SIMULATION AND MODELLING OF HYDROGEN PRODUCTION FROM BIOGAS

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By

RAVINDRA KUMAR
(2K19/Ph.D./ME/17)

Under the supervision of

Dr. Anil Kumar	**Dr. Amit Pal**
(Professor)	(Professor)
Supervisor	Jt. Supervisor

Department of Mechanical Engineering
DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)
Shahbad, Daulatpur, Bawana Road, Delhi-110 042, India

NOVEMBER 2024

DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)
Shahbad, Daulatpur, Bawana Road, Delhi-110042, India

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I Ravindra Kumar hereby certify that the work which is being presented in the thesis entitled "**Simulation and Modelling of Hydrogen Production from Biogas**" in partial fulfillment of the requirements for the award of the Degree of Doctor of Philosophy, submitted in the Department of Mechanical Engineering, Delhi Technological University is an authentic record of my own work carried out during the period from August 2019 to November 2024 under the supervision of Dr. Anil Kumar & Dr. Amit Pal.

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DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)
Shahbad, Daulatpur, Bawana Road, Delhi-110042, India

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(Dr. Anil Kumar)	**(Dr. Amit Pal)**
Professor	Professor
Supervisor	Jt.Supervisor
Mechanical Engineering Department	Mechanical Engineering Department
Delhi Technological University	Delhi Technological University
Delhi (110042)	Delhi (110042)

Date: 01-11-2024

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RAVINDRA KUMAR

ABSTRACT

Hydrogen (H_2) is the most abundant element in the universe. It can serve as a clean fuel when produced using environmentally friendly methods. Hydrogen production is a critical aspect of the global energy landscape, particularly in the context of transitioning to cleaner and sustainable energy sources. H_2 fuel is adopted for the upcoming generation. Switching to H_2 technology is caused of decrement in fossil fuel and changes in climate conditions. There are multiple methods for producing H_2 from conventional and non-conventional resources. For sustainable decentralized power generation in remote and rural areas, development of large-scale H_2 production technology is required. Biogas reforming is an auspicious process for the production of green hydrogen gas as well as for reducing overburden on natural gas and mitigation of greenhouse gas emissions.

In recent times, there has been an amplified interest in exploring fresh applications of biogas, attributed to the rising concerns surrounding climate change and an enhanced emphasis on the utilization of renewable energy sources. The use of fossil fuels in energy systems has environmental consequences, which are driving investigations into H_2 production. Steam-reforming of biogas is a beneficial procedure for producing eco-friendly hydrogen and minimizing the burden on fossil fuels. Steam methane reforming is the most well-known method for producing H_2 using fossil fuels.

In the present study, simulation and modeling of hydrogen production from biogas have been analyzed. This study introduces a zero-dimension (0-D) mathematical model to explore hydrogen production through steam reforming of methane and biogas with varying compositions. The model was simulated by using a batch reactor and incorporated both heat and mass transfer with the chemical reactions occurring in the reactor and calculated product distribution and temperature through the application of energy and mass balances. The model was also used to explain the reaction mechanism involved in the production of hydrogen, and the reaction performance was validated through a simulation analysis using the finite element analysis software (COMSOL Multiphysics 5.6). The presented reactor model closely predicts outcomes from both the 1-D and 2-D non-isothermal models of methane and biogas steam reforming. Therefore, a zero-dimensional model is favored to simplify this study. The model reveals the hydrogen production reaction mechanism and validates its performance through simulation analysis using COMSOL Multiphysics 5.6 software (finite element analysis). The developed model has been validated by available previous experiments and simulation work for biogas reforming with various compositions as well as the methane reforming process. The core aim of this study is to estimate the yield of H_2 for steam methane reforming, and H_2 and CO for steam biogas reforming at steam carbon ratio (S/C) from 1-3 with various temperatures, and find the optimum temperature for the reforming process. The results of the present study show higher yields of hydrogen, achieving 6% and 8.2% respectively, compared to the previous simulation study at a steam-to-carbon (S/C) ratio of 2 and 3, and a temperature of 700°C through steam reforming method. The higher H_2 yields are achieved as 5.33% at 800 ^{o}C, 3.87% at 1000 ^{o}C, and 2.9% at 1200 ^{o}C (average percentage of mol for steam carbon ratio from 1-3) and compared with previous simulation studies at the same operating temperatures through the steam biogas reforming method. It is observed and confirmed that the values obtained from the current simulation enhance the H_2 production rate by almost 4% compared to the previous data. These findings indicate that the proposed work offers a viable method for utilizing renewable methane resources to fuel cells and generate local electricity.

This study explored extensive literature on possibilities of biogas reforming techniques for hydrogen production as well as comprehensive assessment of recent advancements in the domains of dry, bi-, and tri-reforming. A comparative evaluation of various techniques and the exploration of recent catalysts employed in the reforming process and techno-economic biogas conversion applications are also explored in this analysis. Biogas conversion exhibits economic feasibility, typically with a payback period ranging from 4 to 8 years. Opting for a higher reaction temperature within the range of 830-900°C is typically favored as it results in increased CH_4 and CO_2 conversions within the bi-reforming of the biogas process. For Dry and Tri reforming, the temperature range is maintained between 750-850^{o}C and 850-1000^{o}C or above (depending on various factors).

The study presented the thermodynamic analysis for hydrogen production through the steam reforming of biogas (with and without CO_2), considering different CH_4 and CO_2 concentrations and the utilization of various steam-carbon ratios. The study has also discussed the detailed thermodynamic equilibrium study, the path of the reaction, and the kinetic model of these reforming processes. A technical analysis of the steam biogas reforming process and its related energy are also investigated. As the molar ratio of steam carbon (S/C) rises at a particular temperature, it has been noted that the conversion of CH_4 to H_2 results in an increase in the hydrogen output. If the ratio of steam carbon (S/C) is improved from 2:1 to 3:1, the water gas shift reaction occurs, which results in the highest hydrogen production yield (5-6%).

The overall research work has undergone extensive analysis to produce reliable, system-effective results that are nourished by a detailed discussion of the results and conclusions, as well as recommendations for future research.

Keywords: Steam and biogas reforming; Hydrogen production; Numerical Simulation; Thermodynamic equilibrium

LIST OF PUBLICATIONS

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2.	**Ravindra Kumar** and Anil Kumar	Recent advances of biogas reforming for hydrogen production: Methods, purification, utility and techno-economics analysis	International Journal of Hydrogen Energy Volume 76, pages 108-140, Available online 23 February 2024	2024	**7.13**	Elsevier
3.	**Ravindra Kumar,** Anil Kumar, and Amit Pal	Overview of hydrogen production from biogas reforming: Technological advancement	International Journal of Hydrogen Energy Volume 47, Issue 82, 30 September 2022, Pages 34831-34855	2022	**7.13**	Elsevier

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LIST OF SYMBOLS, ABBREVIATION AND NOMENCLATURE

A^f	Forward Frequency factor m^3/s.mol
A^r	Reverse Frequency factor m^3/s.mol
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
C_i	Molar flow rate of the species [mol/s]
C_p	Molar heat capacity of the species [J/(mol·K)]
E^f	Forward activation energy
E^r	Reverse activation emery
F_i^{in}	Molar flow rate of i^{th} component [kmol/hr]
F_j^{in}	Inlet molar flow rates of chemical components j [kmol/h]
$F_{CH_4}^{in}$	Inlet molar flow rate of methane [kmol/h]
H_2	Hydrogen
H_j	Heat of the reaction [J/mol]
i	Chemical component [-]
j	Reaction [-]
k_i	Reaction rate constants [-]
K_i	Adsorption constants of chemical species [-]
$K_{eq}.i$	Equilibrium constants [-]
k^f	Forward Rate constant
n^f	Forward temperature exponent
n^r	Reverse temperature exponent
Pi	Partial pressures of chemical species [bar]
Q	Heat from the chemical reaction [J/(m^3·s)]
Q_{ext}	Heat added to the system per unit volume [J/(m^3·s)].
R	gas constant (J/kmol K),
R_i	Net reaction rate of the species in [mol/(m^3s)]

S/C	Steam to Carbon ratio [-]
$T_{op.}^{in}$	Inlet operating temperature (°C)
V_r	Volume of the reactor [m^3]
$X_{\mathrm{CH_4}}$	Equilibrium conversion of methane [%]
$X_{\mathrm{CO_2}}$	Equilibrium conversion of carbon dioxide
X_{CO}	Equilibrium conversion to carbon monoxide.
Y_{H_2}	Yield of hydrogen [mol]
Y_{CO}	Yield of carbon monoxide [mol]

Greek symbols

η_i	Reaction effectiveness factor [-]
σ_{ij}	Stoichiometric coefficients of chemical components [-]
σ	Stated parameter [-]
θ_j	Inlet Molar Flow Ratio of chemical components j to methane [-]

Abbreviation

BG	Biogas
DRM	Dry reforming of methane
SRM	Steam reforming of methane reaction
RWGS	Reverse water gas shift reaction
RM	Reverse methanation reaction
SBR	Steam biogas reforming

CHAPTER 1

INTRODUCTION

1.1 Overview

The present status of the maximum growth of energy is dependent on traditional resources like fossil fuels. The day-by-day increasing demand for energy and the limitations of fossil fuels underscore the need for alternative energy sources. It is essential to produce clean and environmentally friendly fuel because the environment is greatly affected by air pollution [1, 2]. The rate of fossil fuel consumption is significantly higher than the rate of fossil fuel production by nature. Therefore, the use of renewable energy become more important because it can be conveniently used to produce different kinds of fuels as a form of energy [3]. The environmental degradation and energy crisis have evoked deep concern all over the world, as speedy depletion of natural energy resources [4].

Hydrogen is abundant and is the most available in renewable energy. Furthermore, only water vapor is produced from the combustion of hydrogen. Presently, biogas is one of the main categories of renewable energy sources. Biogas is a mixture of different gases produced by the anaerobic digestion or fermentation of organic matter in the presence of microorganisms [5].

Biogas can be an important path of hydrogen production and is produced through the anaerobic digestion process. The product of biogas consists of mainly methane (CH_4) and carbon dioxide (CO_2) and is associated with traces of other gases like hydrogen(H_2), ammonia (NH_3), hydrogen sulfide (H_2S), nitrogen (N_2), oxygen (O_2) and vapor water (H_2O) [6].

In the current scenario, hydrogen is produced from natural gases (47%), heavy oil with naphtha (30%), coal (18%), electrolysis (4%), and biomass (1%). [7-8]. The application of H_2 as a raw material is used in fuel cells, combustion engines, petrochemicals, and the fertilizer industry, especially in ammonia production. Traditionally, large-scale food processing, hydrogenation processes, the chemical industry, the production of ammonia and methanol, the pharmaceutical industry, Fischer-Tropsch synthesis, and other areas have been significant. The contribution of H_2 production in terms of capacity will increase by 8-10% up to 2025 and nearly double the previous goal of 2005 [9].

Three major techniques used for the conversion of CH_4 present in biogas to H_2 are steam reforming, dry reforming, and partial oxidation reforming which can be used for the production of hydrogen [10].

Biogas reforming for H_2 production is an appealing and promising technique to convert biogas into H_2, especially due to the reduction in the emission of greenhouse gases and its reliability [11]. Another advantage of using biogas as a feedstock for H_2 production is its availability (mostly local) which reduces transportation costs. Therefore, the utilization of biogas in the reforming process has better environmental and economic advantages. Biogas reforming involves CO_2 reforming as well as dry reforming of CH_4. Since this process requires the stripping of oxygen from carbon dioxide and the stripping of hydrogen from methane, there are significant chances of coke deposition on the catalyst surface. That is why most of the reforming studies have been based on the broad and intense analysis of different catalysts. It is used to minimize the costs and the total energy involved in the complete process [12]. The development, modification, and utilization of several catalysts having a higher catalytic activity and stability in reforming processes can reduce the higher temperature needs and increase the reaction rate. In addition, it can also slow the carbon deposition rate and the poisoning of the catalyst, which are the major problems encountered during reforming processes [13]. The most practiced methane/biogas reforming processes for hydrogen production such as steam reforming (SR), Partial oxidation reforming (POR), Auto-thermal reforming (ATR), Dry oxidation reforming (DOR), Dry reforming (DR), Bi-reforming, and Tri reforming. These methods are based on hydrocarbon reforming process.

There are some other unconventional processes for the production of H_2 from methane such as thermal plasma reforming, catalytic decomposition, and solar reforming. Several industries use SR, POR, and DR methods for the large-scale production of H_2 that uses natural gas (≈95 % of CH_4) or naphtha as major sources of hydrocarbons [13].

Generally, reforming processes for H_2 production are performed under low pressure (mostly below 1 atm) in tubular fixed-bed or fluidized-bed reactors, in a wide range of temperatures 600-1000°C (endothermic and reversible reactions) [14]. It also involves predominant catalytic reactions that are mostly combined (see Table 1.1). Reforming processes primarily use natural gas (methane source), but biogas, based on its composition and purity, can also serve as a methane source. Hence, research on methane reforming can be adapted for biogas reforming [15].

The introduction of steam into the biogas dry reforming procedure can substantially mitigate the formation of coke on the surface of the catalyst. The integrated process of steam methane reforming and CO_2 is widely referred to as bi-reforming also known as steam biogas reforming (as shown in Table 1.1 Equation 12) [16]. However, in case of a significant O_2 content, the separation of O_2 from the biogas is necessary to enable the occurrence of the bi-reforming progression. Tri-reforming involves the amalgamation of three distinct methane reforming processes: CO_2 reforming, steam reforming (as shown in Equation 1, and partial oxidation reforming (depicted in Equation 3). Furthermore, during the tri-reforming process, additional reactions are occurring at the same time (Equation 13) [17]. Names of chemical reactions are cited and their respective enthalpy of reaction at 298 K (25°C) has also been shown in Table 1.1.

Table 1.1: Chemical reactions involved in reforming processes [13, 17]

Reaction Equation	**Name of reaction**	**Type of reaction**	**Thermal reaction, ΔH_{298} K (kJ/mol)**
Equation 1	SR	$CH_4 + H_2O \longrightarrow CO + 3H_2$	206.2
Equation 2	Gas-shift reaction	$CO + H_2O \longrightarrow CO_2 + H_2$	−41.2
Equation 3	Combined reaction	$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2$	165
Equation 4	Methane cracking	$CH_4 \longrightarrow C + 2H_2$	74.9
Equation 5	Boudouard reaction	$2CO \longrightarrow C + CO_2$	−172.4

Reaction Equation	**Name of reaction**	**Type of reaction**	**Thermal reaction, ΔH_{298} K (kJ/mol)**
Equation 6	Reduction of CO	$CO + H_2 \longrightarrow C + H_2O$	−131.3
Equation 7	POR	$CH_4 + ½\, O_2 \longrightarrow CO + 2H_2$	−35.6
Equation 8	Complete oxidation	$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$	−801.7
Equation 9	ATR	$CH_4 + ½\, x\, O_2 + yCO_2 + (1 - x - y)\, H_2O \longrightarrow (y + 1)\, CO + (3 - x - y)\, H_2$	≈ 0
Equation 10	DR	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	247.4
Equation 11	DOR	$CH_4 + \beta CO_2 + (1 - \beta)/2\, O_2 \longrightarrow (1 + \beta)\, CO + 2H_2$	$(285\beta - 38)$ $0 \leq \beta \leq 1$
Equation 12	Bi-reforming reaction	$2CH_4 + CO_2 + 2H_2O \longrightarrow 3CO + 5H_2$	453
Equation 13	Tri-reforming reaction	$3CH_4 + CO_2 + H_2O + ½\, O_2 \longrightarrow 4CO + 7H_2$	417

1.1.1 Hydrogen (H_2)

It is the most abundant element in the universe and primarily exists on Earth in water and organic compounds [18]. It is the simplest element, consisting of one electron and one proton, presenting as a colorless, odorless, and flammable gas [18]. With an atomic weight of 1.00794 atomic mass units, rounded to 1.008, hydrogen holds significance in the United States, where October 8th (10/08) is celebrated as National Hydrogen and Fuel Cell Day [19]. Initiated by the Fuel Cell and Hydrogen Energy Association in 2015, this event aims to promote awareness of fuel cell and hydrogen technologies, highlighting their current and future potential, as depicted in Fig. 1.2. This celebration is envisioned to evolve into an international day dedicated to hydrogen energy.

The existence of hydrogen as a chemical substance in nature, with the molecular formula of H_2, is not readily available and it is often in the form of compounds called hydrides with a negative or anionic character, denoted (H^-). The direct production of hydrogen in the industry comes from steam reforming of hydrocarbons. As well as this, other technologies include, for example, electrolysis and thermolysis.

Fig. 1.1: Hydrogen chemical elements and USA National Hydrogen and Fuel Cell Day [19]

1.1.2 Hydrogen as a promising fuel

In recent years, H_2 energy has developed considerable attention as a promising fuel for the future. It offers various applications, including serving as a conduit for energy transport or storage agents. Furthermore, it introduces options free from carbon for traditional fuels [20]. Hydrogen is a secure and flammable fuel that, when reacted, generates in water form and minimal nitrogen oxides. It demonstrates remarkable qualities as a fuel, including efficient combustion, non-toxicity, and no ability to generate ozone. [21]. According to Fig. 1.1, hydrogen has a high energy content of 141.9 mega joules per kilogram (MJ/kg), which surpasses methane (55.8 MJ/kg) by more than double, exceeds the energy capacity of fuels used in transportation (45.8 MJ/kg) by approximately 2.5 times, and is over four times greater than coal's energy content (30.2 MJ/kg) [22]. Typically, clean coal, fossil fuels, nuclear energy, and a variety of renewable sources are used to produce hydrogen. This serves to enhance its potential to emerge as a prominent fuel in the upcoming years.

The literature indicates that there is ample evidence supporting the viability of scaling up hydrogen production for electricity generation using fuel cells in the future [23]. Furthermore, researchers have made significant progress by developing a comprehensive collection of computer algorithms that model the dynamic combustion of H_2 fuel within rocket engines [24]. Furthermore, Akdeniz et al. [25] performed a broad analysis of the utilization of hydrogen fuel in aviation engines, encompassing energy, exergy, and sustainability considerations.

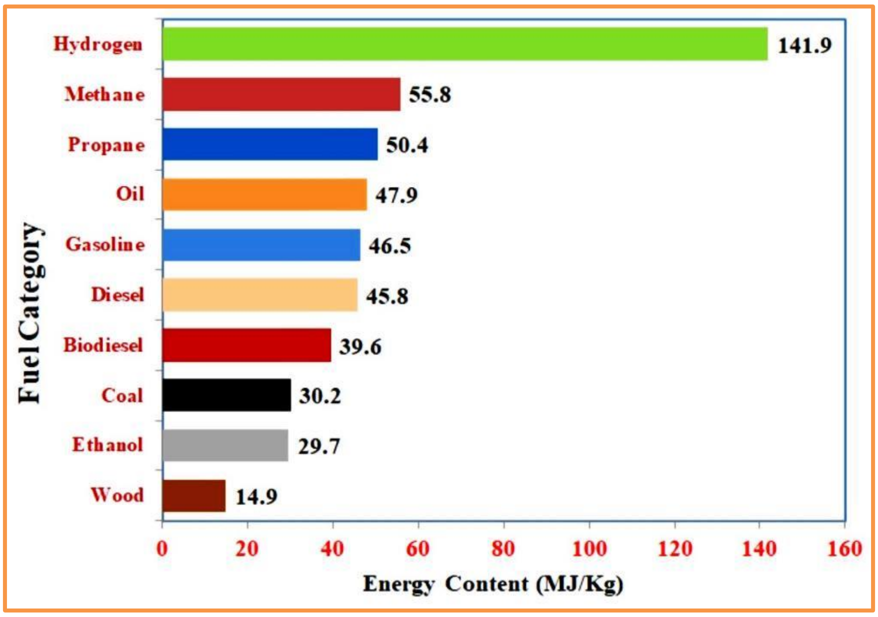


Fig. 1.2: Energy content of various fuels, modified from [22]

1.1.3 History of hydrogen and its accidents

Hydrogen has been recognized as a substance for over 200 years. In the early sixteenth century, the scientist Paracelsus discovered that gas was produced during the interaction of iron with sulfuric acid. This gas was observed to burn, as recorded in the seventeenth century by the scientist Myelin [25].

Robert Boyle created hydrogen in 1761 through the combination of diluted acids and iron filings [42]. Since he presented his major discoveries in a paper to the Royal Society of London in 1776, Henry Cavendish has been recognized as the investigator of hydrogen. He recognized hydrogen as a distinct substance [25, 26].

Antoine Lavoisier produced hydrogen in 1783 [26], and he gave the substance the name hydrogen (Hydrogenium) in 1788, using the word from the Greek word "hydro" (water) [27]. It was originally produced by the English Nicholson and Carlisle in 1800 by the process of electrolysis of water [25, 27].

James Dewar liquefied hydrogen in 1898 [27]. Sir William Robert Grove, a British scientist, created the first fuel cell fuelled by hydrogen in 1839 [26]. In 1900, German Count Ferdinand von Zeppelin created the first balloon that used hydrogen to keep an airframe buoyant [25]. In the 1920s and 1930s, airships were used to travel across the

Atlantic [25]. NASA was established in the United States in 1958 to explore space and has made significant historical contributions to the utilization of hydrogen. By 1961, it was the largest user of liquid hydrogen worldwide and used hydrogen as fuel [25]. The Soviet Union accomplished a flight with TU-155, the first jet engine aircraft in history, and the first space shuttle was launched in 1981.

Since the Hindenburg tragedy on May 6, 1937, which claimed the lives of 35 of the 97 passengers on board the airship [25], and the subsequent incidents as illustrated in Fig. 1.3, hydrogen has been associated with danger due to its exceedingly combustible nature [26]. Even as investigations into the causes of several hydrogen accidents reveal that "organizational and human factors" were involved in over 70% of them [28], these mishaps have been linked to people's inability to handle hydrogen efficiently [28].

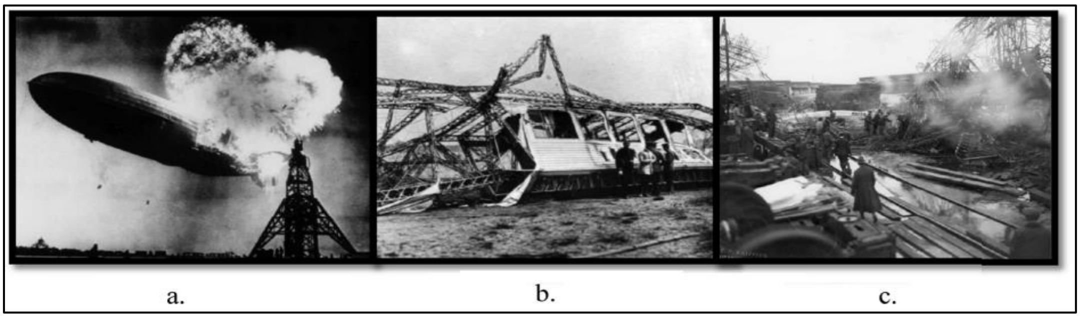


Fig. 1.3: Hydrogen historic accidents: a. Hindenburg, while on fire, b. Wreck of LZ-10 Schwaben at Dusseldorf, c. Airship Roma after ignition [25]

1.1.4 Hydrogen safety

Hydrogen is a much lighter and non-toxic fuel than air since it dissipates quickly upon release, making it safer than other spilled fuels because it may be used relatively quickly in the event of a leak [25]. The main safety concern arises when a leak remains undetected, leading to the accumulation of gas in a confined space, potentially resulting in ignition and causing an explosion [29].

As with all fuels, hydrogen carries inherent risks. Thus, ensuring safe utilization of fuel involves preventing situations where the three elements necessary for combustion—fuel, oxidant, and ignition are concurrently present [25]. To guarantee its safe handling, hydrogen's characteristics, including its broad range of flammable concentrations in the air (4%-75%) and its lower ignition energy requirement (only one-tenth of that needed to ignite petrol), necessitates the implementation of additional engineering controls [29].

To ensure the safe use of hydrogen, it is essential to have a solid understanding of its properties, design safety measures for hydrogen systems, and provide training on safe handling and storage techniques [30, 31]. "As more and more hydrogen demonstrations get underway, hydrogen's safety record can grow and build confidence that hydrogen can be as safe as the fuels in widespread use today," the USA Department of Energy said on its website [25].

1.1.5 Hydrogen properties and applications

Hydrogen has a substantially higher energy content than most fuels (gasoline, for example, has an energy content of 44 MJ/kg at 298 K), with a higher heating value of 141.8 MJ/kg at 298 K and a lower heating value of 120 MJ/kg at 298 K [30, 31].

However, when compared to hydrocarbon fuels like petrol, liquid hydrogen possesses a volumetric energy density approximately four times lower (8 MJ/l compared to 32 MJ/l) [32,33]. Due to its poor energy density by volume but good energy density by weight, hydrogen gas requires larger storage tanks than hydrocarbons [32].

A significant amount of the risk involved in using hydrogen is due to its combustible nature and relatively low ignition temperature [26]. Additionally, because of its small molecule size and destructive ability (hydrogen embrittlement), it can pass through materials and cause mechanical degradation and failure in some materials to the point of leaking [31, 34]. Table 1.2 shows the comparison of hydrogen properties with other important fuels.

Hydrogen is considered as the cleanest energy source. Hydrogen is also deemed to be a suitable solution to environmental problems if it is produced from renewable resources. The advantages of hydrogen are zero emission of greenhouse gases if it is produced using renewable energy.

Hydrogen is a gas that accounts for 75% of the universe's mass. Hydrogen is found on Earth only in combination with other elements such as oxygen, carbon and nitrogen.

To use hydrogen, it must be separated from these other elements. Today, hydrogen is used primarily in ammonia manufacture, petroleum refinement and synthesis of methanol. It is also used in NASA’s space program as fuel for the space shuttles, and in fuel cells that provide heat, electricity and drinking water for astronauts. Fuel cells are devices that directly convert hydrogen into electricity. In the future, hydrogen could be used to fuel vehicles and aircraft and provide power for our homes and offices.

Hydrogen is having high energy; an engine that burns pure hydrogen produces almost no pollution. NASA has used liquid hydrogen since the 1970s to propel the space shuttle and other rockets into orbit [35]. The production of hydrogen from biofuel resources is considered one of the most promising techniques due to its high organic content and availability.

Table 1.2: Comparative properties of hydrogen and other fuels [36]

Properties	**Hydrogen**	**Methane**	**Propane**	**Methanol**	**Ethanol**	**Gasoline**	**Units**
Chemical formula	H_2	CH_4	C_3H_8	CH_3OH	C_2H_5OH	CxHy (x=4-12)	-
Molecular weight	2.02	16.04	44.1	32.04	-	-	-
Density (NTP)[a]	0.08375	0.6682	1.86	791	789	751	kg/m^3
Viscosity NTP)[a]	8.81×10^{-4}	1.10×10^{-3}	8.01×10^{-4}	9.81×10^{-2}	0.119	0.037-0.044	Pa s
Normal boiling point	-252.8	-161.5	-42.1	64.5	78.5	27-225	°C
Flash point	<-253	-188	-104	11	13	-43	°C
Flammability in air	4-75	5-15	2.1-10.1	6.7-36.0	4.3-19	1.4-7.6	Vol.%
Auto ignition temperature in air	585	540	490	385	423	230-480	°C
Higher heating value (at 25°C and 1 atm)	141.86	55,53	50.36	19.96	29.84	47.50	MJ/kg
Lower heating value (at 25°C and 1 atm)	119.93	50.02	45.60	18.05	26.95	44.50	MJ/kg

[a] NTP = 20 °C and 1 atm
[b] Properties of a range of commercial grades

1.1.6 Categories of Hydrogen

The classification of hydrogen into grey, blue, and green categories depends on the type of energy source and production method, as depicted in Fig. 1.4. Thermochemical reforming, electrolytic conversion, biological route, and water splitting using solar are commonly utilized for H_2 production at large scale.

Grey hydrogen is the term used to describe hydrogen generated through processes like thermal cracking and steam methane reforming [37]. Fig. 1.4 demonstrates that methane steam reforming leads to substantial CO_2 production. However, these CO_2 emissions are captured, securely stored in containers, and deposited in safe storage facilities. On the other hand, blue hydrogen refers to hydrogen obtained from sources such as natural gas, syngas, and biogas.

In the case of blue hydrogen, the CO_2 gases formed during production cannot be stored and are released into the atmosphere. However, in comparison to grey H_2, blue H_2, mainly obtained via natural gas, offers a significant decrease in CO_2 emissions by capturing and recycling carbon. Fig. 1.5 depicts that both the production of grey and blue H_2 pathways lead to the creation of CO_2 as a side product. On the contrary, green H_2 production methods attain a complete absence of carbon emissions. The primary methods used for green hydrogen production are solar and wind technologies, although the availability of other technologies as such catalytic reforming with the potential to generate green hydrogen. Examples include gasification of biomass and thermal and chemical by nuclear pathways, which offer the potential for carbon emissions reduction. However, there are significant challenges to address, including costs of production technology, durability of the system, reliability, safety, and infrastructure, as highlighted in reference [38].

Yan et al. [39] state that the current global production of hydrogen amounts to approximately 75 million tonnes per year. Out of this total, around 76% is attributed to blue hydrogen sourced from natural gas (equivalent to 205 billion cubic meters or 6% of the present worldwide natural gas consumption), while 23% is accounted for by grey hydrogen produced from coal (equivalent to 107 million tonnes equivalent to 2% of the current worldwide usage). Nonetheless, this hydrogen production results in around 830 million tonnes of CO_2 emissions each year, which are emitted as greenhouse gases into the atmosphere, constituting approximately 2% of the total annual global emissions.

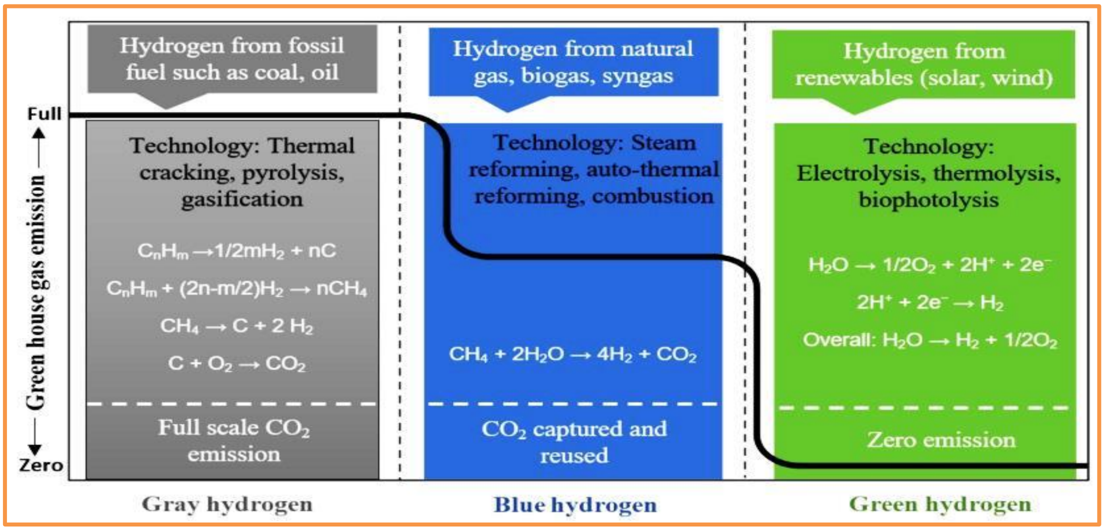


Fig. 1.4: Hydrogen types, feedstock sources, and technological approaches [40, 41]

1.2 Hydrogen production

Hydrogen production from fossil fuels involves heating hydrocarbons, steam, and sometimes air or oxygen before combining them in a reactor. Hydrogen is extracted from both water and hydrocarbons, with H_2, CO, and CO_2 forming as water molecules and hydrocarbons break down. Another approach involves heating hydrocarbons without steam or air to decompose them into hydrogen and carbon. Alternative primary energy sources are necessary for generating hydrogen.

The maximum production of hydrogen is generated from fossil-based fuels through advanced technology as shown in Fig. 1.5. It is realized that 48% use natural gas through steam reforming process in order for hydrogen production and others like coal (18%) and Oil (30%) obtained through the partial oxidation process. There is minimum utilization of water 4% for production of hydrogen through electrolysis process [42, 43].

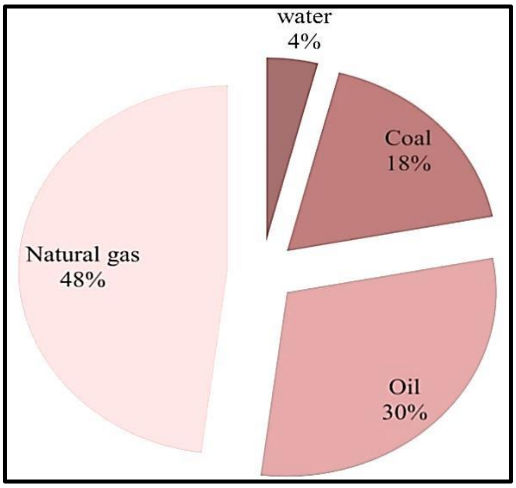


Fig. 1.5: Modes of global hydrogen production [42, 43]

The most popular techniques include gasification of coal, partial oxidation of petroleum, steam iron treatment, and catalytic steam reformation of natural gas. Furthermore, among the processes used to obtain hydrogen as a by-product during the production of other industrial products, some examples include the production of counter-chlorine from chlor-alkaline, the production of light gases during the refining of crude oil, the production of coke from coal in coke ovens, and chemical hydrogenation processes in the margarine industry [44, 45].

1.2.1 Biogas as Hydrogen feedstocks

Biogas generally carries of different percentage of gases (55%-65%) CH_4, (35-45%) CO_2 and (1%) N_2 in sewage digesters while (60% - 70%) CH_4, (30%- 40%) CO_2 and (1%) N_2 in organic waste digesters and (45% - 55%) CH_4, (30%- 40%) CO_2 and (5% - 15%) N_2 [46]. It is generally produced in bio-waste digesters, landfills, and sewage sludge which include animal wastes, agricultural wastes, animal dung, energy crops, etc. [47]. The unwanted component of biogas is hydrogen sulfide (H_2S). It is corrosive gas and can damage accessories and equipment during the process of producing energy. Other impurities like CO_2 and humidity decrease the calorific value of biogas in direct combustion for thermal plants. [48].

Biogas can be obtained through landfills; such a gas is known as ‘landfill’ gas. The typical composition of biogas and landfill gas in comparison to natural gas is shown in Table 1.3. The composition of biogas varies from site to site, depending on type of feedstock and also the type of anaerobic digesters used. The composition of CH_4 in biogas and landfill gas is nearly similar, the former showing slightly higher composition. In comparison to natural gas, both kinds of biogas exhibit lower CH_4 content thus lowering the calorific value of the gas. In contrast to natural gas, biogas shows presence of NH_3 and O_2. On the other hand, higher hydrocarbons are absent in biogas/landfill gas. But both biogas and natural gas typically contain H_2S and N_2 as minor compounds.

Table 1.3: Composition of landfill gas and biogas along with natural gas [49]

Component	AD-biogas	landfill biogas	Natural gas	Unit
CH_4	53-70	30-65	80-90	(vol%)
CO_2	30-50	25-47	0.67-1	(vol%)
H_2S	0-2000	30-500	0-2.9	(ppm)
NH_3	<100	0-5	NA	(ppm)
H_2	NA	0-3	NA	(vol%)
N_2	2-6	<1-17	0.28-14	(vol%)
Light HC	NA	NA	3.5-9.4	(vol%)
O_2	0-5	<1-3	0	(vol%)
Total chlorine	<0.25	0-0.225	NA	mg/Nm^3
Siloxanes	<0.08-0.5	<0.3-36	NA	µg/g-dry

The major problems associated with combustion of biogas are presence of high amount of H_2S and silicon compounds as they generate the SO_2 pollutant and silica particulates which damage combustion engine parts and heat exchanger surfaces. In reductive catalytic environments, the H_2S would also act as catalyst poison. Anaerobically produced biogas exhibits higher H_2S content than landfill gas and natural gas. Similarly, more halogens are present in landfill-derived biogas in comparison to the other two.

Currently, there are no such reviews that examine the potential of hydrogen generation from biogas with respect to India. The current status of hydrogen production from biogas in India was analysed to determine the recent developments. The focus was to determine the right processes to produce hydrogen from biogas based on reactor type and process conditions. As catalyst is the most important part of the hydrogen production process, the use of various catalyst formulations in different biogas reforming processes was extensively examined. Factors affecting the performance of the catalyst i.e. preparation method, surface area, pore size, crystallite sizes and carbon formation were compared to determine the best formulation for biogas reforming technology implementation in India [49].

According to literature on reforming, the research has highlighted cost and energy-saving catalysts. The use of catalysts with higher catalytic activity and stability in reforming route can lead to a decrease in the high temperatures commonly used, which can be accompanied by improvement in the reaction rate and a slowdown in the catalyst deactivation process. Poisoning effect, additional impurities, and carbon deposition (coke) are often severe problems [13].

The most important technology for large-scale production of H_2 is to facilitate the reforming of light hydrocarbons (HCs), predominantly methane (CH_4) which is the main component of biogas [50]. However, some of these routes produce a combination of CO and H_2, also called synthesis gas, widely used in industry [51]. The production of pure H_2 via synthesis gas is quite expensive due to the need to remove CO [52].

1.2.2 Biogas potential

Biogas is a viable, sustainable, and efficient energy resource because of its plentiful supply of low-cost feedstock. The countless applications such as in power sector, heating, fuel, and hydrogen production by chemical processing and biofuels through raw materials. Worldwide, biogas-based power generation capacity has been increasing from 65 GW (year 2010) to 120 GW (year 2019) [53].

The global capacity of biogas plants was approximately 19.5 GW at the end of the year 2019 with growth driven by factors such as high prices of fossil fuels, easy access to low-cost biomass feedstock and more concerns over global warming and emissions [54, 55]. The development of biogas accounted 0.25% energy market and 27% biofuel market worldwide in 2011 [56]. In 2005, biogas digesters (small households) were available to nearly 16 million worldwide, but most were in India and China. In India, firewood was switched by biogas as an equivalent of 16 million tons (MT) up to 1996, while in China; about 4% of total energy demand is fulfilled by 7 million biogas digesters [56].

Production of biogas and its utilization have numerous benefits. It offers greenhouse reduction, alternative fuel, heat and electricity, fertilizer as by-product, waste recycling, and safety of environment from pollutants. Biogas arrangements could be renovated manure or organic domestic waste materials into gas to light and cook. The waste products like rice, fruits, and vegetables can be transformed into energy rather than disposed of. The waste materials storage and disposal invite insects and pests. Biogas supports waste management and donates to enriched hygiene in rural zones [49].

Biogas is primarily used as fuel for cooking purposes and stationary engines. Biogas potential has not yet been fully explored and used. To promote domestic biogas, the Indian government established the National Biogas Development Project (NPBD) in 1981. The number of biogas plants in India has increased from 1.23 million in 1990 to 4.54 million in 2012, despite the enormous potential of 12.34 million digesters [57]. The installation of biogas plants has increased related to its potential by approximately 26% - 37% from 2002 to 2012. Domestic scale (biogas plants) leads to an expected saving of 4.0 million tons of fuel (wood type) every year, as well as producing one Mt of enhanced organic manure [58]. In Europe, the production of biogas has been growing nearly from 9.29×10^9 L (2009) to 1.65×10^{10} L (2016) through the using biogas technology [55].

1.3 Biogas Purification and Utilization: Technology Outline

1.3.1 Biogas purification technology

In biogas, impurities like nitrogen (N_2) and hydrogen sulfide (H_2S) can be present, which have the potential to degrade the fuel quality. To ensure the desired fuel quality for different utilization technologies, it is crucial to employ upgrading and purification technologies. These technologies have a significant role in managing and reducing the concentrations of contaminants in biogas, based on the specific requirements of various utilization methods. By implementing effective upgrading and purification processes, the impurity levels in biogas can be controlled, meeting the quality standards necessary for different utilization applications [59].

Numerous kinds of research have been studied for biogas purification and upgradation on H_2S, CO_2, and water removal and also used advanced solutions for up-gradation [60-62]. Similarly, in a comprehensive summary by Gaj [63], various established techniques for eliminating siloxanes and other impurities were compiled. Furthermore, Munoz et al. [64] conducted a review that specifically focused on the elimination of H_2S, H_2O, CO_2, and minor elements, such as halocarbons, siloxanes, N_2, and O_2. Notably, their review placed particular emphasis on the application of biotechnologies in the purification process. The primary techniques utilized for upgrading and purifying biogas as shown in Fig.1.6 (a). These mainstream technologies serve the purpose of enhancing the quality and purity of biogas through various processes.

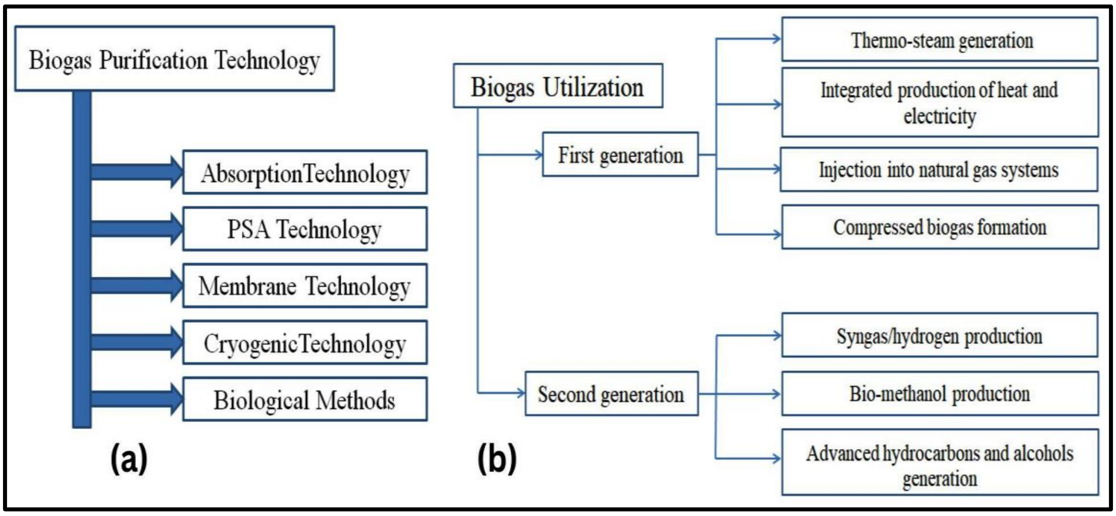


Fig. 1.6: (a) Illustrate biogas techniques for the purification process and (b) the utility of biogas in different areas

1.3.1.1 Absorption

The varying degrees to which different gases expand in liquid solvents form the basis for the separation method known as absorption. Physical absorption techniques are often employed, including Organic Physical Scrubbing (OPS) and High-Pressure Water Scrubbing (HPWS). These techniques involve the use of liquid solvents to selectively remove impurities from biogas based on their solubility characteristics. HPWS is a well-established technology extensively employed in various industries because water is both cost-effective and widely accessible as a solvent. In the HPWS process, compressed biogas is introduced at the bottom of the absorption column, while water flows in a counter-current manner. Functioning under a pressure of 6 to 10 bar, this setup makes it possible to effectively extract both CO_2 and H_2S from biogas at the same time. Both CO_2 and H_2S exhibit higher solubilities in water compared to CH_4, allowing for their efficient separation during the absorption process [65]. Regarding the principles of absorption, OPS and HPWS are comparable, but OPS uses organic cleaning solutions instead of water. These organic solvents require less solvent and electricity due to their higher solubility in CO_2 and H_2S. Common solvents employed in the OPS method include propylene carbonate, N-methyl pyrrolidone, polyethylene glycol ethers, and methanol [66].

Chemical absorption is dependent on the interactions that take place between gases and solvents through chemical reactions. Similar to physical absorption, a counter-current process is employed in the chemical scrubber system. However, the operational pressure within the chemical scrubber arrangement is low, typically ranging from 1 to 2 bar [61]. In the process of removing CO_2 and H_2S, the solutions of inorganic alkaline and alkanolamine are commonly employed. The absorbents frequently utilized for this purpose include sodium hydroxide (NaOH), monoethanolamine, potassium hydroxide, methyl diethanolamine, diglycolamine, dimethylethanolamine, ammonia, and calcium hydroxide [67].

1.3.1.2 Pressure swing adsorption (PSA)

This approach relies on disparities in the forces of van der Waals between different gases and adsorbent surfaces. This technology finds widespread use in numerous industrial sectors and can attain a substantial at least 97% CH_4 concentration along with an impressive CH_4 recovery rate of 94% [68].

The untreated biogas is initially introduced into an adsorption column where porous adsorbents operate under increased pressure (4 to 10) bar to capture and retain impurities such as CO_2, H_2S, N_2, water, and other contaminants [69]. Once the adsorbents reach saturation with CO_2, the biogas is directed to a separate column. Subsequently, the pressure within the saturated column is decreased, leading to the desorption of CO_2. To ensure the continuous operation of pressure swing adsorption (PSA), a specific order of opening and closing multiple columns must be observed [70].

The selection of suitable adsorbents for PSA requires considering their specific surface area, porosity, capacity, and ability to selectively interact with various gases. Activated carbon, carbon molecular sieves, synthetic resins, silica gels, and zeolites are among the commonly used adsorbents in the PSA process. Additionally, there has been a growing application of novel materials in recent times for PSA operations. In a study by Wu et al. [71], a novel adsorbent metal-organic framework (MOF) called MOF 508b was synthesized, resulting in reduced energy consumption in the PSA process. Another innovative material, Mg-MOF-74, developed by Bao et al. [72], exhibited significantly improved adsorption capabilities in order to CH_4 and CO_2 compared to zeolite 13X.

1.3.1.3 Membrane technology

Membrane separation relies on the selective permeability of the membranes, allowing some chemicals to pass through while preventing others. The driving force behind the separation process is the pressure difference between the two sides of the membrane. Membrane separation primarily encompasses two main processes: gas-gas separation under high pressure and gas-liquid separation through absorption. Gas-gas separation typically occurs at high operating pressures ranging from 20 to 40 bar [60], although in certain systems, it can be carried out at lower pressures of 8-10 bar [70]. During membrane separation, the selective permeability of the membrane allows CO_2, H_2S, and other impurities to pass through while retaining CH_4, resulting in the enrichment of CH_4 and higher concentrations of CH_4 in the separated gas stream. At pressures close to atmospheric levels, gas-liquid separation is performed. CO_2 and H_2S pass through the membrane and are removed using absorption solutions that simulate the action of chemical adsorption on the opposite side of the membrane. Inorganic components often found in commercial membranes include zeolites, activated carbon, and MOFs, while examples of organic polymers include polyimide and polycarbonate.

1.3.1.4 Cryogenic technology

The separation of cryogenic is an emerging technique that relies on the variations in boiling pressures and temperatures of different constituents within biogas. In this method, the biogas is subjected to a cooling process, typically achieving temperatures between 173 and 203 K, while maintaining an exceedingly high-pressure level of 40 bar. In the condensation and distillation process of cryogenic separation, the separation of CO_2, H_2S, N_2, H_2O, and additional impurities takes place. This technique allows for the extraction of CH_4 and CO_2 with high levels of purity. On the other hand, the utilization of multiple compressors and heat exchangers in cryogenic separation significantly increases the initial investment cost, operational expenses, and energy consumption [73].

1.3.1.5 Biological methods

Conventional bio-desulfurization methods have been extensively utilized in the biogas industry to target H_2S removal. The process involves injecting biogas into a filter along with a controlled proportion of air, typically ranging from 2% to 5%. By creating a controlled environment, the conditions are optimized for desulfurization bacteria to effectively oxidize H_2S, leading to the generation of elemental sulfur. This method is typically complemented by water scrubbing, as the filter provides ample surface area for efficient gas-liquid contact and creates favorable conditions for bacterial growth. The Shell-Paques system, which employs a two-step procedure combining bio-oxidation and adsorption, has proven to be a successful method for removing H_2S [67].

In a study by Fernandez et al. [74], the bio-desulfurization of biogas was investigated through the utilization of an anoxic biotrickling filter that incorporated open-pore polyurethane foam. They achieved an impressive removal efficiency of 99% by optimizing the operational parameters in the study. In the context of methane enrichment, a novel approach utilizes hydrogenotrophic methanogens, which employ microorganisms to convert CO_2 and H_2 into CH_4. The outcome of this inventive technology resulted in an impressive methane (CH_4) concentration of 98% in the final product gas [61].

Yan et al. [75] conducted a study where they employed a photo-bioreactor designed as a microalgae bag. Their approach aimed to achieve both biogas enhancement and purification of biogas slurry simultaneously, utilizing the photosynthetic capabilities of microalgae. According to the findings presented by Wang et al. [76], the concurrent enhancement of biogas and purification of wastewater have shown significant advancements when microalgae were co-cultured with activated sludge or fungi.

1.3.2 Biogas utilization: first-generation

The biogas has more CH_4 concentration; it is a common approach to utilize upgraded biogas directly as an energy source for generating heat and electricity. There are several widely utilized methods in industrial processes as shown in Fig.1.6 (b).

1.3.2.1 Thermo-steam generation

The traditional approach to utilizing biogas is through heat and steam production. Biogas serves as a significant energy source for lighting and cooking purposes in numerous nations [77].

Enhancing heat generation through biogas combustion is an area of ongoing research. In their study, Li et al. [78] discovered that conditions enriched with H_2 and O_2 contributed to improved heat-releasing properties and combustion of biogas. Furthermore, the utilization of biogas for combustion in boilers to produce steam has seen widespread adoption because of its capacity to accommodate a broad spectrum of biogas purity, frequently obviating the need for hydrogen sulfide (H_2S) removal.

1.3.2.2 Integrated production of heat and electricity

The idea of combined heat and power (CHP) was initially sponsored by the Council of the European Union in 1974 [79]. This concept, which allows for the simultaneous generation of heat and electricity, has gained significant traction and interest in recent decades. Its ability to achieve both energy outputs concurrently has contributed to its growing recognition and attention over the years. Biogas presents a favourable and cost-effective fuel option for this process. CHP units have been reported to exhibit an efficiency level of 90% (with 40% electrical and 50% thermal components) under ideal operating conditions [80].

Presently, CHP plants have gained significant popularity and have become a prominent feature of the biogas industry in Germany, the UK, Denmark, and the U.S. [73]. In the case of this technology, it is crucial to restrict H_2S concentrations in biogas to below 250 ppm to prevent engine corrosion in CHP units [81].

1.3.2.3 Injection into natural gas systems

The imminent depletion of natural gas reserves in several nations highlights the urgent need for biogas to serve as a viable substitute for natural gas. Biogas must undergo purification using effective methods such as membrane separation and absorption before it can be safely injected into natural gas grids to meet natural gas quality standards and prevent equipment deterioration. The differing criteria of the United States and the European Union (EU) serve as an example of how petroleum quality standards vary among nations. In the USA, the minimum methane (CH_4) content should range from 93.5% to 95.5%, while the maximum hydrogen sulfide (H_2S) content must be limited to 6–88 mg/m^3. Conversely, the EU mandates a minimum CH_4 content of 70–98% and a maximum H_2S content of 2–15 mg/m^3. These variations underscore the need to meet specific gas quality criteria depending on the country [82].

1.3.2.4 Compressed biogas formation

Typically, purified biogas, which has a methane (CH_4) content exceeding 97%, undergoes a conversion process to enhance its storage and quality for future utilization. One common approach involves compressing the biogas into bio-compressed natural gas (bio-CNG), also known as compressed biogas, at pressures ranging from 20 to 25 MPa [83]. Another method involves liquefying the biogas into LBG by subjecting it to extremely low temperatures of around -162°C [79]. Both these conversion techniques aim to reduce the volume of the biogas during storage while improving its overall product quality. Due to its similarities to compressed natural gas (CNG) and the depletion of fossil fuel stocks, bio-compressed natural gas (bio-CNG) is becoming increasingly popular as a car fuel. Since 1996, Sweden has developed significant expertise in using biogas as a vehicle fuel and has been at the forefront of developing standards for its use in this context [66]. In addition, this approach has emerged as a significant strategy in numerous European countries, including France, Germany, and the UK. When it comes to heavy vehicles, bio-compressed natural gas (bio-CNG) stands out as an environmentally friendly option, exhibiting reduced emissions of sulfur, lead, and greenhouse gases (GHGs) in comparison to compressed natural gas (CNG) and other conventional fuels [81].

1.3.3 Biogas utilization: second-generation

In the context of first-generation technologies, biogas is utilized as a fuel for the direct production of heat or electrical power, or it undergoes conversion into alternative forms without undergoing significant chemical transformations. In recent times, numerous researchers have redirected their focus toward novel avenues to unlock the full potential of biogas. Second-generation concepts, involving catalytic reactions, have positioned biogas as a valuable chemical feedstock, generating increasing attention and intrigue. In these catalytic reactions, biogas holds the potential to generate more valuable products with enhanced applicability in chemical engineering and various other domains. The second-generation approaches for utilizing biogas primarily involve the production of syngas/hydrogen, methanol, and higher hydrocarbons and alcohols. These methods aim to unlock the full potential of biogas by transforming it into higher-value substances, opening up new avenues for its utilization, and expanding its scope in various industries [74].

1.3.3.1 Syngas/hydrogen production

Syngas, predominantly composed of H_2 and CO, is a highly appealing and valuable gas compound with numerous potential applications in chemical engineering. It functions as a flexible foundational element for diverse chemical processes, encompassing the creation of Fischer-Tropsch oil, gasoline, methanol, and various other known chemical products. Syngas is typically generated through catalytic reforming reactions, which involve methods such as methane reforming with steam, dry, and partial oxidative. These reforming techniques enable the transformation of methane-rich biogas into syngas, unlocking its potential for diverse chemical engineering applications [72].

Several large-scale enterprises already produce hydrogen using steam reforming technology. According to reports, steam reforming is responsible for producing between 80 and 85 percent of hydrogen worldwide [84]. Along with the water-gas shift (WGS) reaction, the primary reaction, steam methane reforming, frequently occurs. Ni-based catalysts are commonly used, and recent years have seen a continued focus on the development of innovative catalysts with higher performance. For instance, Janewit Phromprasit et.al [85] created and synthesized Ni-Zr-CaO and Ni-Ce-CaO catalysts to enhance the efficiency of steam reforming. Daneshmand-Jahromi et al. [86] involved the examination of a Ni/SBA-16 oxygen carrier that had been subjected to modification with a yttrium promoter. The research resulted in the achievement of the highest methane (CH_4) conversion rate of 99.83% at a temperature of 650°C.

Dry reforming is an encouraging approach to convert the primary components of biogas, namely CH_4 and CO_2, into syngas as well as hydrogen production through a chemical reaction. The process typically demands a temperature range of 700-900°C due to its endothermic nature. Similar to steam reforming, catalysts hold significant importance in facilitating the production of syngas. The cost-effective nature of Ni-based catalysts has led to significant interest. However, the issue of carbon deposition can adversely impact catalyst performance. In contrast, noble metal catalysts such as Ru-, Pt-, and Rh-based catalysts have shown superior capability in managing the deposition of carbon and enhancing the rate of conversion process when correlated to catalysts made from non-noble metal [87].

The partial oxidative reforming process involves the partial oxidation of CH_4 using O_2, resulting in the production of syngas. The process of partial oxidative reforming entails partially oxidizing CH_4 with O_2, leading to the generation of syngas. This exothermic reaction predominates at temperatures below 600°C [84].

Tri-reforming is an approach that integrates partial oxidative reforming with both dry and steam reforming, aiming to achieve equilibrium between heat liberation and absorption. A recent research conducted by Chai et al. [88] resulted in the successful formulation of a nanocomposite catalyst with a Ni-foam structure, effectively enhancing the partial oxidative reaction. Moreover, the operational parameters for this catalyst were extensively examined. Hassan et al. [89] carried out an investigation in which they studied the partial oxidation of methane under supercritical water conditions, particularly at 658 K temperature and 26 MPa pressure. The findings suggested that increasing the O_2/CH_4 ratios could potentially enhance syngas production [90].

1.3.3.2 Bio-methanol production

The growing demand for methanol can be attributed to its significant value in the textile industry, pharmaceuticals, and other chemical engineering sectors. Methanol acts as an essential precursor in the manufacturing of various compounds such as dimethylformamide, acetic acid, formaldehyde, dimethyl ether, methylamine, and various other chemical blends.

In the last few years, methanol production via methane has gained significant attention, attracting numerous advanced studies. For example, in a publication in Nature, Shan et al. [91] presented their findings on CH_4 conversion to acetic acid and methanol using mononuclear Rh/zeolite and Rh/TiO_2 catalysts. Notably, this conversion process occurs under relatively gentle circumstances at a temperature of 150°C, facilitated by the presence of CO and O_2. In a publication highlighted in Nature, Snyder et al. [92] explored the complexities of the active site accountable for the hydroxylation of CH_4 at low temperatures within iron-containing zeolites. Their research yielded profound insights into the underlying mechanism of this process, offering a deeper understanding of the role played by iron-based zeolites in facilitating CH_4 hydroxylation at lower temperatures. In a significant scientific contribution published in Science, Sushkevich et al. [93] demonstrated that a zeolite catalyst containing copper successfully transformed CH_4 into methanol with remarkable selectivity, reaching as high as 97%. This ground-breaking research highlights the potential of copper-based zeolites as effective catalysts for the direct CH_4 transformation into methanol, offering new possibilities for sustainable chemical synthesis.

1.3.3.3 Advanced hydrocarbons and alcohol generation

A rising trend involves the exploration of biogas as a resource for producing enhanced hydrocarbons and alcohols. While microbiological methods are commonly employed for hydrocarbon production, the use of catalysts for example, Ni-Cr-Al-Co-based catalysts has also proven to be more effective in biogas conversion into more complex hydrocarbons [94]. Researchers have been actively exploring these approaches to enhance the conversion of biogas into valuable products with potential applications in various industries. While direct conversions of biogas into higher alcohols have been limited, prominent advancements have been achieved in the evolution of indirect techniques. These approaches involve the initial production of syngas through reforming processes, and then the syngas is converted into alcohols of greater complexity. Among these methods, syngas fermentation stands out as an auspicious technology in order to butanol and ethanol production. This process utilizes the path of acetyl-CoA within microorganisms to efficiently convert syngas into desired alcohols [84]. Furthermore, researchers have been investigating novel catalysts to enhance the production of higher alcohols. These catalysts include methanol synthesis catalysts modified with Fe, Ni, or Co, as well as Mo-based catalysts modified with alkali. These studies aim to enhance the effectiveness and process selectivity for higher alcohol synthesis [95].

In conventional first-generation approaches, biogas is typically utilized directly. However, recent advancements in technology have shifted the focus towards exploring more valuable applications of biogas, opening up broader research prospects. Among these innovative techniques, dry reforming has emerged as a highly competitive pathway. It offers the advantage of utilizing both CO_2 and CH_4, the primary biogas constituents, without the need for their prior separation. This eliminates the costs associated with gas separation and helps avoid CO_2 waste, making dry reforming an attractive and sustainable option.

1.4 Present status of hydrogen production

Most researchers and specialists adopted that hydrogen holds excellent potential as energy in the future. Two factors, such as economic growth and industrialization of developing countries have grown the world's energy demand. Balat [96] reported the world H_2 production was nearly 44.5 million tons per annum or 500 Bm^3 by the end of the year 2008 and the estimated demand for energy will touch nearly 600- 1000EJ up to 2050 [97]. Hosseini [97] reviewed the H_2 fuel cell as favourable technology for future energy supply. Currently, resources of fossil fuels such as coal, natural gas, and crude oil provide approximately 80% of planetary energy demand [98]. It is assumed that consume petroleum in each day nearly 18.3 million barrels can replace hydrogen fuel cell-powered vehicles (cars and light trucks) by the year 2040. It is also accepting that hydrogen-based powered vehicles are more efficient (2.5 times) than improved vehicles of gasoline and to full fill, the petroleum reduction would meet the requirement of hydrogen nearly 150 million by 2040. The overall net energy can be saved by the use of petroleum approximately 11 million barrels /day from all H_2 production through petroleum reforming [99]. Rohland et al. [100] focused 36% shares from renewable resources by 2025 increased to world total energy 69% shares by 2050 from the same energy and 11% by 2025 grown to 34% from hydrogen up to 2050. Nadaleti et al. [101] highlighted Brazil's potential and economic viability in producing biogas-derived hydrogen from urban waste. The country can produce 457 million cubic meters of hydrogen annually from wastewater treatment plants (WWTPs) and 2.87 billion cubic meters per year from landfills. This hydrogen from landfills could replace 0.64% of the national car fleet and 4.82% of the national bus fleet. By 2050, the International Energy Agency (IEA) projects that the Net Zero Emissions scenario will require 530 million tonnes of hydrogen for the energy sector. Of this demand, 60% will be met through electrolytic processes powered by green energy sources such as wind, solar, hydro, and biomass [102].

1.5 Techno-Economic Analysis of Biogas Conversion

An economic analysis of converting biogas into energy in the setting of small pig farms in Thailand was carried out by Pipatmanomai et al. [103]. The analysis took into account a 45% government subsidy for these farms, which had 255 puppies and 170 reproduction piglets.

Without H_2S removal, the system had a payback period of around 4 years, but with H_2S removal, it extended to approximately 8 years. The payback period is significantly influenced by the cost of electricity and the subsidy from the government. Although incorporating H_2S removal can result in significant operational expenditures for the suggested setup, it is strongly advised to reduce pollution gas emissions and avoid rusting of the reactor unit [103]. To enhance conversion efficiency, an alternative approach involves utilizing biogas for generating products other than electricity. A small-scale biogas conversion system investigation was done by White et al. [104] on numerous farms in Ontario, Canada. The results showed the potential for running economically sound and appealing biogas systems on beef operations with over 78 animals and dairy farms with more than 33 animals.

Hydrogen possesses a high calorific value, making it a valuable fuel option. Its utilization for energy purposes offers significant benefits as carbon emissions and greenhouse gases are zero. However, it's essential to remember that hydrogen is extremely flammable and might explode.

Madeira et al. [105] performed an economic and exergetic assessment of transforming biogas made from cassava wastewater into hydrogen. The estimated production cost for biogas was \$0.0518 per kilowatt-hour (kWh), while for hydrogen; it was \$0.13 per kilowatt-hour (kWh).

A techno-economic analysis of producing hydrogen from biogas was done by Lache'n et al. [106]. Water, energy, catalyst, biogas, cobalt ferrite, membrane, and iron oxide were among the raw materials taken into account by the study. A yield of 68% pure hydrogen was produced by the biogas conversion process at a temperature of 575°C.

Depending on the exact working temperature between 475 and 575°C and predicted the production cost from \$4.49 to \$16.85 per kilogram (i.e., 4€ to €15 per kilogram).

In general, conversion operations for biogas can result in the production of wax, heat, hydrogen, methanol, liquid fuel, and compressed natural gas (CNG). Depending on the precise kind of product produced, the total efficiency of biogas conversion might range from about 35% to 80%. The economic feasibility of biogas conversion is typically illustrated by a standard payback period ranging from 4 to 8 years.

The economic feasibility is affected by a number of factors, including the price of raw materials, the plant's feed capacity, government subsidies, and the market price of the finished product. Using a tri-reforming method and FTS-based technology, T2C-Energy LLC, situated in Tampa, Florida, has completed a pilot-scale test that successfully converted landfill gas (LFG) into liquid fuels. Despite the success of the pilot test, commercial operations are still ongoing.

Two companies, Velocys in Plain City, Ohio, and Fulcrum Bio Energy Inc. in Pleasanton, California, have created cost-effective technology to convert municipal garbage into liquid fuels (carbon-free). Although the majority of biogas is now used to generate electricity or turned into compressed natural gas (CNG), there are currently no commercial operations using biogas to produce liquid fuels or chemicals. The biogas reforming sector has a number of difficult challenges, including the need to keep costs down in order to make these procedures more profitable. Techno-economic assessments shown in Table 1.4 provide a summary of the economic viability of using and applying biogas. These studies, which may be carried out for both small-scale and large-scale systems, make use of tools like Aspen Plus and Aspen HYSYS v 9.0. Low conversion efficiency, which is, barring special instructions, calculated based on energy recovery, is a significant barrier in biogas application.

Table 1.2: Techno-economic analysis of biogas conversion application at different scales

Product	**Conversion Route**	**Product Price**	**Payback Period (Year)**	**Plant size/Farm**	**Conversion Efficiency (%)**	**Ref.**
Electricity	Engine with electric generator	0.067 US$)/kWh	4-8	Pig farm at small-scale	20.8	[103]
Electricity	Use an engine		10	Cattle farms at small scale	35	[104]
Hydrogen	PSA, shift reaction, and steam reforming	-	7	Wastewater plant at Large-scale (producing approx.4019 m^3 /day biogas)	79	[105]
Hydrogen	Steam-iron method and dry reforming of biogas	Approx.9.99 US$)/kg	-	Model of the plant (1,350 kg/h biogas)	>45	[106]
Hydrogen	Biogas auto-thermal reforming	-	-	Plant biorobur (producing 100 Nm^3 of H_2 per hour)	65	[107]
Liquid Fuel	Tri-reforming and FTS	Approx.0.79 US$)/ kg (diesel)	Not economically feasible	Model of the Plant (27.22 kg/s of natural gas with higher CO_2 content)	54 (carbon conversion efficiency)	[108]
Liquid Fuel	Hydrocracking, FTS, cleaning and reforming of biogas, and distillation	-	-	Model of the plant (2,000 Nm^3 per hour of biogas)	54 (mass basis)	[109]
Liquid Fuel	Tri-reforming and FTS	-	-	Plant model at commercial scale (2,500 scfm LFG)	45	[110]
Methanol	Methanol production, biogas cleaning, and reforming	0.9 US$)/gallon	-	Model of the plant (12,080,000 m^3 of	-	[111]

				biogas annually)		
Methanol	Methanol synthesis, biogas cleaning, and reforming	Approx.400 US$)/ metric ton	Not economically feasible	An enormous plant produces 5,900 Nm^3 of biogas every hour.	-	[112]
Compressed Natural Gas	Adding pressure to the gas and removing impurities	-	-	Model for a modest landfill	-	[113]
Wax	Steam reforming of biogas, FTS, and separation of products	Approx.2.77 US$)/kg	Approx.7	Plant model at small scale (generating approx. 200 kg/h biogas)	56	[114]

1.6 Motivation for Work

- The motivation for hydrogen production from biogas lies in its potential to offer renewable, clean energy, mitigate climate change, enhance energy security, and drive sustainable development.
- Hydrogen production from biogas reforming has many unrevealed areas where significant research effort is required. Several researchers have conducted experimental investigations to find the effective operating conditions for smooth functioning of the system but very little work has been done in the area of simulation. The demands of present era in any research investigation are changing. Simulation work, primarily validated with the benchmark experimental work conducted by learned researchers, has become indispensable in finding the best suitable operating conditions. The motivation for the present study is to simulate the physical problem in a well-validated and effective manner with less effort time and resources to reduce the dependence on expensive experimental set-up and empirical correlations that are being presently used.
- Simulation and modelling optimize biogas reforming for hydrogen production by exploring various conditions, designs, and catalysts to maximize yield and

minimize energy use. They drive innovation, enabling virtual testing of new concepts and accelerating the development of advanced hydrogen production systems. Overall, they address optimization, understanding, scale-up, integration, assessment, analysis, policy support, and innovation for a sustainable energy future.

1.7 Thesis Layout

The thesis has been organized into five chapters. An overview of each chapter is given as follows:

Chapter 1: Introduction

In this chapter, a detailed introduction to hydrogen production from biogas has been presented. A brief description with an overview and modes of global H_2 production are discussed. Further, a detailed description of the status of hydrogen production and then a discussion of Hydrogen as a promising fuel, history of hydrogen, characteristics, safety, and category of hydrogen are delivered. The change of modes of flow is discussed. The biogas potential, utilization of biogas, and biogas purification methods are also described. Finally, the motivation for the present research is presented.

Chapter 2: Literature Review

Chapter 2 describes a literature review of the main possibility of hydrogen production methods from biogas and a comparison between them is summarised. The findings by various researchers and scientists in the field of research work are presented. The review includes experimental and simulation approaches undertaken from time to time, along with the development of numerical solutions to the problems of biogas reforming for hydrogen production. The identification of gaps in the literature and the objectives of the present research are presented.

Chapter 3: Methodology

Chapter 3 presents a detailed description of the 0-D mathematical model developed to analyse and predict the hydrogen yields at different temperature using a SMR and

WGS reaction through a batch reactor using COMSOL software. It also describes the simulation model, procedure of simulation work, model assumptions, governing equations, and kinetic models.

Chapter 4: Results and Discussion

In this chapter, the results of the tested 0-D model under different operating conditions (Temperature, pressure, CH_4/ CO_2, S/C ratio, CO_2/CH_4, H_2/CO) are analysed and discussed. The current model has been validated with experiment as well simulation data for steam methane and biogas reforming process. The experimental data from the literature on work done under similar operating conditions was used to support the majority of the results. A study is conducted to determine the ideal operating conditions.

Chapter 5: Conclusion, Future Scope and Social Impact

Finally, Chapter 5 summarizes the conclusions from the study, presents the scope for further research, and social impact.

CHAPTER 2

LITERATURE REVIEW

The most prevalent element on Earth is hydrogen (H_2), which is made up of two atoms. Under normal circumstances, the gas is odourless and colourless. Its name (derived from Greek) means "water-former" because of its role in burning to produce water [115]. Hydrogen is always present in other substances like natural gas, coal, oil, or water because it mixes well with other chemical constituents. It can also be found in biomass that is naturally occurring, such as plants and animals. Hydrogen is regarded as an energy carrier as a result [116]. It can be employed to transport as well as supply energy. The production, storage, and distribution of H_2 come with prohibitive costs and technical difficulties [115].

The primary application of hydrogen lies in water creation. Additionally, it serves as a crucial industrial product employed in synthesizing various compounds, particularly methanol and ammonia. Ammonia, the primary ingredient in fertilizer, is formed through the reaction between nitrogen and hydrogen. Approximately half of the world's hydrogen production is utilized in the production of ammonia [117].

Pure hydrogen can also be employed as a power source. For instance, hydrogen and oxygen atoms are combined in hydrogen fuel cells to generate energy. When these two things come together, electricity is produced. The efficiency of a fuel cell is two to three times higher than that of an internal combustion engine powered by petrol. In an engine, only water vapour is released when H_2 is burned. On the other hand, when fossil fuels are burned, CO_2 is released into the atmosphere, raising its concentration. Hydrogen will therefore be essential to the required switch from fossil fuels to a sustainable energy system, and it is anticipated to grow into a major fuel that will significantly improve the quality of the air in the atmosphere [118].

2.1 Hydrogen production methods from biogas

An enormous variety of approaches are possible for producing H_2 based on the raw materials utilized. The important methods can be divided into two main categories, namely, conventional and advanced methods from biogas. Fig. 2.1 shows the various methods for hydrogen production via biogas.

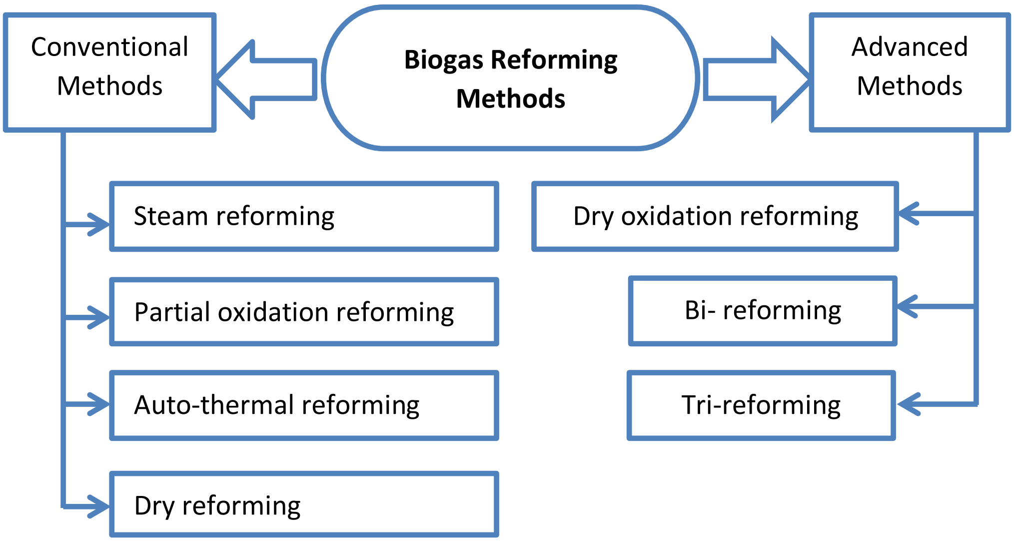


Fig. 2.1: Hydrogen production methods from biogas reforming process

There is an interesting way that methane is the part of biogas component and biogas is generated from waste materials as a renewable source. Therefore, biogas reforming seems renewable energy from conventional techniques for the production of hydrogen [119].

To produce pure hydrogen, additional steps are included in any kind of reforming process. A conversion reactor is utilized for converting the CO into CO_2 by using shift reaction [13]. The final process for hydrogen purification is done in a separate unit by pressure swing adsorption (PSA) [119]. H_2 could be obtained through the methane or reforming of biogas in a various temperature limit (873–1273K) over reversible reactions and exothermic or endothermic. The reforming reactions are done by low pressure and high temperature. In several kinds of reforming methods, biogas is responded to along with representatives like oxygen or air and steam to generate syngas with H_2 and along with other gases [15].

There are some purification techniques available for removal of toxic and undesirable substances which is present in biogas: physiochemical and biological treatment [13]. Fig. 2.2 presents the important steps for the production of H2 from biogas. Consequently, the biogas reforming reactions are parallel to natural gas (CH4) reforming.

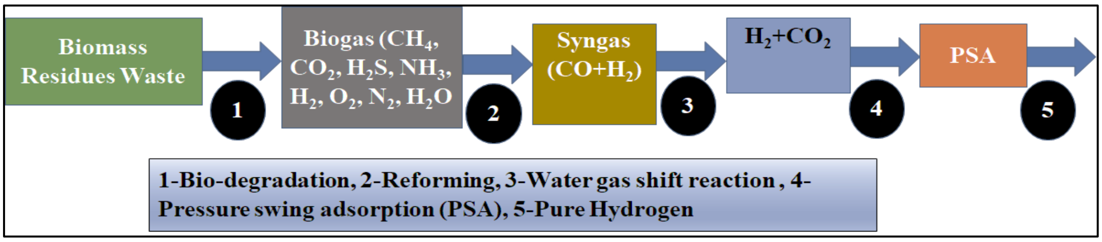


Fig. 2.2: Flow process of hydrogen generation from biogas [120]

2.1.1 Conventional methods

As shown in Fig. 2.1, fossil fuels are the first category of processes, which includes the methods of hydrocarbon reforming. Hydrogen gas can be produced from hydrocarbon fuels through basic technologies such as Steam reforming (SR), Partial oxidation reforming (POR), Auto-thermal reforming (ATR), and Dry oxidation reforming (DOR).

Carbon monoxide (CO) is produced in large quantities by these methods. Preferential oxidation (PrOx) or methanation reactions come next, after which one or more chemical reactors are utilised to primarily transform CO into carbon dioxide (CO_2) via the WGS. Furthermore, the elimination of sulphur, which is included in the majority of fossil fuels, is a major undertaking in the development of the hydrogen-based economy. Consequently, the process of desulphurization will also occur [115].

2.1.1.1 Steam reforming (SR)

Steam reforming is a kind of technique to produce hydrogen through different feedstock (higher hydrocarbon, acetone, ethanol, methanol, ethane and methane) with different catalysts. Methane is a more favourable feedstock to others because of better by-product formation [121]. This technique can produce hydrogen in multiple stages, as shown in Fig. 2.3.

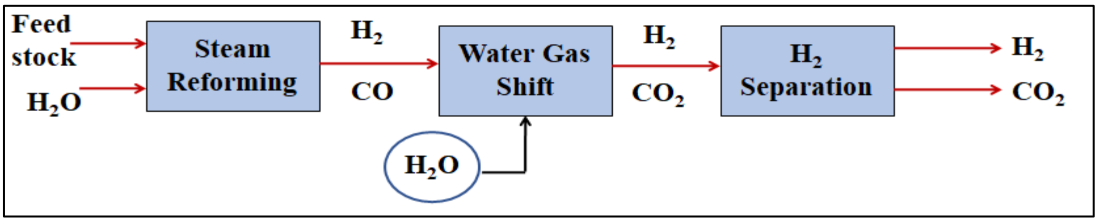


Fig. 2.3: Flow process of multistage for production of hydrogen [121]

Steam methane reforming of natural gas is a well-established technology that is used to generate hydrogen with the presence of steam through the conversion of hydrocarbon and the first industrial application of steam methane was in 1930 [122]. The steam methane reforming process involves catalytically reforming or (syn-gas) production, gas purification or methanation and water gas shift. It is operated at a higher temperature range of 700-900^{o}C with the endothermic process [123]. The general equation for SMR from biogas or methane is mentioned below [124-126].

$$CH_4 + H_2O_{(Steam)} \rightarrow CO + 3H_2 \qquad \Delta H_{298K} = +206.2\ (kJ/mol) \qquad (2.1)$$

In this process, methane molecule reacts with steam molecule in the presence of a suitable catalyst to generate syngas and reaction takes place at high temperature. This process includes steam reforming (SR), water gas shift (WGS) and combined steam reforming reactions [120]. First, methane is reacted with water vapor in SR to form syngas containing carbon monoxide (CO) and hydrogen (H_2) in the presence of an appropriate catalyst (Equation 2.1). Syngas gas (mixture of CO+H_2) is then cooled to a temperature between 300°C-500°C and fed into the WGS reactor, where carbon monoxide (CO) reacts with water (H_2O) to reduce the CO content and produce carbon dioxide (CO_2) and hydrogen (H_2) (Eq. 2.2) [120]. Additionally, combined or direct steam reforming reaction is sum of SR and WGS reaction (Eq.2.3).

Water gas shift reaction:

$$CO + 2H_2O_{(Steam)} \rightarrow CO_2 + 2H_2 \qquad \Delta H_{298K} = -41.2\ (kJ/mol) \qquad (2.2)$$

Combined reaction:

$$CH_4 + 2H_2O_{(Steam)} \rightarrow CO_2 + 4H_2 \qquad \Delta H_{298K} = +165\ (kJ/mol) \qquad (2.3)$$

The ratio of H_2/CO is close to 3, which means higher yield of H_2 (above 70%). Methane requires a high temperature (840-950°C) for reaction, but a higher temperature can be managed by a suitable catalyst [127]. Most industrial steam reforming units use ceramic-based nickel catalysts operating at temperatures of 700-1000°C and a pressure between 15-30 atm [128].

The main detriment of this process is that enormous heat is required to shift the equilibrium reaction rightward with the formation of H_2 and CO. The reason is that the reaction is endothermic and requires an external heat source [129].

Hydrogen production process from steam reforming of biogas is considered a promising alternative route to steam methane reforming with similar efficiency [13] and presented a detailed assessment of hydrogen production method using biogas [130]. Noble metals offer a higher conversion rate with low temperatures than Ni metal, which offers a high conversion rate with high temperatures.

The main challenge in developing catalysts in hydrogen production via biogas is avoiding deposition of carbon in energetic phase to raise its life. Furthermore, it involves improving the catalyst resistance to poising sulphur content and increasing catalyst surface area in order to promote activity [21].

2.1.1.2 Partial oxidation reforming (POR)

Partial oxidation is another standard route to H_2 production, which uses oxygen and hydrocarbon or methane fuel. The syngas (H_2 + CO) and a mixture of CO_2, N_2, H_2O, and a small amount of products such as methane are produced through partial oxidation. In a general way, oxidizing fuel is a requirement of energy balance in the presence of air. If sufficient air is not added, the fuel will oxidize incompletely, yielding mainly CO and H_2. However, it provides sufficient air yielding, mainly CO_2 and H_2O as well. However, if the air present becomes half, at that time the chemical equilibrium will predict the mixture of CO and H_2, along with small traces of CO_2 and H_2O [131].

Two-step reactions consist of partial oxidation of methane. In the first step reaction, total methane combustion in the presence of O_2 to get CO_2 and H_2O. This is now followed by steam reforming of unreacted methane and CO_2 to receive syngas. The reaction accumulates with the reaction of water gas shift to obtain CO_2 and H_2O. The reactions of reforming are endothermic, however, but total oxidation of methane is an exothermic process [132]. POR is a methane reforming process for cost-effective H_2

production, involving exothermic reactions with air or oxygen. The general equation of partial oxidations reaction is as follows.

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad \Delta H_{298K} = -35.6 \text{ (kJ/mol)} \qquad (2.4)$$

In this process, methane molecule is partially oxidized to generate a mixture of CO and H_2, which requires temperature between 700-900°C at atmospheric pressure, ratio of H_2/CO to nearly 2 and H_2 yield almost 67% and reduces the soot formation [133].

One important characteristic to consider during processing is the molar ratio (O_2/CH_4). A higher molar ratio (O_2/CH_4) results in complete combustion by fuel, as seen in Eq. (2.4), which is an exothermic reaction type that increases the temperature of reaction, which can initiate the development of hot spots and coke on the catalyst surface in the reactor and decrease the yield of H_2 compared with SR process [13].

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H_{298K} = -801.7 \text{ (kJ/mol)} \qquad (2.5)$$

Nickel-based catalysts are regularly used for POR reactions. Several selective and highly active catalysts for POR methane have been described, such as mixed crystals of NiO-MgO, Ca-Sr-Ti-Ni and Ni-Mg-Cr-La-O. Among the most suitable catalysts for POR reaction, the Ru-based catalyst has excessive coke resistance at very high temperatures. Since ruthenium oxide has good thermal and chemical stability and more resistance to chemical corrosion, it increases the selectivity of H_2 production and conversion of methane [134].

Partial oxidation of biogas has several benefits over SRB, including compactness, less sensitivity, and better response time for fuel variants. The reactors of partial oxidation increase interest in energy conversion for high temperatures utilized in fuel cell. It is a faster chemical reaction than SRB due to its exothermic reaction [135].

Hydrocarbon (HC) conversion to syngas via partial oxidation process can occur at high temperatures lacking catalysts. Conversely, the operating temperature will be significantly decreased using catalyst. Most of the studies via partial oxidation catalysts are same as catalyst used in steam reforming process as noble metal and transition metallic elements such as Ni, Fe and Co [136].

2.1.1.3 Auto thermal reforming (ATR)

This approach is combined with steam reforming and POx methods in an adiabatic reactor. This technique also provides the neutral reaction of pairing the endothermic as steam reforming and exothermic as partial oxidation. H_2 yield is low than steam reforming, a better alternative option for fuel reforming due to neutral reaction thermodynamically [137].

To mitigate the disadvantages of the endothermic nature of SR process and low H_2 recovery from POR process, auto-thermal reforming (Eq. 2.6) was developed as combined group of the two processes [21].

$$\mathrm{CH_4} + \frac{1}{2}\mathrm{H_2O_{(Steam)}} + \frac{1}{4}\mathrm{O_2} \rightarrow \mathrm{CO} + \frac{5}{2}\mathrm{H_2} \qquad \Delta\mathrm{H_{298K}} = 0\ (\mathrm{kJ/mol}) \qquad (2.6)$$

The term ‘Auto-thermal’ denotes no need for heat required through the external source for the reaction. It manages the demand of heat of endothermic reaction by releasing heat through the exothermic reactions and can be reflected as an effective process for H_2 production [122]. Partial oxidation and methane reforming reactions are injected by steam and oxygen simultaneously. The higher H_2 yield is around 74%, with the ratio of H_2/CO close to 2.8 [119].

In an ATR reformer, partial oxidation reaction consists in the thermal zone and producing heat to steam reforming occurs in the catalytic zone [24]. The major drawbacks associated with the ATR process are soot formations in combustion zone that feed steam to cause upturns in capital and operating cost of reformer [21]. Higher plant efficiencies achieved by biogas reforming via ATR process are 75%, operating temperature range varies from 500 -700°C and molar ratio of O/C from 0.80-0.90. Generally, maximum temperate is applied for the process since low temperature raises molar ratio H_2/CO due to the enlarged content of the non-reacted CH_4. Additionally, a low temperature is suitable for further removal of CO [138].

Number of research is limited to auto-thermal reforming of biogas (ATRB). Araki et al. performed ATRB model biogas with catalyst (30wt% Ni/Al_2O_3) and reported the effect of the ratio of S/C and O_2/C at the same temperature. Optimal results were achieved with steam-to-carbon (S/C) ratios of 1.5-2.5 and oxygen-to-carbon (O_2/C) ratios of 0.44-0.56 at 750 °C, achieving a 90% conversion of CH_4 [139].

2.1.1.4 Dry reforming (DR)

In the DR process, methane reacts with CO_2 to generate CO and H_2 and reaction temperature increases above 640°C. The general equation for dry reforming process is as follows [134].

$$\mathrm{CH_4 + CO_2 \rightarrow 2CO + 2H_2} \qquad \Delta \mathrm{H_{298K}} = 247\ (\mathrm{kJ/mol}) \tag{2.7}$$

The reaction of DR is the conversion of methane and carbon dioxide into syngas. In addition to reactions, other chemical reactions can also take place at the same time during the process. A typical side reaction is reverse water gas shift (RWGS) (Eq.2.8) which can reduce the ratio of H_2/CO in syngas products. Though it may be undesirable in syngas production, this reaction helps establish the correct H_2/CO ratio for higher hydrocarbon production [140].

$$\mathrm{CO_2 + H_2 \leftrightarrow CO + H_2O} \qquad \Delta \mathrm{H_{298K}} = 41\ (\mathrm{kJ/mol}) \tag{2.8}$$

Particular side reaction contributes formation of coke during the process. The methane (CH_4) decomposition presented by Eq.9, wherein methane decomposed completely toward solid carbon over the catalytic surface and emitted H_2. The CO disproportionation is termed as Boudouard reaction, presented in Eq.10. The hydrogenation of CO_2 and CO is in Eq. (2.11 and 2.12), respectively, wherein CO_2 reacts with H_2 to develop solid carbon (C) and water vapor (H_2O) [141].

$$\mathrm{CO_4 \leftrightarrow C + 2H_2,} \qquad \Delta \mathrm{H_{298K}} = 74.9\ (\mathrm{kJ/mol}) \tag{2.9}$$

$$\mathrm{2CO \leftrightarrow C + CO_2,} \qquad \Delta \mathrm{H_{298K}} = -172.4\ (\mathrm{kJ/mol}) \tag{2.10}$$

$$\mathrm{CO_2 + 2H_2 \leftrightarrow C + 2H_2O,} \qquad \Delta \mathrm{H_{298K}} = -90\ (\mathrm{kJ/mol}) \tag{2.11}$$

$$\mathrm{CO + H_2 \leftrightarrow C + H_2O,} \qquad \Delta \mathrm{H_{298K}} = -131.3\ (\mathrm{kJ/mol}) \tag{2.12}$$

There is a need for an external heat source due to endothermic reaction and also this process is attractive for biogas because of two basic elements involved in raw biogas such as CH_4 and CO_2. This process leads to molar ratio H_2/CO of nearly 1 and yield of H_2 of approximately 50% [13]. The main problem with DR is that coke can build up, deactivate the catalyst and blockage the reactor. From previous processes, catalytic materials with H_2 selectivity and thermal stability have been used and countless interests to reduce carbon deposition [13]. Although catalysts based on Ru, Rh, and Pt improve the production of H_2, they have not received industrial development due to limitations of availability and their high cost, while catalysts based on Ni and Co are widely used [116,138]. Circulating bed reactors and regenerators is a technical process often used to deposit coke on catalysts to avoid catalyst deactivation during continuous operation. The coke formation accumulated on the catalyst surface is removed by incineration, and the generated heat can be used for endothermic dry reforming [138].

This method's main benefit is using greenhouse gases such as CH_4 and CO_2. This process uses CO_2 for reaction and provides heat source from external due to its endothermic reaction in nature. The key problem of DR process is the development of coke over the catalyst surface during the process due to deficient steam and methane reaction, and this coke formation can blockage the rector. The research on Hydrogen production from DR method has been directed toward thermal stability and growth of carbon tolerant and well-suited noble metallic elements such as Pt, Ru and Rh for DR process, but these metals are more costly. Hence it becomes expensive and unattractive for industries. On the contrary, Ni-based catalysts have been invested for availability and cost factors [21]. The need for high temperature for DR reaction and high carbon content as in reactant makes those metals disposed to deactivate through carbon deposit and sintering. Various researchers investigated bimetallic catalysts in dry reforming of biogas (DRB) process as Ni-Co [142], Ni-K [143] and Ni-B [144].

2.1.2 Advanced methods

In the recent period, a lot of advancement has been achieved in optimizing reaction conditions and understanding the catalysis mechanism, leading to notable advancements in the performance of biogas dry reforming. These developments have effectively enhanced the process efficiency. The proper selection of metal-support pairing for catalyst formation for example, Ni-Zr on CeO_2 Substrate, maintaining the pressure at 1 bar, operating temperature above 800°C, and fine-tuning the various reactants composition are crucial parameters that significantly impact the stability of catalytic efficiency and minimize the deactivation during the biogas dry reforming process. These considerations are important key in ensuring the performance and durability of the catalyst for this application.

2.1.2.1 Dry oxidation reforming (DOR)

DOR process has been developed by combining two processes dry and partial oxidation reforming of methane and used for controlling the carbon deposition on catalyst surface. The general equation (Eq.2.13) of DOR is following [13,138].

$$\mathrm{CH_4} + \frac{1}{2}\mathrm{CO_2} + \frac{1}{4}\mathrm{O_2} \rightarrow \frac{3}{2}\mathrm{CO} + 2\mathrm{H_2} \qquad \Delta\mathrm{H_{298K}} = 123.5\ (\mathrm{kJ/mol}) \qquad (2.13)$$

Combined feed of O_2 with CH_4 and CO_2 offers the following additional benefits: Minimized overall energy consumption, increased conversion of CH_4 and enlarged yield of product at low temperatures, increased stability of catalyst and better resistance of deactivation and managed the ratio of H_2/CO by adjusting the O_2 flow condition [145]. This route additionally diminutions the reaction of energy demand as the exothermic partial oxidation system releases heat and is more useful for dry oxidation process (endothermic). The ratio of H_2/CO correspondingly improves and generates H_2 yield of approximately 60% [138].

2.1.2.2 Bi-reforming

The process of reforming methane using both CO_2 and steam is known as dual methane reforming (DMR), and it is referred to as "bi-reforming" in this context. It describes the conversion of a mixture containing CH_4, CO_2, and H_2O into syngas. DMR presents intriguing possibilities for various setups, including the biogas steam reforming and the utilization of CO_2 through its integration into the reforming process of natural gas or methane. In this system, both CO_2 and H_2O serve as oxidants, playing crucial roles in the reaction [146]. The combined reaction of bi-reforming is shown by equation 2.14.

$$2CH_4 + CO_2 + H_2O \rightarrow 3CO + 5H_2 \qquad \Delta H_{298K} = 453\ (kJ/mol) \qquad (2.14)$$

Similar to dry reforming, bi-reforming possesses the capacity to employ CO_2 for the generation of more valuable components within syngas as well as H_2 production. Bi-reforming can also be used to produce syngas from natural gas that contains a lot of CO_2, Additionally; it may make it possible for CO_2 to be converted from flue gases via the burning of fossil fuels [147]. Bi-reforming, as opposed to dry reforming, produces an H_2/CO ratio of 2/1, which is perfectly compatible with subsequent industrial operations. Additionally, according to the information that is currently accessible, one advantage of bi-reforming is its ability to adapt the H_2/CO ratio flexibly by changing the H_2O/ (H_2O+ CO_2) ratio in accordance with the various requirements of downstream applications [148,149].

Coke prevention in biogas reforming presents several challenges, including the need to operate the reaction at lower temperatures to save energy and prevent catalyst deactivation, the variability in H_2O content originating from different biogas sources, and the requirement for more advanced catalysts. To prevent coke formation in biogas reforming, it is necessary to operate at reaction temperature (above 500°C) and maintain a higher ratio of (CO_2 + H_2O): CH_4. The introduction of H_2O into the biogas stream is effective in reducing coke formation as it facilitates reactions that lead to the destruction of coke [150].

2.1.2.3 Tri-reforming

Tri-reforming, which integrates CO_2 dry reforming, methane oxidation, and steam methane reforming, has developed a revolutionary strategy to reduce CO_2 emissions. This combined process offers a promising approach to mitigating CO_2 emissions [151]. The general equation for tri-reforming reforming is as follows.

$$CH_4 + CO_2 + H_2O + \frac{1}{2}O_2 \rightarrow 4CO + 7H_2 \qquad \Delta H_{298K} = +417\ (kJ/mol) \qquad (2.15)$$

A fundamental distinction between tri-reforming and CO_2 reforming is the integration of O_2 and H_2O within the tri-reforming procedure. This inclusion of O_2 and H_2O helps minimize carbon formation on the catalyst, setting it apart from CO_2 reforming [152].

Additionally, the resulting H_2/CO ratio in tri-reforming reactions typically falls within the desired range of 1.5/2, which is highly advantageous for a range of chemical production techniques that make use of synthesis gas [153]. Considerable focus has been dedicated to advancing new catalysts and investigating optimal operational parameters in the domain of tri-reforming.

By introducing supplementary components such as O_2 and H_2O into the biogas, it is possible to accomplish the expected transformations of reactant and attain the preferred ratio of H_2/CO. There is a big challenge in sustaining a high-performing reforming operation while keeping the low costs of processing [150].

The researchers achieved product compositions rich in H_2 and CO by operating at relatively low pressure. High temperature and low-pressure conditions were favorable for achieving higher conversion of CO_2 and a higher rate of H_2 production during the process. Moreover, increasing the ratio of O_2/CH_4 ratio led to a substantial enhancement in the conversion of CH_4, particularly at temperatures below 850°C [154].

During the tri-reforming process, methane acts as a limiting reactant. As the H_2O content increases, the transformation of CO_2 reduces due to the higher chemical reactivity of H_2O with CH_4 compared to CO_2. Increased quantities of O_2 and H_2O present in the feed could potentially cause a decrease in both CO_2 conversion and H_2 yield. To enhance CO_2 conversion, it is beneficial to operate at relatively low pressure. Nonetheless, transforming syngas from biogas reforming into fuels such as liquid hydrocarbon using the Fischer-Tropsch synthesis (FTS) requires high pressure such as 20 bar [154].

2.1.3 Comparison of Hydrogen Production Technologies

In this section, a comparison of the major hydrogen production processes is presented. The merits and demerits of each process are summarised in Table 2.1.

Table 2.1: Merits and demerits of H_2 Production from biogas reforming

Technology	**Merits**	**Demerits**	**Remarks**
Conventional Methods			
SR	✓ Carbon formation is low. ✓ Purity of H_2 is high. ✓ Yield of H_2 is high. ✓ No need O_2 for operation.	✓ Costly catalyst ✓ Need higher temperature ✓ Need to add H_2O (vapour) ✓ Highest CO_2 emissions are high. ✓ Air emissions are also high. ✓ Need huge size reformer.	✓ Mostly used in industry applications. ✓ Requires removing CO_2 from biogas.
Partial oxidation	✓ Operating temperature is relatively low. ✓ Energy efficiency is high. ✓ Lower methane slip. ✓ No need for feedstock desulfurization.	✓ Hot spot seems during increasing temperature on catalyst surface. ✓ Low Co selectivity can oxidize CH_4 completely. ✓ Low H_2 yield compares to SR. ✓ H_2/CO ratio is low. ✓ Highly exothermic reaction leading to catalyst deactivation by formation of hot spots.	✓ very few industrial applications ✓ Unite with other methods. ✓ Need air or O_2. ✓ Catalyst deactivates due to exothermic reaction.
ATR	✓ No requires external heat. ✓ Low cost. ✓ Energy efficiency is high. ✓ Main content can be used as CH_4 and CO_2 from biogas. ✓ Reformer size is compact.	✓ Need various types of catalysts. ✓ Hydrogen yield is low compared to SR. ✓ Need control of complex processes. ✓ Need air or O_2. ✓ Separate unit is required for using oxygen.	✓ Combination of SR and POR process. ✓ ATR improves temperature control and decreases hot spot formation and increases temperature control. ✓ Self-sustaining method.
DR	✓ Conversion efficiency is high. ✓ Both greenhouse gases can be used from biogas as CH_4 and CO_2 . ✓ Environment friendly using biogas.	✓ High formation of carbon. ✓ Operating temperature is high. ✓ Expensive catalyst. ✓ Reformer size is large. ✓ Commercial experience is low.	✓ Biogas is much more suitable for this process as both content (CH_4 and CO_2) are available.
Advanced Methods			
ODR	✓ Formation of carbon is low. ✓ Conversion efficiency is high. ✓ Improved deactivation resistance and catalyst stability. ✓ Decreased total energy	✓ Production of CO_2 is more. ✓ Expansive catalyst. ✓ Limited availability of catalyst. ✓ Another metal is needed for catalyst stability.	✓ Industrial application is low. ✓ Combination of DR and POR process. ✓ Exothermic or endothermic reactions depend on O_2 feeding.

Technology	Merits	Demerits	Remarks
	involved.	✓ Complicated control process.	
Bi-Reforming	✓ Enhanced hydrogen production ✓ Efficient use of biogas ✓ Reduced carbon emissions ✓ Reduction of greenhouse emissions ✓ Help to reduce coke deposition	✓ Low CO_2 conversion ✓ Energy consumption is high ✓ Dependency on biogas quality ✓ Complex process control	✓ Combination of SR and DR ✓ CO_2 utilized ✓ Active research and development for industrial implementation
Tri-Reforming	✓ Increase yield of hydrogen ✓ Carbon utilization ✓ Reduced catalyst deactivation ✓ Cost effectiveness ✓ Required high temperature ✓ Effectively prevent coke formation	✓ Maintain O_2 amount ✓ Reduced CO_2 due to higher H_2O amount ✓ Complex process ✓ Technical challenges such as catalyst development, process optimization, and carbon management	✓ Energy efficient and economically viable ✓ Combination of SR, DR, and POR ✓ Higher operating cost ✓ Environmental benefits ✓ Integration with renewable energy

From the above summary, it can be noted that some reforming methods are still under development and currently being researched. Research and development programs are currently concerned with the development of small-scale technologies for biogas reforming to enable distribution of hydrogen and improve delivery infrastructure.

Hydrogen production through biogas claims to be a sustainable system from environment point of view. However, significant efforts are still required for its generation process to be estimated from a comprehensive environment-viable system. The main important aspect of the production of H_2 from biogas is the advance of catalysts unaffected by carbon and sulphur content. H_2 production with SMR is broadly studied and used commercially. However, the main problem with SRB is the existence of CO_2, which affects the catalyst performance. Water gas shift reaction occurs during the SR process and negatively affects CO_2 conversion [155].

The incorporation of H_2O in the bi-reforming method serves as a barrier for the production of coke on catalysts in contrast to biogas dry reforming. As a result, in the bi-reforming procedure, it is not necessary to eliminate moisture from the basic biogas. The existence of water can also result in a reduction in the energy required to complete the bi-reforming operation. This is especially advantageous because biogas reforming at high temperatures of reaction might result in more expensive processing.

The incorporation of oxygen into tri-reforming, as opposed to biogas bi-reforming, provides further advantages by further reducing coke production, which aids in preventing catalyst deactivation. Moreover, existing O_2 contributes to lowering energy consumption, thereby reducing overall costs associated with the process.

2.2 Literature on experimental approach for biogas reforming methods

2.2.1 Steam reforming of biogas (SRB)

Hydrogen production process from steam reforming of biogas is considered as a promising alternative route to steam methane reforming with similar efficiency [13] and presented a detailed assessment of hydrogen production method using biogas [130]. The noble metals offer a higher conversion rate with low temperatures than Ni metal, which offers a high conversion rate with high temperatures.

The main challenge in developing catalysts in hydrogen production via biogas is avoiding deposition of carbon in energetic phase to raise its life. Furthermore, it involves improving the catalyst resistance to poising sulphur content and increasing catalyst surface area in order to promote activity [21].

Ahmed et al., (2015) evaluated catalyst (4wt%Rh/La-Al_2O_3) through SBR in hydrogen production. The catalyst performance was analysed in order to temperature variation from (590–685 °C), the molar ratio of steam to carbon range (1.28-3.85), molar ratio of CO_2 /CH_4 (0.54-1.50) and the range of GHSV (9810-27000 h^{-1}). It was observed that highest conversion of CH_4 and lowest conversion of CO_2 at 650 °C at GHSV 9810 h^{-1} and 1.32 S/C. low CO_2 conversion rate due to low temperature of reaction results in more contribution of WSR reaction. The increasing S/C positively affected CH_4 conversion, resulting in higher H_2 yield and the marginal effect of GHSV on their process performance [155].

Effendi et al., (2002) performed the comparison of fluidized and fixed bed reactors at catalyst (11.5 wt% Ni/Al_2O_3), molar ratio of H_2O/CH_4 (2.2), GHSV (18,000 h^{-1}) and along with temperature 750°C. The fluidized bed reactor was evaluated to offer (5-

15%) better performance than fixed bed reactor. Higher feeding of ratio (gas to steam) was introduced to strong carbon formation due to reduced fluidization in reactor and carbon formation was minimized by increased steam feed. The poor performance of fixed bed produces cold spot formation in the bed of catalyst [156].

Izquierdo et al., (2012) estimated the result of various compositions on bimetallic Rh-Ni and Ni catalyst performance in steam biogas reforming at temperature 800°C, ratio of CH_4/ CO_2 (1.5) and WHSV (131.6 $g_{gas}/g_{cat}\ h^{-1}$), whereas catalyst (13 wt% Ni/Ce-Zr-Al_2O_3) observed at steam methane ratio of one gives 99.5% of CH_4 conversion and 67% of CO_2 conversion [157]. In addition, as per **Ahmed et al., (2015)** [155], increasing ratio of S/C was a positive advantage in CH_4 conversion, but CO_2 conversion was unfavorable, resulting in improvement of WGS over the catalyst (4 wt% Rh/La-Al_2O_3).

Despite higher conversion of CH_4 and CO_2, catalyst presented low H_2 yield compared with the catalyst of Ni/Ce-Al_2O_3 and Ni/Zr-Al_2O_3. The catalysts activity and stability are affected by H_2S, which is present in biogas. Sulphur content from H_2S reduced the catalyst activity because it reacts with active metals, limiting access of reactants to active sites. Furthermore, the development of stable metal adsorbate bonds could lead to non-selective side reactions [158].

Additionally, H_2S acts as a toxic gas for metal-based catalysts, but a certain amount of H_2S in the feed increases the reforming activity of the catalyst [159]. Due to the toxic effect, the content of H_2S in biogas sharply reduces the catalytic activity. Therefore, several purification methods have been used to remove H_2S, such as membrane technology, adsorption, and biological methods [120].

In contrast, **Appari et al., (2014)** reported catalyst activity loss of 98% with catalyst (15wt% Ni/Al_2O_3) suffering from suphur poising effect [160].

Ashrafi et al., (2008) observed that temperate is independent of H_2S concentration and depends on sulphur content over the catalyst's surface in loss of catalyst activity. The poisoning effect of catalyst at the temperature (700°C) is not recovered by elimination of H_2S content through the feed, but from temperature (800°C) could be reversed by eliminating H_2S content through the feed. The deactivation of catalyst activity was recovered at (800°C) and fully deactivated at (700°C); with increasing temperature H_2S removal increases the catalyst regeneration limit.

Efficient removal of sulphur content could be costly in biogas applications but it can be economical to operate the reformer with a higher feed of H_2S biogas at higher temperatures. Reformers process at high-temperature conduct extensive issues such as hot spot formation, sintering metal crystallites, and decreased surface area of catalyst, etc. These issues generate loss in activity, stability, and catalyst life [161]. Catalyst such as Ni-based is more active in SR of biogas process. In maximum applications, conversion of CO_2 was low compared to conversion of methane, while some research also described high conversion of CO_2. The high conversion of methane and CO_2 has been expressed in higher hydrogen yield [161].

Avraam et al., (2010) presented an experimental and theoretical study for the biogas steam reforming reaction over 5% Ru/Al_2O_3 catalyst. The experimental reactor was modeled as an isothermal pseudo-homogeneous fixed bed reactor. Five reactant species, CH_4, CO_2, H_2O, CO and H_2, were included in the model, whereas the feed consisted of the first three. Steam reforming and water gas shift were the main reactions. Experimental results and theoretical predictions match closely, stability of the catalyst was assured and an optimal operational window was identified, at GHSV = 10,000-20,000 h^{-1}, T = 700-800 ^oC, CH_4/CO_2 = 1.0 -1.5 and H_2O/CH_4 = 3.0 -5.0 [162].

Shapovalova et al., (2012) described a new type of syngas and hydrogen generator that requires no catalyst but can convert low-quality biogas with a CO_2 content of up to 60%. The generator is based on the recently developed volumetric permeable matrix reformers with effective heat recovery. The work is investigating the possibility of using low-quality biogas to produce syngas and hydrogen via its partial combustion in volumetric (3D) permeable matrixes [163].

Effendi et al., (2005) studied the steam methane reforming of biogas using fluidized bed reactor. The steam reforming of biogas was performed over 11.5 wt% Ni/Al_2O_3 and a molar CH_4/CO_2 ratio of 1.5 was employed as clean model biogas. Excess steam resulted in strong inhibition of carbon formation and an almost complete CH_4 (more than 98%)

conversion was achieved. The final product compositions following low-temperature CO shift reaction (steam to dry gas ratio of 1.5 at 483 K) yielded H_2 at 68% and a CO concentration of 0.2% (equivalent to CO conversion of more than 99%) [164].

Tuna et al., (2018) investigated the performance of $NiAl_2O_4$/g-Al_2O_3 catalyst in order to compare its catalytic activity under CH_4/ CO_2 reforming conditions and evaluate its resistance to carbon formation with a Ru/g-Al_2O_3 catalyst. The effect of operating conditions, including a CH_4/CO_2 molar feed gas ratio of 1.5:1 and 1:1, and temperatures ranging from 650 to 850°C, on CH_4 and CO_2 conversions, as well as the H_2/CO ratio, for the two catalysts under study was investigated using an experimental pilot unit. It was found that 7.4% Ni/$NiAl_2O_4$/g-Al_2O_3 with aluminate layer and 3.1% Ru/g- Al_2O_3 were effective as catalysts, given that they showed high CH_4 conversion, CO and H_2 selectivity, resistance to carbon deposition, and low activity loss. The effect of CH_4: CO_2 ratio revealed that both catalysts have the same behavior. Optimal performance has been achieved in a CH_4: CO_2 ratio of 1.5:1. H_2 yield was 60% for both catalysts at their respective operating temperature. Prototype dimensions and catalyst preparation and characterization are also presented [165].

Silva et al., (2015) evaluated Syngas and hydrogen production by methane reforming of biogas (CH_4/CO_2 = 2.85) using carbon dioxide in a fixed bed reactor with a Pd-Ag membrane in the presence of a nickel catalyst (Ni 3.31% weight)/γ-Al_2O_3) at 773 K, 823 K, and 873 K and 1.01×105 Pa. A mathematical model was formulated to predict the evolution of the effluent concentrations. Predictions based on the model showed similar evolutions for yields of hydrogen and carbon monoxide at temperatures below 823 K for operations with and without hydrogen permeation. The hydrogen yield reached approximately 21% at 823 K and 47% at 873 K under hydrogen permeation conditions [166].

A fixed-bed reactor with a Pd-Ag/H_2 selective membrane was used to convert biogas into syngas by a reforming process. The performance of a nickel catalyst (3.31% weight)/γ-Al_2O_3) was evaluated at 773 K, 823 K, and 873 K and 1.01×10^5 Pa with and without hydrogen permeation.

Roy et al., (2015) performed steam reforming of biogas with the catalysts Metal-foam-coated 0.09wt%[Pd(7)-Rh(1)]/($CeZrO_2$–Al_2O_3) compared along with commercially available alumina-supported 8.0 wt% Ru and 13.0 wt% Ni catalysts. The experiments were conducted in a tubular reactor using a feedstock with the steam-to-methane ratio of 1.50 at 1 atm pressure and 20,000 h^{-1} GHSV.

The experimental results demonstrate that the metal-foam-coated Pd–Rh/($CeZrO_2$-Al_2O_3) catalyst performs better for syngas production through steam-biogas reforming compared to the Ru and Ni catalysts. The catalyst performance in the temperature range of 923-1123 K was compared with commercial Ru/Al_2O_3 and Ni/Al_2O_3 catalysts used in steam methane reforming [167].

2.2.2 Partial oxidation of biogas (POB)

Partial oxidation of biogas has several benefits over SRB, including compactness, less sensitivity, and better response time for fuel variants. The reactors of partial oxidation increase interest in energy conversion for high temperatures utilized in fuel cell. It is a faster chemical reaction than SRB due to its exothermic reaction [135].

Hydrocarbon (HC) conversion to syngas via partial oxidation process can occur at high temperatures lacking catalysts. Conversely, the operating temperature will be significantly decreased using catalyst. Most of the studies via partial oxidation catalysts are same as catalyst used in steam reforming process as noble metal and transition metallic elements such as Ni, Fe and Co [168].

Pantaleo et al., (2015) described a supported catalyst (La_2O_3, CeO_2 and combined CeO_2-La_2O_3) with Ni catalyst from Partial oxidation of methane. The support of Ni catalyst is prepared from wet impregnation and co-precipitation. Carbon is formed on Ni/ La_2O_3 and Ni/CeO_2 and carbon is not formed on combined support (CeO_2-La_2O_3) during the test [169].

Chen et al., (2018) analyzed a spiral type Swiss roll reactor via catalytic partial oxidation of methane (CPOM) with Rh-based catalyst. Three types of biogas are considered for studies: sewage, landfill, and farm biogas. Syngas yield was found at 2.80 mol/mol of CH_4) and 31.12% CO_2 conversion. The conversion of CH_4 (99%) and the yield of H_2 (exceeding 1.49 mol per mol of CH_4), along with the H_2/CO ratio, were higher than those reported in other studies [170].

Tsyganok et al., (2004) evaluated catalyst Pt-, Rh- and Ru-based via joint operation of both dry and partial oxidation of methane (CH_4) and supported on Mg-Al mixed oxides. The experiment was conducted at 850 °C and 1 atm, using the ratio of O_2/CH_4 (0.46) and GHSV (79 NL $CH_4/(g_{cat}\cdot h)$) [171]. The authors investigated Rh-and Ru-based catalysts with high activity performed during the experiment and no carbon deposit for 5 hours [153]. **Moral et al., (2018)** studied syngas production from biogas catalytic partial oxidation and dry reforming used by several Rh-based catalysts with different support SiO_2, CeO_2 and γ-Al_2O_3. It was measured that the molar ratio O_2/CH_4 (0.45) was favorable for higher hydrogen yields and maximum CH_4 conversion. The results were obtained by feeding various amounts of O_2 and the mixture of biogas in catalytic performance using dissimilar Rh-based catalyst and conducting the experiment with GHSV value of 150 NL $CH_4/(g_{cat}\cdot h)$ and temperature at 700°C [172].

Rafiq et al., (2011) studied through the experimentally and thermodynamic analysis in a plasma assisted gliding arc reactor using Ni catalyst via partial oxidation model biogas as CH_4 (60%) and CO_2 (40%) and reported highest CH_4 conversion as 90%, while the ratio of CH_4/O_2 as 3 at temperature 800°C [173]. The ratio of CH_4/O_2 as 2, methane conversion was obtained as 97.5% using Ni catalytic filter in tabular reactor without considering hydrogen. These studies also show that calcium silicate could be a good base material for catalytic filters from partial oxidation of biogas mixture [174].

Camacho et al., (2018) investigated the conventional random foam and homogeneous lattice support structures for the production of hydrogen from the ATR reaction. 15-0.05 wt%-Ni-Rh/$MgAl_2O_4$-SiSiC structured catalyst and $LiFeO_2$-SiC monolith were selected for the conversion of biogas to hydrogen and the syngas post-treatment process, respectively. The tests were performed using a GHSV of 10,000 per hour, an S/C ratio = 2.0 and O/C ratio = 1.1 (design values) was used for the experiment section. The catalyst activation in both pilot plants was performed at 750°C for 2 h using a mixture of 25% H_2 and 75% N_2. Model biogas composed of clean methane and carbon dioxide (60:40 vol: vol) was used in this study. The activation procedure was successful and a long duration test was carried out using a space velocity of 4000, S/C =2.0, O/C = 1.1 and T_{in} = 500°C. A thermodynamic equilibrium and a methane conversion higher than 98% were achieved [175].

2.2.3 Auto thermal reforming of biogas (ATRB)

Research in the field is constrained to auto-thermal reforming of biogas (ATRB). This means that the scope of investigation is limited to studying the process of ATRB and its associated parameters, rather than exploring a broader range of reforming methods or alternative technologies for biogas utilization.

Rau et al., (2019) developed and studied a pilot plant for the Bio-Robur project, producing 50 Nm^3/h of hydrogen through auto-thermal biogas reformation with a noble metal catalyst. All required reactants are internally generated or stored, without synthetic gas purification. Their study investigated temperature, oxygen-to-carbon ratios, and gas hourly space velocities to evaluate efficiency and workload variation, demonstrating reliable operation at ≥20% workload [176].

Vita et al., (2014) investigated catalyst (Ni/CeO_2) in auto-thermal reforming of biogas (ATRB). The conversion of CH_4 (97.3%) and CO_2 (90.5%) with ratio of S/C (0.3) and ratio of O_2/C (0.1) was reported (Table 2.2). The performance of catalyst was tested 150 hours with minor sign of deactivation. The catalyst activity was retained due to NiO distribution over the catalyst surface [177].

Izquierdo et al., (2013) reported that the catalyst (13wt% $Ni/Ce\text{-}Zr\text{-}Al_2O_3$) also utilized in SRB method and ATRB method observed with ratio of S/C (1), O_2/C ratio (0.25), and WHSV (161 per hours). Bimetallic catalyst ($Rh\text{-}Ni/Ce\text{-}Al_2O_3$) exposed the maximum yield of H_2 in ATR process among the catalysts inspected [178].

Bawornruttanaboonya et al., (2018) investigated catalyst ($Re\text{-}Ni/g\text{-}Al_2O_3$) in auto thermal reforming of biogas. Micro-reactor (Channel type) was compared to novel micro-reactor and noted that novel reactor was optimum condition was O_2: H_2O: CO_2:CH_4 (25:5:28:42) % (v/v) at 730°C and pressure 1 bar [65].

Camacho et al., (2018) examined homogeneous (lattice structure) and convention (random form) for H_2 production via ATR reaction. Structured catalyst (15-0.05 wt%-Ni-Rh/$MgAl_2O_4$-SiSiC) and monolith ($LiFeO_2$-SiC) were chosen for biogas conversion to H_2 gas. The investigations were executed using a ratio of S/C (2), ratio of O/C (1.1), and GHSV (10,000 per hour) through the experimental section and achieved more than 98% methane conversion [175].

2.2.4 Dry reforming of biogas (DRB)

The biogas dry reforming reaction is distinctive for its substantial endothermic characteristics, requiring higher reaction temperatures that can lead to catalyst deactivation. The deactivation of the catalyst poses a limitation when incorporating biogas dry reforming into industrial applications. To avert catalyst deactivation and ensure the durability of catalysts, scientists have engaged in the exploration and advancement of a variety of catalyst types.

Evans et al., (2014) investigated the dry reforming of the biogas method using catalysts such as Ni/$SrZrO_3$, which demonstrated a notable preference for the reforming reaction, leading to the formation of syngas. However, the transformation of CH_4 was restricted as a result of the limited availability of CO_2 as a reactant [180].

Zhang and Li (2015) observed that the catalysts (core-shell Ni@SiO_2) demonstrated excellent activity and stability. The amorphous SiO_2 shell of the catalyst facilitated the creation of both micropores and mesopores, effectively preventing the growth of carbon filaments. The pores present in the SiO_2 shell allowed gas molecules to reach and interact with the Ni cores (nanoparticles). The type of catalyst, its structure, and the interaction between the metal and support are crucial factors that greatly influence the ability of the catalyst to resist the deposition of carbon [181].

Bian et al., (2016) investigated the dry reforming of biogas using catalysts such as Ni-Mg PSNTS@silica (multicore-shell type). These catalysts showcased exceptional stability and achieved high conversion rates throughout a continuous 72-hour operation. In the absence of the silica coating, the Ni-Mg PSNTS (Porous Silica Nanotube Structures) experienced pronounced deposition of coke as a result of the breakdown of the nanotubular type structure at elevated temperatures around 750°C. The introduction of the silica coating resulted in a remarkable enhancement in the thermal stability of Ni-Mg PSNTS@silica, with the silica material forming a strong and durable connection with both the inner and outer PSNTS surfaces [182].

Cruz-Flores et al., (2020) observed the catalysts (Ni-SiO_2) verified nominal deposition of carbon during short a time-on-stream of approximately 4 hours. However, with a longer time-on-stream around 50 hours, the Ni particles experienced severe sintering. A profound comprehension of the catalyst's reaction mechanism is vital for catalyst design, the execution of reforming reactions through biogas, and the precise analysis of reaction outcomes [183].

Khoja et al., (2018) introduced a reaction mechanism depicting the biogas dry reforming with the utilization of catalysts (Ni/Al_2O_3-MgO). In this process, the activation of CH_4 occurred on Ni while deposited carbon was gasified on MgO. The catalyst support facilitated the adsorption of components and intermediates comprising H, O, C, and oxy-carbonates on its surface and active sites. Plasma played a role in initiating the dissociation of both CH_4 and CO_2 [184].

Das et al., (2019) investigated the dry reforming of biogas employing a catalyst transformed with Ru (Ru-Mg-Ce/SiO_2). The adsorption of CO_2 was primarily observed to occur on the MgO surface, resulting in the formation of the surface-adsorbed layer of CO_2. The adsorbed CO_2 underwent a transformation process using Ce_2O_3. A fraction of CO_2 was activated on surface of the catalyst, resulting in the oxidation of activated Ru metallic. Following this, the Ru metal that had been oxidized was reverted back to its metallic state with the assistance of the produced H_2. CH_4 experienced specific dissociation across the metal (Ru) surface, resulting in the creation of a carbon layer on the exterior part of the catalyst. Afterward, the carbon that had been deposited underwent oxidation through interaction with the oxygen present on the catalyst surface, leading to the development of CO [185].

Bobadilla et al., (2017) presented a reaction mechanism outlining the process of biogas dry reforming with the utilization of Rh/$MgAl_2O_4$ catalysts. The initial step involved the disintegration-driven CO_2, resulting in the formation of oxygen species in an active state situated at the metallic Rh sites. The presence of reactive oxygen entities facilitated the initiation of CH_4, leading to the production of H_2. The resulting H_2 set in motion a dual-functional mechanism, where CO_2 experienced activation on the alkaline sites of the support surface. The transformation of CO_2 to CO occurred through hydrogen-assisted dissociation at the interface between the metal and support, as well as direct dissociation on the metallic sites of Rh [186].

Hossain et al., (2019) found that changing the Gas Hourly Space Velocity (GHSV) within the range of 10,000 -60,000 h^{-1} influenced the conversions of CH_4 and CO_2. Optimal conversion of CH_4 and CO_2 was attained when the GHSV was set at 35,000 h^{-1}. At high temperatures during the reforming process, methane pyrolysis may become the dominant reaction leading to carbon development due to the increased thermodynamic unfavorability of the Boudouard reaction. There was a rise in the conversion of CH_4 from 43% -55% and along with an increase in the conversion CO_2 from 86% - 99% with an increase in the reaction temperature within the range of 700 to 900°C [187].

To recapitulate, academia has conducted numerous studies on the biogas dry reforming method. A GHSV implies an increased duration of exposure to reactants on the surface of the catalyst, potentially resulting in higher transformations of reactants. As the reaction temperature rises, the CH_4 conversion also increases. Noble metal-based catalysts, such as Ru/SiO_2 and Ir/Al_2O_3, show superior performance in biogas dry reforming compared to Ni-based catalysts like $Ni@SiO_2$ and $Ni\text{-}W/Al_2O_3$, primarily as a result of the remarkable noble metals stability. Catalyst development has seen significant progress in reducing carbon deposition. Researchers have explored the incorporation of specific metals, such as La, Fe, Sn, and Zr, to effectively address this issue [188-190].

Recent literature on dry reforming method extensively covers the utilization of various catalysts in hydrogen production through the reforming process. For example, **Dang et al., (2021)** studied the effective catalysis of dry reforming of methane at 600°C and utilising Pd-promoted $Ni\text{-}CaO\text{-}Ca_{12}Al_{14}O_{33}$ multifunctional adsorbent/ catalyst materials. The findings indicate a noteworthy 67% conversion rate for CO_2, 68% conversion rate for CH_4, and an almost unity H_2/CO ratio. Remarkably, the catalyst remains active for 50 hours at 600°C without showing signs of deactivation during an ongoing on-stream dry reforming of methane (DRM) process. The higher performance is explained by the increased CH_4 dissociation activity that Pd facilitates [191].

Sun et al., (2021) examined Co based catalyst (1Co-1Ce/AC-N) and kinetics study of dry reforming of methane. The study focused on methane dry reforming kinetics at 800°C, covering temperatures ranging from 650°C to 850°C. To conduct the investigation, CH_4/CO_2 ratios were varied between 0.3 and 3.0. Three standard kinetic models successfully fit the experimental results such as Eley-Rideal, Langmuir-Hinshelwood, and Power Law [192].

Kaviani et al., (2024) produced a core-shell catalyst by covering Ni-SiO_2 with SiO_2 and utilized it in the dry reforming of the biogas process. The findings showed that as the TEOS (Tetraethylorthosilicate) content increased, the amount of carbon deposition progressively reduced. The sandwiched core-shell catalyst with 2 ml TEOS demonstrated high methane and CO_2 conversions of 71.5% and 91.5% under T = 700°C and CH_4/CO_2 = 1.5 for 20 hours, respectively [193].

Genc et al., (2023) [194] examined the impact of sulphur content on biogas dry reforming using catalysts based on Ni and Fe. Iron was added to the catalyst structure to react with H_2S at a high temperature and maintain nickel activity in the dry reforming reaction. During examining the activity tests of bimetallic catalysts, it was noted that they revealed no resistance to H_2S at high concentrations (50 ppm) and quickly lost their activity. However, they retained their activity when exposed to low concentrations of H_2S (2 ppm).

González et al., (2020) prepared various catalysts based on nanograins and nanofibers γ-Al_2O_3 with Ni and Ni/Ce and studied in the dry reforming of simulated biogas. The nanofiber alumina containing 5 wt% Ni and 1.5wt%Ce (NiCe/NFA) demonstrated the highest catalytic activity and stability during the process (CH_4/CO_2 =1.5), attaining 98% CO_2 conversion at 750°C. The fibrous shape of the alumina support is responsible for the NiCe/NFA material's exceptional catalytic activity. Because of their enhanced dispersion due to this shape, the supported Ni metal particles become smaller and have more active sites available for the dry reforming reaction to take place [195].

Similarly, **Ha et al., (2022)** presented catalysts featuring low Ni loading (2.5wt %) for the dry reforming of methane-rich gases (CH_4/CO_2 = 2). These catalysts are subsequently modified with Gd, Sc, or La. At 750°C, the most effective catalyst achieves a 49% conversion of CH_4 and a 95% conversion of CO_2. The rare earth elements have been introduced to Ni/MgO-Al_2O_3. With negligible activity loss, this modification effectively imparts resistance to Ni agglomeration and coking in the dry reforming of methane. These new catalysts demonstrate superior performance in converting CH_4-rich feed compared to others. Notably, the Gd.Ni/$Mg_{1.3}AlO_x$ catalyst exhibited the lowest coking rate and the highest activity at both 630°C and 750°C [196].

Introducing suitable metals such as Fe, La, Zr, and Sn into Ni-based catalysts has been found to enhance the carbon-inhibition characteristic. Particular catalysts like Ni-Mg PSNTS demonstrated a notable coke formation rate reaching as high as 0.022 g coke/(gcat*h). On the other hand, the Ni-Mg PSNTS@silica catalysts demonstrated minimal coke rate due to the occurrence of O_2 vacancies in MgO and the supporting role of the silica material.

Dry reforming of biogas primarily utilizes catalysts based on Ni and Ir, both of which showcase higher levels of activity. However, Ir is classified as a noble metal, and its widespread utilization has the potential to contribute to higher costs, employing small amounts of noble metals to decorate economically advantageous metals (e.g., Ni) integrated into the catalysts proves to be an effective approach. Nickel, being one of the most commonly utilized metals, holds significant popularity in the field of dry reforming.

2.2.5 Dry oxidation reforming of biogas (DORB)

In general, DORB is vital to the advancement of sustainable biogas utilisation and helps to forward the goals of resource efficiency, carbon emission reduction, and the development of a more circular economy. To realise the full potential of DORB technology and expedite the shift to greener and more sustainable energy sources, research and development on the technology are necessary.

Lai et al., (2012) performed biogas (CH_4-50%: CO_2 -50%) as equimolar in ODRB. Experiment results from ODR showed that adding a significant amount of oxidant could increase the methane conversion rate, but unnecessary oxidation can reduce the CO_2 conversion efficiency [197].

Lau et al., (2011) simulated biogas model via oxidative reforming was obtained higher efficiency. In addition, the catalytic activity level of (0.5% Ce)/Ni/SiO_2 measures the equilibrium condition and is comparatively stable throughout 24 hours of ODRB [198].

Asencios et al., (2014) tested the experiment on Ni catalyst support via ODRB and represented the various pH conditions with Al_2O_3. Commercially available Ni-Al_2O_3 showed the highest activity at 750°C reaction temperature, but it was deactivated after 3 h. The synthesized Ni-Al_2O_3 catalyst showed good stability during the 6-hour test at more pH conditions close to 7 but obtained only 70% methane conversion rate while the CO_2 conversion maintained the equilibrium. The catalyst activity is based on the low acidity of the carrier, so less coke is deposited on the catalyst. The low acidity of the substrate reduces the CO_2 reaction in the main Al_2O_3 core, which leads to an acid-base interaction that promotes this reaction [199].

Rosha et al., (2018) optimized the dry oxidative reforming (DOR) process parameters for producing H_2-enriched biogas by using response surface methodology. It examines the impact of CH_4/CO_2 and O_2/CH_4 ratios on DOR catalytic performance within a temperature range of 800–900 °C. The optimal reaction conditions were determined to be 900°C, with a CH_4/CO_2 ratio of 1.5 and an O_2/CH_4 ratio of 0.10. Under these conditions, the experimental results showed a maximum H_2 enrichment of 38.7%, with CH_4 and CO_2 conversions of 82.9% and 90.8%, respectively. The regression model and dry oxidative biogas reforming technology combined offer an attractive solution for increasing H_2 yield in product gases, thereby enhancing energy density and promoting the generation of environmentally friendly gas [200].

Kathirazer et al., (2017) developed highly active and coke-resistant ceria-promoted Ni/SiO_2 catalysts through an in-situ self-assembled core-shell precursor method. Under the studied conditions, it was found that a low ceria loading of 0.5 wt% was beneficial in both mitigating carbon deposition and increasing the activity of oxidative biogas reforming. This low ceria loading was shown to have a positive effect by anchoring ceria at interfacial points on the Ni/SiO_2 support. This allowed Ni and SiO_2 to interface closely within the mesopore wall by forming nickel silicates with strong metal-support contact [201].

2.2.6 Bi-reforming of biogas

The bi-reforming of biogas is significantly influenced by reaction conditions. Researchers have focused on establishing a wide range of catalysts to attain the desired conversions of reactants and specific H_2/CO ratios. The bi-reforming of biogas was investigated as follows.

Li et al., (2015) utilized Ni/ZrO_2 catalysts modified with different MO_2C loadings (0.2 to 3.0wt %). According to their research findings, these modified catalysts showed improved catalytic stability and efficiency when compared to the original catalyst [202].

Olah et al., (2015) observed that the increasing temperature from 830 to 910°C resulted in higher conversions of both substances such as CH_4 and CO_2. However, there was a minor decrease observed in the H_2 to CO ratio with the increase in temperature. Conversely, there was a reduction in the conversion of CH_4, but a slight enhancement in the ratio of H_2/CO during increasing pressure range from 7- 42 bar [203].

Park et al., (2015) found that with the temperature rising (750-900°C), there was an amplification in the conversions of both CH_4 and CO_2. However, the ratio of H_2/CO demonstrated a decline as the temperature increased. The decrease in the H_2/CO ratio was linked to the depletion of H_2 caused by the formation of carbon on the catalyst surface as the temperature rose [204].

Li et al., (2015) investigated the bi-reforming method from biogas using LA-Ni/ZrO_2 catalysts and found that these catalysts exhibited enhanced catalytic performance, including improvement in the conversions of both CH_4 and CO_2 in comparison to traditional Ni/ZrO_2 catalysts. The enhanced catalytic performance of LA-Ni/ZrO_2 catalysts can be attributed to various factors, such as a stronger interaction between Ni and the catalyst support, improved dispersion of Ni particles, an increase in oxygen vacancy size, improved reducibility of NiO facilitated by oxygen vacancy, and a higher content of t-ZrO_2 in the catalysts. The increase in GHSV from 24,000 to 72,000 $mL*g^{-1}\ h^{-1}$ resulted in a decrease in the conversions of CH_4 and CO_2. This decrease can be attributed to the shorter residence time of reactants on the catalyst surface and the limited availability of active sites to accommodate the higher amounts of reactants at the elevated GHSV [205].

Zhang et al., (2022) investigated Co-Ce/AC-N catalysts for combined steam and dry reforming of methane. Four separate methods were used to manufacture a series of catalysts using nitrogen-doped activated carbon as the support, cobalt as the active ingredient, and cerium as the auxiliary agent. The catalyst synthesized using impregnation exhibited the highest catalytic activity and stability when compared to the other three preparation methods. The initial conversions of CO_2 and CH_4 were 64.4% and 71.6%, respectively, at 650°C. There was a 1.5 H_2/CO ratio. Only around 2% of the CH_4 and CO_2 conversion was lost after the 12-hour reaction [206].

Poggio et al., (2023) tested catalyst NiCeSnRh/Al_2O_3 for bi-reforming of biogas process with sulfur-resistant. It was found that the multimetallic sample under study helped convert synthetic biogas into a syngas stream. The carbon dioxide conversion consistently outperformed the methane conversion, which is consistent with the observed lower H_2/CO ratio close to 2/1, suggesting that sulfur may be obstructing the active sites for H_2O activation. Deposits of graphitic and disordered carbon were discovered during the catalysts' investigation [207].

Zhang et al., (2024) synthesized various $MgAl_2O_4$ spinel catalysts, denoted as $Ni_xMg_{1-x}Al_2O_4$, for application in the biogas bi-reforming process. Alongside mitigating sintering and carbon deposition, the strong metal-support interaction and efficient CO_2 adsorption/activation of nano $Ni_xMg_{1-x}Al_2O_4$ contribute to outstanding catalytic stability [208].

Farooqi et al., (2021) studied a comprehensive analysis that emphasizes the ability of Ni-based catalysts to reform methane through the steam and dry routes, a process known as "bi-reforming of methane". It was discovered that Ni-based catalysts, due to their lower cost compared to many expensive alternatives, exhibited favourable reaction activity [209].

Lulianelli et al., (2021) examined the performance of an Rh (1%)/$MgAl_2O_4$/Al_2O catalyst in membrane reactors for conducting the biogas steam reforming reaction. CH_4 conversion was moderate, reaching approximately 25% (the optimal value), when employing a supported PdAu/Al_2O_3 membrane with low hydrogen perm-selectivity and high hydrogen permeability in a membrane reactor operating at 823 K and 150 kPa. Despite the modest CH_4 conversion, the membrane exhibited robust hydrogen recovery, achieving 80% under the same operating conditions [210].

2.2.7 Tri-reforming of biogas

Tri-reforming method of the biogas procedure, the addition of supplementary H_2O (water) and O_2 (oxygen) is employed to attain a targeted H_2/CO ratio, typically falling within the range of 1.7 to 2.2. This ratio holds value for the facilitation of Fischer-Tropsch Synthesis (FTS) and contributes to improving the conversion of CH_4 (methane). Through the incorporation of partial oxidation and steam reforming of methane, there exists the potential to generate an H_2/CO ratio of 3.

The concept of tri-reforming process from methane was initially introduced by **Song and Pan (2004)** since then, researchers have explored and developed various kinds of catalysts with different supports and have investigated different compositions of biogas to enhance the catalytic activity for the method of tri-reforming biogas [211].

Both the reforming methods of biogas such as bi and tri-reforming can generate syngas products with a desirable molar ratio of H_2/CO as 2:1 as compared to dry reforming. These resultant syngas can be transformed into valuable end products like liquid fuels, all without requiring a water-gas shift reactor, as reported by **Zhao et al., (2018)** [212].

Pandey et al., (2024) developed a specialized nanonickel metal catalyst distributed on mesoporous zirconia for controlled synthesis gas production with a targeted H_2/CO molar ratio of 1.5-2 through methane tri-reforming. The catalysts underwent testing in a fixed-bed reactor operating at 600-850°C and 1 atm. Achieving maximum conversions of approximately 86% for CH_4 and 28% for CO_2, this occurred at the optimal feed ratio $CH_4:CO_2:O_2:H_2O:N_2$ = 1:0.5:0.1:0.013:1. The results from the catalyst characterization and time-on-stream investigation revealed the coke-resistant and thermally stable characteristics of the nanosized nickel metal particles dispersed on mesoporous zirconia [213].

Gupta et al., (2023) explored the tri-reforming of methane using mesoporous Ni-Al_2O_3 catalysts with Ni weight percentages ranging from 5 to 15. Characterization revealed that metal loading influences catalyst's metal-support interaction. Increasing Ni loading led to rising conversions and yields, reaching a maximum of 82.4% for CH_4 and 19.7% for CO_2 at 15 wt%. No carbon was detected at 600°C, and the H_2/CO ratio exceeded 3 throughout the process [214].

Anchieta et al., (2022) assessed Ni/CeO_2 catalysts for methane tri-reforming, revealing strong activity in the synthesized catalyst using an ionic liquid. The catalyst produced syngas with an H_2/CO molar ratio ranging from 1.3 to 2.2, influenced by metal-support interactions. Performance improvement was achieved by increasing the CO_2 or O_2 load, with maximal CH_4 and CO_2 conversions reaching 95% and 55%, respectively [215].

Kumar et al., (2021) revealed excellent catalytic activity and observed enhanced CH_4 and CO_2 conversions in methane tri-reforming. This was achieved using cylindrical-shaped MgO-Al_2O_3 supported Co-Ru catalyst extrudates generated through a straightforward incipient wetness co-impregnation process [216].

Singha et al., (2016) performed an investigation on the tri-reforming of biogas using Ni/ZrO_2 catalysts. In their research, these catalysts displayed remarkable performance, showing no signs of deactivation for a period exceeding 100 hours. Furthermore, they achieved nearly whole conversions of amounts such as CH_4, CO_2, and H_2O, making them highly effective throughout the process [217].

Damanabi et al., (2019) revealed that there was a noticeable decline in the conversions of both CH_4 and CO_2, as the pressure was raised from 1-10 bar. The pressure effect on product selectivity in the processing reactor (tri-reforming) is an important consideration. In the reactor, the ratios of H_2/CO vary with temperature, showing values of 3.73 at 600°C and 2.2 at 800°C [218].

Tri-reforming method of biogas represents an emerging technology and is a simplified process for syngas/hydrogen production. For certain target applications, sufficient reactant transformations and an appropriate H_2/CO ratio must be obtained. It is common to introduce additional steam and oxygen into the reactor system. However, it is extremely important to take into account that the addition of steam and oxygen may lead to increased costs associated with the process.

2.3 Literature on Simulation and Modelling Approach

There are multiple reports in the literature about simulation and modelling research on utilizing biogas for hydrogen production.

Hajjaji et al., (2016) conducted a study; they used Aspen Plus software to simulate a hydrogen production plant that utilized steam reforming of biogas. Their study directed that utilizing biogas for hydrogen production through steam reforming offered significant benefits based on a life cycle assessment approach [219].

Rosa et al., (2018) utilized Aspen Plus to optimize the process conditions. Based on their thermodynamic simulations, they recommended the most effective operating parameters to be a pressure (1 bar), a temperature range (1008 to 1063 K), and ratios of O_2/CH_4 ranging from 0 to 0.1, as well as S/C ratio ranging from 2.4 to 3.0. These optimized conditions were determined through their experimental work [220].

In a study by **Minutillo et al., (2020)** two distinct hydrogen production plants from biogas were simulated using Aspen Plus. The simulations focused on steam reforming and auto-thermal reforming methods. The outcomes exposed that the energy efficiency of steam reforming was 19% greater than that of auto-thermal reforming [221].

Hwanglo et al., (2018) used a network modeming approach to combine biogas supply with a conventional methane steam reformer to account for variable demand scenarios. The main outcomes of the study presented a noteworthy decrease of 24% in the overall cost of producing hydrogen [222].

Pashchenko et al., (2021) conducted an exploration of the steam methane reforming process within a micro-channel reformer employing a Ni-based catalyst. The results of the reformer such as temperature and reforming products were obtained through experiments, CFD modeling, and numerical analysis. Initial conditions encompassed a temperature range of 327-727 °C, Reynolds numbers (10, 50, and 100), and heat flux values (500 W/m^2, 1000 W/m^2). It was observed that as inlet temperature, heat flux, and Reynolds number increased, methane conversion in the reformer decreased. Specifically, at 727 °C, Re = 10, and heat flux 1000 W/m^2, methane conversion was 39%, compared to the equilibrium conversion of 63% [223].

Lu et al., (2021) developed and validated a 0-D model for the steam methane reforming process. The process employs a Ni-based catalyst with spherical particles having a diameter of 4 mm. This model incorporates six gaseous chemical species such as CH_4, H_2O, CO_2, CO, N_2, and H_2. The new model predicts both internal temperature and species mass fractions within the particle, along with surface-averaged temperature and species mass fractions at the particle level. The validity of the 0-D model has been confirmed by comparison with an extensive 3D-CFD-based model that addresses bulk flow, temperature, and species boundary layers around the particle, and the convection-diffusion processes occurring within the porous catalyst particle. CFD calculations showed that the temperature and species mass fractions within the particle changed significantly when the ambient temperature increased from 527-727°C [224].

Pashchenko et al., (2020) performed the pressure drop in the fixed-bed reactor and examined both experimental and numerical simulation approaches to investigate the flow dynamics within a fixed-bed reactor containing porous particles. The simulation models the flow dynamics, and experimental data are utilized for result validation. Demonstrating the utility of a commercial CFD code, the pressure drop characteristics for fixed-bed reactors with porous particles were determined with less than a 10% average error. This level of error is deemed acceptable for design purposes. The results suggested flow through the fixed-bed reactor porous elements when the pore size is over 0.5 mm. Conversely, if the pore size is less than 0.5 mm, there is no flow through the porous medium, treating the particles as solid bodies in numerical analysis. When the pore size is increased from 0.2 mm to 2 mm, it decreases the pressure drop by more than three times [225].

Pashchenko et al., (2021) studied experimental and thermodynamic investigation of carbon deposition during steam methane reformation using a Ni-based catalyst. Experiments tested diverse operating conditions, including temperatures of 600°C and 800°C, S/C ratios (0.5, 1.0, and 2.0), and pressure. Thermodynamic analysis determined equilibrium carbon formation zones for these conditions, and experimental results were compared with the analysis outcomes. The results showed that at a residence time of around 5 kg_{cat} .s/molCH_4, methane conversion approaches equilibrium. When the steam-to-carbon (S/C) ratio was 0.5, the methane conversion was significantly reduced. On the other hand, there is very little methane conversion for S/C = 2.0 and S/C = 1.0. The rate of carbon deposition on the stream has an approximately linear relationship on time when the steam-to-methane ratio is larger than 1. The carbon deposition rate is roughly 0.12 g/h for S/C = 2 and T = 800 °C, 0.21 g/h for S/C = 2 and T = 600 °C, 0.29 g/h for S/C = 1 and T = 800 °C, and 1.02 g/h for S/C = 1 and T = 600 °C [226].

Kong et al, (2020) presented a study on an iron-based chemical looping technology as an alternative pathway to convert biogas into H_2. This chemical looping process requires neither upstream biogas compression and purification, nor downstream CO_2 removal and H_2 purification, hence achieving a great level of process intensification. The chemical looping process, as well as the conventional steam methane reforming and mixed reforming processes for biogas to H_2 conversion, are simulated in ASPEN to compare their performance. The CL-BTH technology provides an alternative conversion pathway to produce high-purity H_2 from biogas [227].

This study confirms that CL-BTH is a novel technology that can produce H_2 from biogas of various compositions with competitive CGE (Cold gas efficiency) and ETE (Effective thermal efficiency) while achieving 100% CO_2 capture, demonstrating its great potential to be applied to a future carbon negative economy. The CL-BTH, SMR-BTH, and MR-BTH (Methane reforming biogas to hydrogen) processes are simulated in ASPEN plus V11 under the same system setup.

The system CGE and ETE decrease with increasing CO_2 vol% in biogas. However, the reduction in CGE and ETE only becomes significant when the biogas CO_2 vol% increases from 50% to 60%.

Chattanathan, et al., (2014) investigated the effect of a major impurity (i.e., H_2S) on a commercial methane reforming catalyst during hydrogen production. The effect of temperature on CH_4 and CO_2 conversions was studied at three temperatures (650, 750 and 850^oC) during catalytic biogas reforming. The experimental CH_4 and CO_2 conversions thus obtained were found to follow a trend similar to the simulated conversions predicted using ASPEN plus. The study found that even with the introduction of small amount of H_2S (0.5 mol%), the CH_4 and CO_2 conversions dropped to about 20% each as compared to 65% and 85%, respectively in the absence of H_2S. Although there are different reforming techniques, the focus of this work was on dry reforming of biogas for the conversion of both CH_4 and CO_2 to more useful syngas: H_2 and CO. Syngas can be converted to liquid hydrocarbons in the presence of Fe and Co catalysts via Fischer-Tropsch synthesis. Dry reforming of biogas was carried out in a fixed-bed reactor. Reforming reactions were performed at temperatures from 650^oC to 850^oC and atmospheric pressure using a commercial CH_4 reforming catalyst. Experiments were carried out for 5 h to test the stability of the catalyst under different experimental conditions. The effect of H_2S on the CH_4 and CO_2 conversions was studied by using three H_2S concentrations. It was noticed that even with the introduction of 0.5 mol% H_2S drastically reduced the CH_4 and CO_2 conversions from 67% and 87% to 19% and 22%, respectively [228].

Cipitì, et al, (2016) aimed to develop and test a biogas steam reforming reactor. A mathematical model has been developed in order to describe, the performance of the above-cited steam reforming reactor (packed bed). To study the effects on reaction performance, a parametric analysis was performed under varying operating conditions such as inlet temperature and reagent molar ratio. The model was validated by comparing the calculated data with the experimental data obtained with a proprietary Ni/CeO_2 based catalyst in packet bed micro-scale reactor at different temperatures. The purpose of the model is to investigate the performance of the reactor in order to enhance optimization and control of the steam reforming unit. The model can be used to predict the experimental data for the product distribution and the reactor performance description as well as a tool to advance the reactor design for fuel reforming technology [229].

Sadooghi and Rauch (2015) worked on experimental and theoretical studies of steam methane reforming reactions with different amount of hydrogen sulfide in the feed gas are presented. A two-dimensional pseudo heterogeneous model is developed to simulate methane steam reforming reactions in a packed bed tubular reactor. This model is based on mole and energy balance equations for the catalyst and the fluid phases. The catalyst used in these experiments is a nickel-based catalyst supported by alumina, ($NiAl_2O_3$). Compare the experimental data with simulation data with different parameters like space velocity, H_2S (with and without used condition), S/C ratio along temperature. It is shown that even presented in the gas at very low concentration levels (ppm), sulfur drastically decreases the conversion of methane. The obtained results play a key role in design and optimization of an actual reactor [230].

Hamedi. et al.,(2014) reported a computational fluid dynamics (CFD) model based on a detailed kinetic mechanism developed for exhaust gas reforming of biogas to synthetic gas (H_2 and CO). The work concludes by validating the experiment data with CFD model as different parameters like O_2/CH_4 ratio and GHVC (gas hourly space velocities). A three-dimensional CFD model for a heterogeneous PO_X reactor with a rhodium catalyst was developed. The model was validated with the experimental results published in earlier work. Commercial CFD package ANSYS Fluent 13.0 software (ANSYS Inc.) was used to perform the simulation. This study shows that with sophisticated control over parameters such as O_2/CH_4 ratio, GHSV and inlet temperature, biogas can be implemented in a REGR system to generate hydrogen enriched gas for IC engine emissions control [231].

Balaji et al., (2020) focused on the production of hydrogen from biomass via anaerobic digestion of waste biomass and dry reformation of biogas. This process consumes carbon dioxide instead of releasing it and uses only renewable feed materials for hydrogen production. It is recognized that if biogas containing 52 mol% methane, 38 mol% carbon dioxide, and 10 mol% water (or steam) is used for hydrogen production by dry reformation at a temperature of 837.5°C and a pressure of 101.3kPa; optimal values of 89.9% methane conversion, 99.99% carbon dioxide conversion and hydrogen selectivity 1.21 can be obtained. Dry reformation of biogas can give hydrogen selectivity above 1 and yield above 2. End-to-end process Simulation model developed with HYSYS, MOSAIC modelling and MATLAB [232].

Roy et al., (2018) utilized Aspen Plus simulations and experimental data to investigate the steam-biogas reforming (SBR) method for hydrogen production from biogas. Various S/C ratios, temperatures, and CH_4/CO_2 ratios were examined for the SBR process. The study evaluated the influence of temperature and S/C ratio on feed conversion and other performance indicators. Comparatively, the SBR process is expected to achieve higher CH_4 conversion rates than dry reforming of CH_4. At 873 K and the entire S/C ratio range studied, over 50% of the equilibrium CH_4 conversion was attained. SBR simulations were conducted within a temperature range of 873-1123 K for biogas feeds with CH_4/CO_2 ratios of 40/60, 50/50, and 60/40 at S/C ratios of 1.0-2.0. Experimental results indicated positive CO_2 conversion [16].

Chouhan et al., (2021) developed a non-isothermal 1-D mathematical model to investigate steam reforming of biogas (SRB) in an industrial-scale packed bed reactor. The model demonstrated good agreement with previous modelling studies on steam reforming of biogas, which were utilized for model validation. Simulations were conducted to assess the performance of an industrial-scale steam reformer for SRB under varying biogas compositions (CH_4/CO_2 ratios of 40/60, 50/50, 60/40, 70/30, and 80/20) and heat flux values ranging from 0 to 70 kW/m^2 [233].

The above section covers the technological advancement in essential hydrogen production methods from biogas. Various H_2 production methods such as SMR, POR, ATR, DR, DOR, Bi-, and Tri-reforming are used for the conversion of methane and biogas. Various methods have been studied experimentally and simulation work for hydrogen production process but steam methane (SR) and steam biogas (Bi-)

reforming were adopted for simulation work. The mentioned literature survey shows extensive work on conventional and advanced methods of essential hydrogen production methods from biogas/methane (Table 2.2).

Table 2.2: Summary of simulation and modeling approach

Production Method	**Simulation Tool**	**Outcomes**	**Ref. & year**
Steam biogas reforming	ANSYS Fluent 13.0 software	This study shows that with sophisticated control over parameters such as O_2/CH_4 ratio, GHSV and inlet temperature, biogas can be implemented in a REGR system to generate hydrogen enriched gas for IC engine emissions control.	[231] (2014)
Steam methane reforming	-	The catalyst used in these experiments is a nickel-based catalyst supported on alumina, ($NiAl_2O_3$). Compare the experimental data with simulation data with different parameters like space velocity, H_2S (with and without used condition), S/C ratio along with temperature.	[230] (2015)
Steam biogas reforming	Aspen Plus	The steam-biogas reforming (SBR) process to convert biogas to high hydrogen syngas was studied experimentally and using Aspen Plus simulations. SBR simulations were conducted for biogas feeds with CH_4/ CO_2 ratios of 40/60, 50/50 and 60/40 at S/C ratios of 1.00–2.00 over a temperature range of 8731123 K.	[16] (2018)
Steam biogas reforming	HYSYS, MOSAIC modelling and MATLAB	Simulation model developed with HYSYS, MOSAIC modelling and MATLAB. Parameters are CH_4/CO_2 ratio, H_2/CO, mole fraction of CH_4, CO_2, and H_2O.	[232] (2019)
Steam biogas reforming	COMSOL Multiphysics	The model aims to investigate the performance of the reactor in order to enhance optimization and control of the steam reforming unit.	[229] (2016)
Steam biogas reforming	COMSOL Multiphysics	This study develops a concise CFD model for water gas shift in untreated biogas reformate, examining $3Ni5Cu/Ce_{0.5}Zr_{0.33}Ca_{0.17}$ catalyst interaction with fluid transport in fixed bed and membrane reactors. The CFD model closely aligns with literature and experimental data, yielding average absolute deviations of 8.59% and 6.32% during validation with fixed bed and membrane reactor experiments, respectively.	[234] (2020)
Steam biogas reforming	Aspen Plus	Reforming temperatures of 800°C and an H_2O/CH_4 ratio of 3 were found to be the ideal parameters for BG reforming in order to maximize hydrogen generation while minimizing the concentrations of methane and carbon monoxide.	[219] (2016)

Production Method	**Simulation Tool**	**Outcomes**	**Ref. & year**
Steam biogas reforming	ASPEN plus	According to the analysis, 735°C is the ideal temperature to convert pure methane into hydrogen, with O_2/CH_4 and H_2O/CH_4 equal to 0.05 and 1.45, respectively. The optimal biogas conditions are 50–60% CH_4, O_2/CH_4 = 0-0.1, and H_2O/CH_4 = 3-2.4, with reforming reactor conditions at T = 790–735°C.	[220] (2018)
SBR and ATR	Aspen Plus	The research indicates that steam reforming is the preferred method for efficient hydrogen production, boasting high energy efficiency (59.8%) and energy-based efficiency (59.4%). While the ATR layout is suitable for addressing increased local heat demand (73.9% energy efficiency, 54.8% exergy), steam reforming remains the top choice for simultaneously producing heat and hydrogen (73.5% energy efficiency, 64.4% exergy).	[221] (2020)
Combine SMR and SBR		To address varying demand scenarios, a network modeling technique integrates biogas supply with a conventional methane steam reformer. The primary outcome of the study was a noteworthy 24% decrease in the overall cost of hydrogen production.	[222] (2018)
SMR	CFD modeling (ANSYS Fluent)	Examining steam methane reforming within the temperature range of 600–1000 K and Reynolds numbers (Re) of 10, 50, and 100, alongside heat flux values of 1000 W/m^2 and 500 W/m^2, the study revealed a reduction in methane conversion with rising Reynolds number, heat flux through the walls, and inlet temperature.	[223] (2021)
SMR	CFD modelling (ANSYS Fluent)	Development and validation of a novel 0-D sub-model for methane steam reforming were undertaken. A satisfactory correlation was observed between the 3D CFD-based model and the newly developed 0-D model.	[224] (2021)
SBR	MATLAB software	The developed model has been validated using existing modeling studies on both industrial methane steam reforming processes and lab-scale biogas steam reforming. The biogas-fed industrial reformer exhibits hydrogen yields (1.022-2.28) and methane conversions (93.08-85.65%) that closely approximate thermodynamic equilibrium.	[233] (2021)

2.4 Thermodynamic equilibrium of steam reforming of biogas without CO_2

2.4.1 Formation of hydrogen amount

In this analysis, the biogas is considered as a pure methane (absence of CO_2), also known as steam methane reforming process. The syngas conversion from the ideal chemical reaction of steam-reforming methane is represented by Equation 2. One mole of methane (CH_4) is required to convert by 1 mole of water (H_2O). Typically, in this process, an abundant amount of steam is employed, which is determined by the molar ratio of steam-carbon (S/C). Fig. 2.4 depicts the thermodynamic equilibrium of a mixture containing CH_4 and H_2O, showcasing three distinct molar ratios of S/C. Fig. 2.4 illustrates the presence of significant products that exist in substantial quantities under these equilibrium conditions. All products are formed in the gaseous state apart from solid carbon and other known hydrocarbons are formed in small amounts nearly 10^{-6} -10^{-14} mol like ethane, acetone, ethylene, and methanol. Various small quantities of hydrocarbons and solid-state carbon are not presented here.

Fig. 2.4 (a) shows the equimolar ratio of H_2O/CH_4 (S/C). Hydrogen starts to form beyond 180°C and its concentration increases as the temperature rises, and CO_2 is formed at a temperature range from nearly 280-800°C but CO_2 is an undesirable by-product. The formation of syngas is favorable above 800°C thermodynamically under these conditions.

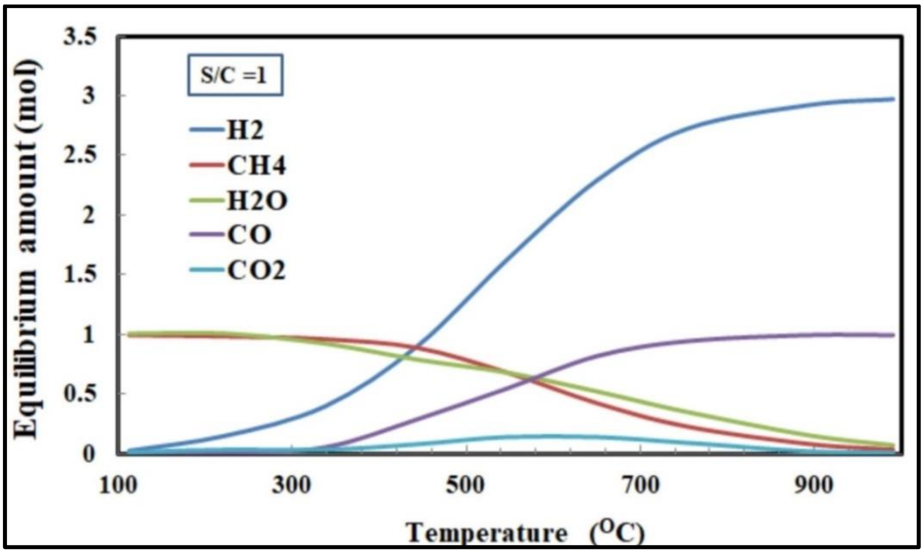


Fig. 2.4 (a): Thermodynamic equilibrium at atmospheric pressure of the mixture containing at 1mol CH_4 and 1mol H_2O [10]

Fig. 2.4 (b) shows the molar ratio of H_2O/CH_4 (S/C = 2). Hydrogen is more amount compared to the equimolar ratio due to an excess amount of water mol, methane is converse above 800°C, and CO_2 amount is increased at nearly 600°C due to WGS reaction and excess water mol. when molar S/C ratio 3 refers to Fig. 2.4 (c), methane product is completely consumed at nearly 720°C, hydrogen product is more, and the main benefit is utilizing a higher molar S/C ratio. However, an excess of water (more than 50%) sturdily burdens on process energy balance, and CO_2 is omnipresent exceeding more than 200°C due to the WGS reaction.

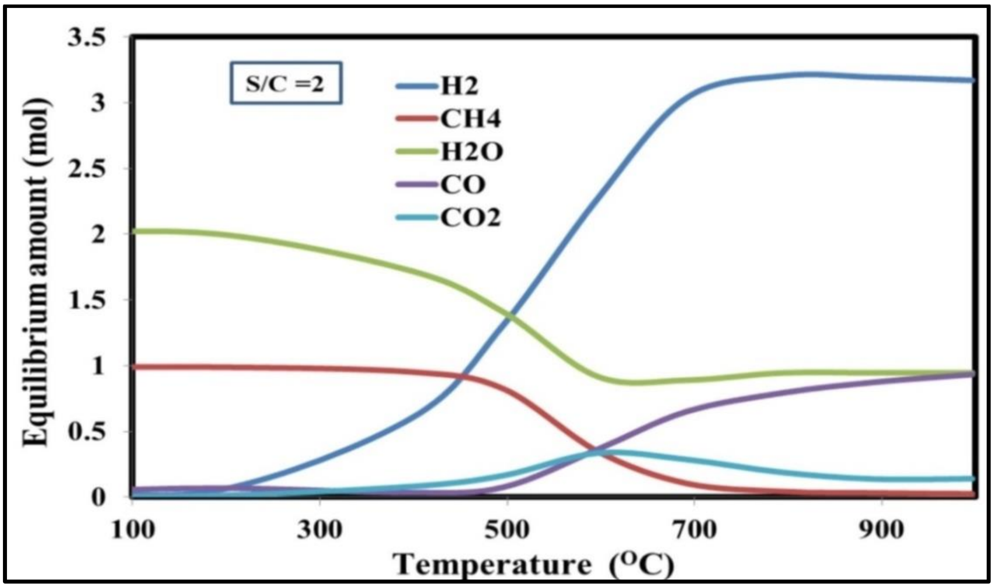


Fig. 2.4 (b): Thermodynamic equilibrium at atmospheric pressure of the mixture containing at 1 mol CH_4 and 2 mol H_2O [10]

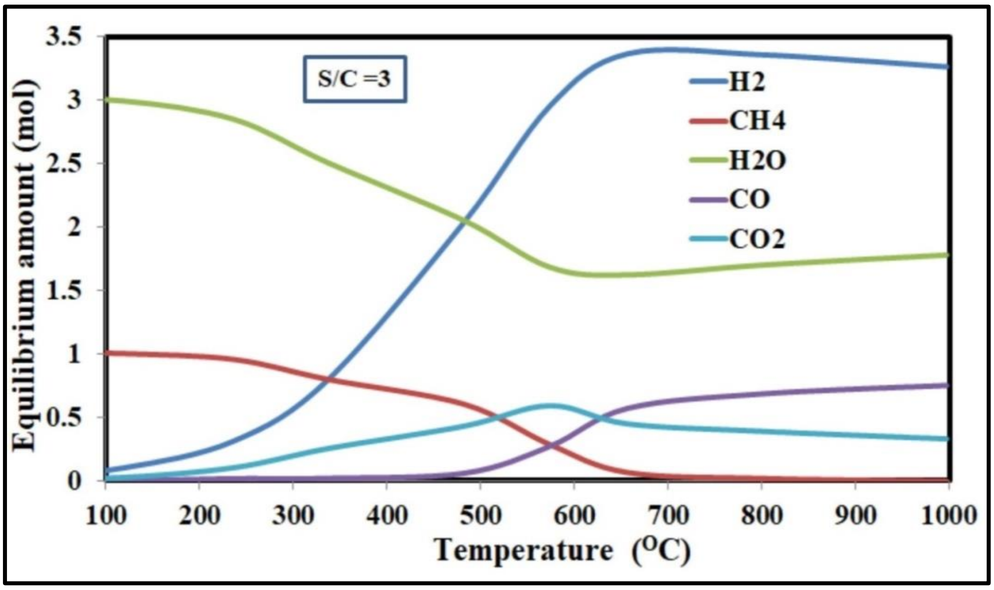


Fig. 2.4 (c): Thermodynamic equilibrium at atmospheric pressure of the mixture containing at 1 mol CH_4 and 3 mol H_2O [10]

2.4.2 Influence of methane conversion and yields of H_2, CO, and CO_2

Fig. 2.5 (a) shows the effect of methane conversion between varying molar ratio of steam carbon (S/C = 1-3) and reaction temperature at thermodynamic equilibrium. CH_4 conversion rises with reaction temperature when the S/C ratio is increased, while the amount of unconverted methane decreases in relation to reaction temperature.

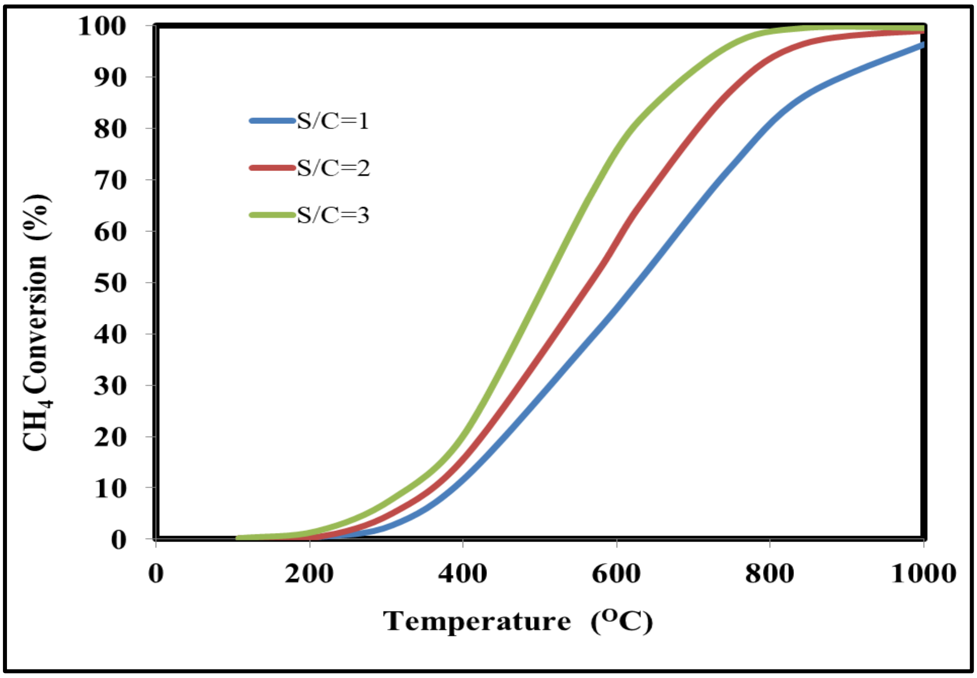


Fig. 2.5 (a): Effect of the molar ratio of S/C (1, 2, and 3) vs. temperature at thermodynamically on conversion of CH_4 [10]

The quantity of H_2 yield increases along with molar ratio of S/C at a certain temperature, as formerly observed in methane conversion, refer to Fig. 2.5 (b). Hydrogen amount touches the maximum yield caused by the existence of WGSR as well as increasing S/C ratio from 2:1 to 3:1.

The amount of CO attained after 400°C, also increases its amount with a certain temperature. The CO amount is slightly affected by the molar ratio of S/C at nearly 600°C, after that temperature, the increasing molar ratio is favored by WGS and thus starts to reduce the CO amount in Fig. 2.5 (c).

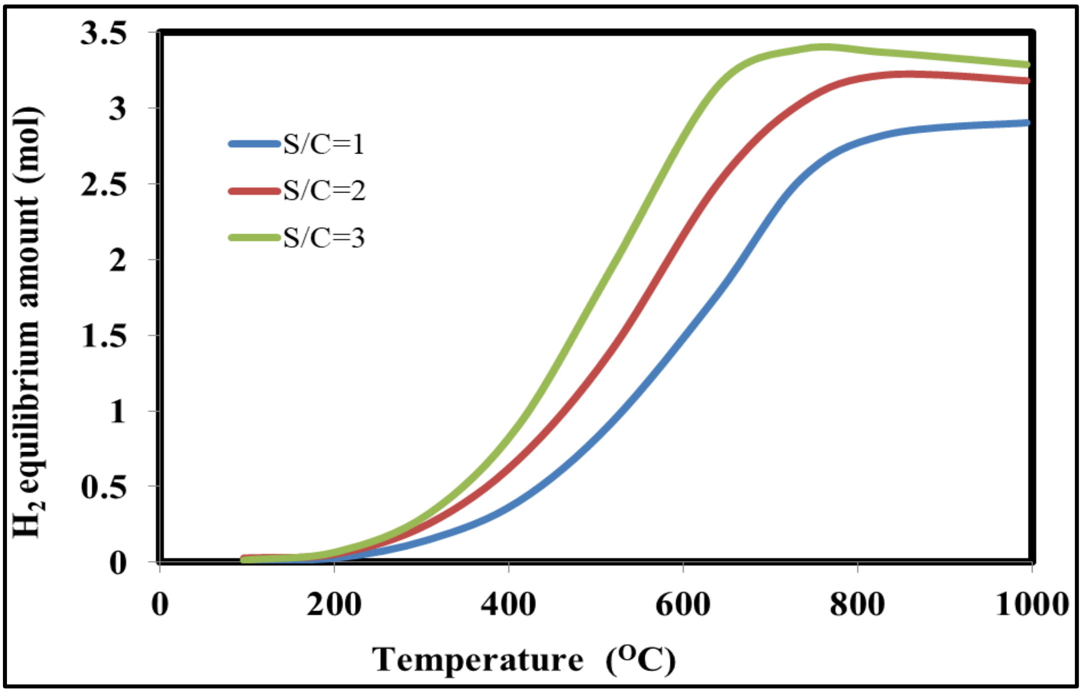


Fig. 2.5 (b): Effect of the molar ratio of S/C (1, 2, and 3) vs. temperature at thermodynamically on H_2 yield [10]

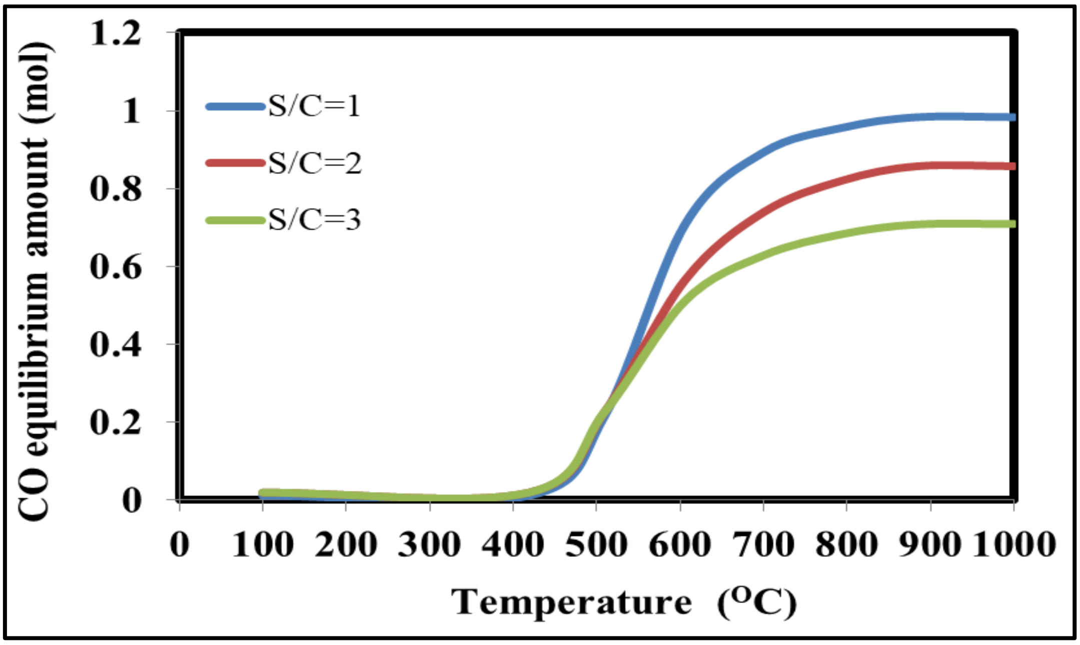


Fig. 2.5 (c): Effect of the molar ratio of S/C (1, 2, and 3) vs. temperature at thermodynamically on CO yield [10]

In SMR, the water gas shift (WGS) reaction is liable for producing quantity of CO_2 and it is also an assessment of CO_2 amount in Fig. 2.5 (d). The quantity of CO_2 gains as well as increases the S/C molar ratio at a certain temperature and it touches a maximum nearby 600°C for each molar ratio. After the above, this reaction temperature reduces amount with increasing reaction temperature [10]. It seems from these results, SMR is extremely preferred using an S/C ratio above 1.5/1 and a temperature of nearly 700°C at atmospheric pressure.

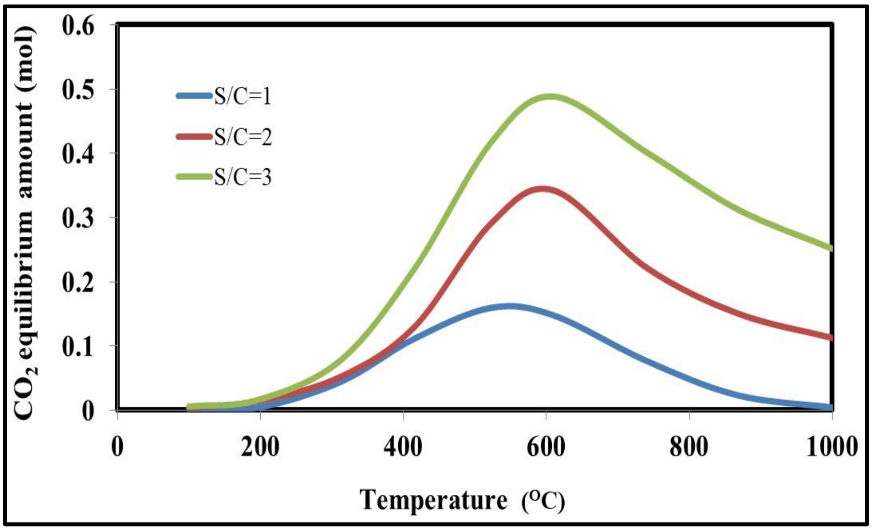


Fig. 2.5 (d): Effect of the molar ratio of S/C (1, 2, and 3) vs. temperature at thermodynamically on CO_2 yield [10]

2.5 Thermodynamic Equilibrium of Steam Reforming of Biogas (SRB) with CO_2

SRB is also known as dual methane reforming, it refers to syngas production from a mixture of (CH_4 + CO_2) and H_2O. This arrangement is mainly interesting to different kinds of arrangements like biogas steam reforming and carbon dioxide (CO_2) valorization by its combination into the natural gas or methane reforming. Therefore, the role of oxidants is played by both H_2O and CO_2 in the reforming process. The WGS equilibrium is also affected by the simultaneous occurrence of using both CO_2 and H_2O.

Here, following two cases are considered for analysis.

i.) Different quantities of water (H_2O) are added while maintaining a constant mixture composition of CH_4 and CO_2.

ii.) Various amounts of CO_2 are added while keeping a constant mixture composition of CH_4 and H_2O.

2.5.1 Influence of methane and CO_2 conversion, coke selectivity, and yields of H_2 at various compositions of steam

The effect of thermodynamic equilibrium analysis of mixtures is comprising 1mol of CH_4 and CO_2 and mol of H_2O (0.5, 0.8, 1.2, and 2) at 1 bar as shown in Fig. 2.6. A composition containing an equal molar mixture of CH_4 and CO_2 can serve as a representation of biogas or purified landfill gas. There are not many more benefits of increasing the water content in this mixture for methane conversion to nearly 700°C. The methane conversion is decreasing with increasing water content up to 600°C due to water content formation from a mixture of methane and CO_2 via WGSR. But, adding water content leads to a slight improvement in methane conversion above 700°C. Therefore, it is possible to touch 100% methane (CH_4) conversion, refer to Fig. 2.6 (a).

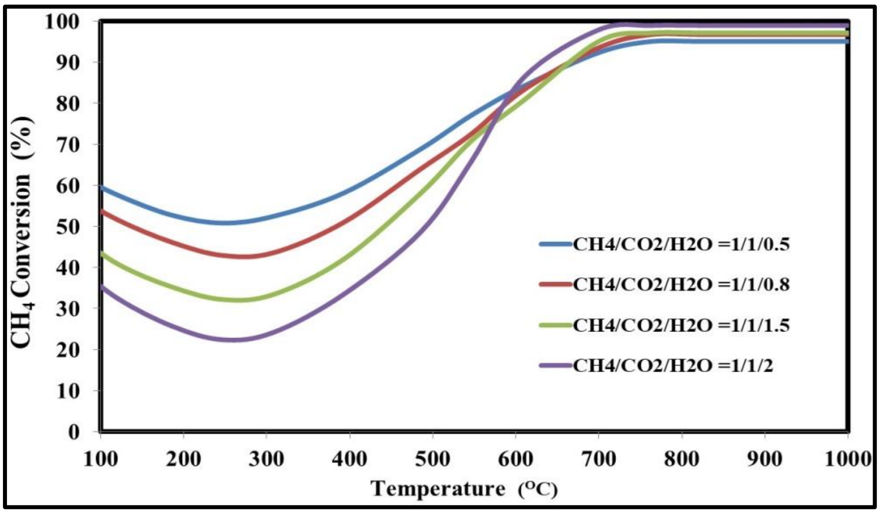


Fig. 2.6 (a) Effect of thermodynamic equilibrium analysis at 1 bar on conversion of CH_4 [10]

Fig. 2.6 (b) also shows the effect of decreasing CO_2 conversion with an increasing amount of water content added to the mixture due to the reason of WGS. Conversely, there is also strongly affects the various amounts of solid carbon (Coke), hydrogen yield, and content of CO by adding the quantity of H_2O to the system. Fig. 2.6 (c) illustrates coke selectivity for different operating conditions of $CH_4/CO_2/H_2O$ as a function of reaction temperature. Coke selectivity indicates that Coke or solid carbon can be well controlled by adding water to the system. Coke formation can be reduced with increasing water content in the mixture at a given specific reaction temperature. It is found that no coke formation takes place above 700°C using H_2O content more than one [243].

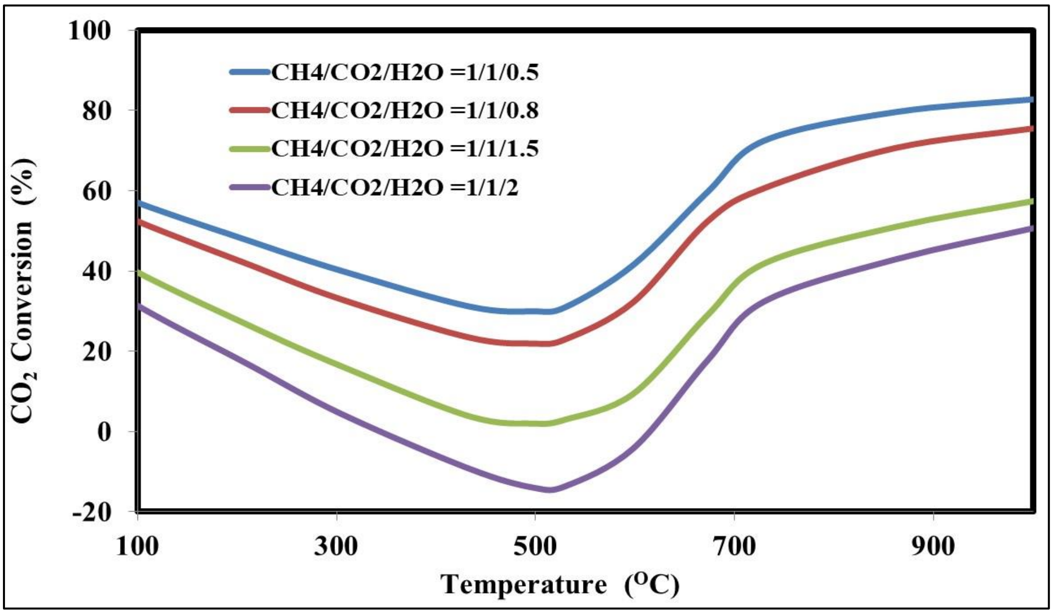


Fig. 2.6 (b): Effect of thermodynamic equilibrium analyses at 1 bar on CO_2 conversions [10]

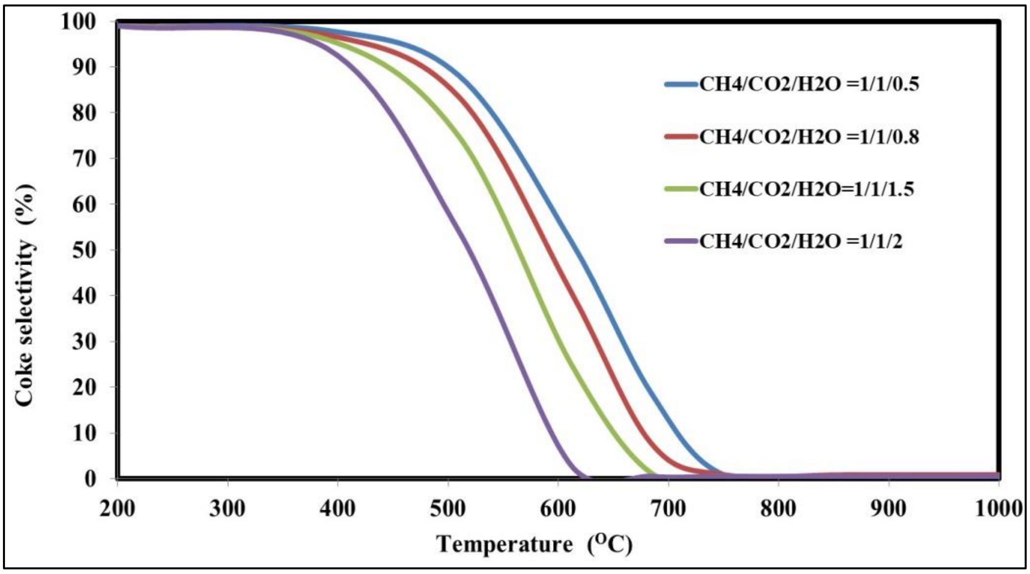


Fig. 2.6 (c): Effect of thermodynamic equilibrium analysis at 1 bar on coke selectivity [10]

The formation of hydrogen is strongly influenced and favorable by adding water to the system due to coke gasification, and due to the presence of WGS touches the maximum hydrogen yield amount as shown in Fig. 2.6 (d).

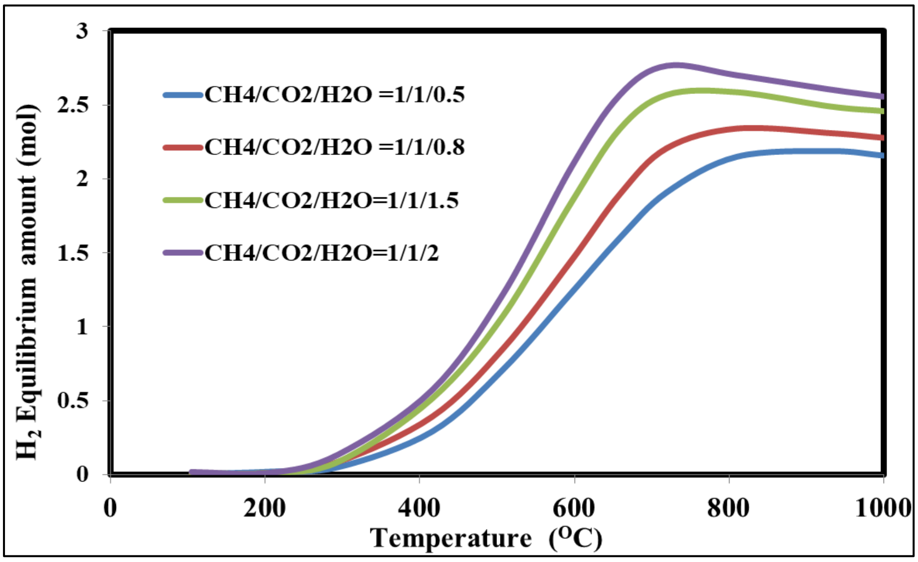


Fig. 2.6 (d): Effect of thermodynamic equilibrium analysis at 1 bar on H_2 yields [10]

2.5.2 Influence of various chemical equilibrium amount and H_2/CO ratio at various compositions of CO_2

Fig. 2.7 illustrates the influence of thermodynamic analysis of mixtures comprising CH_4 (2 mol), H_2O (1 mol), and CO_2 mol with various mol conditions (0.5, 0.8, 1.2, and 2) at pressure 1 bar. In this condition, the major quantities of CH_4 and H_2O remain constant, while the quantity of CO_2 varies. The addition of CO_2 predominantly enhances CH_4 conversion below approximately 700°C, but its effectiveness diminishes at higher reaction temperatures, as depicted in Fig. 2.7 (a).

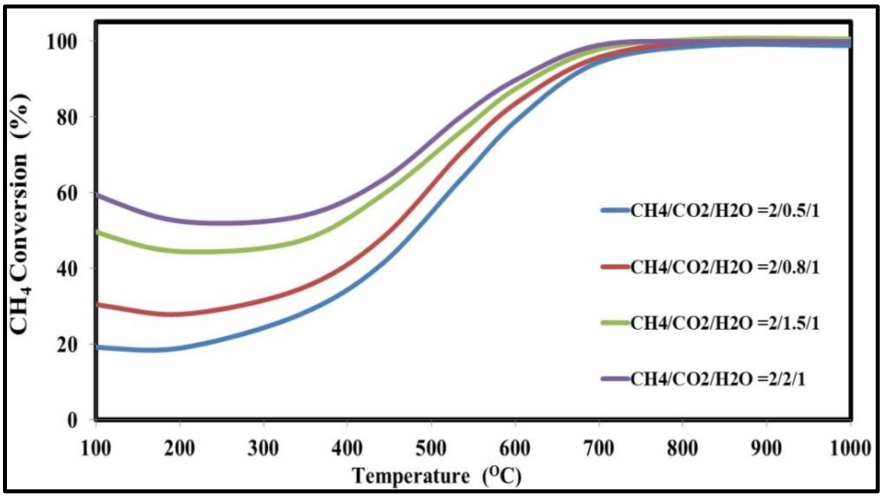


Fig. 2.7 (a) Effect of thermodynamic equilibrium analysis at 1 bar on CH_4 conversion [10]

The primary quantity of CO_2 slightly affects the conversion of CO_2 as shown in Fig. 2.7 (b) and H_2 yield in Fig. 2.7 (d). However, CO_2 amount has a sturdy impact on coke formation as depicted in Fig. 2.7 (c), CO formation in Fig. 2.7 (e), and molar ratio H_2/CO in Fig. 2.7 (f). Coke selectivity is sharply limited with increasing CO_2 amount, which is explained by coke gasification through CO_2 to form CO amount at temperatures above 550°C. This observation further highlights the beneficial effect of the initial quantity of CO_2 on CO production. As the initial amount of CO_2 increases, the molar ratio of H_2/CO decreases. This phenomenon can be attributed to the significant impact of the initial CO_2 amount on CO formation, whereas the yield of H_2 is comparatively less influenced.

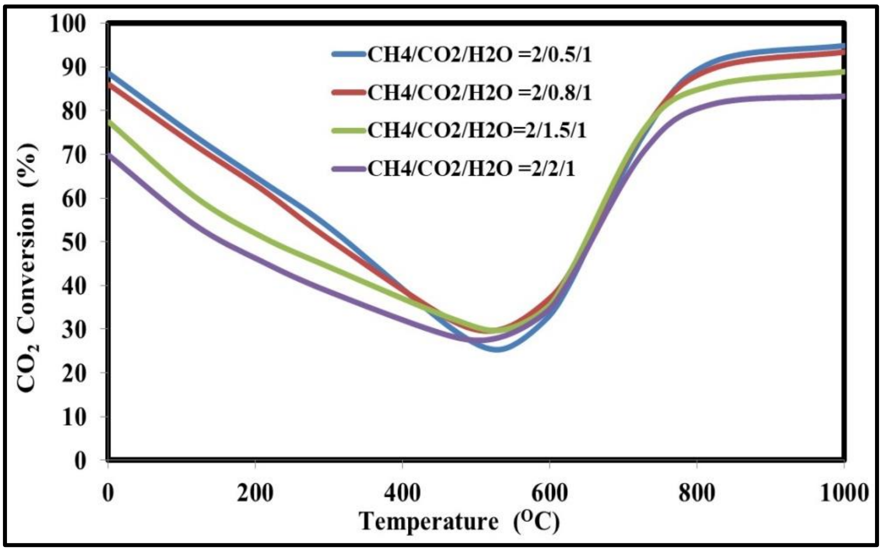


Fig. 2.7 (b) Effect of thermodynamic equilibrium analyses at 1 bar on CO_2 conversions [10]

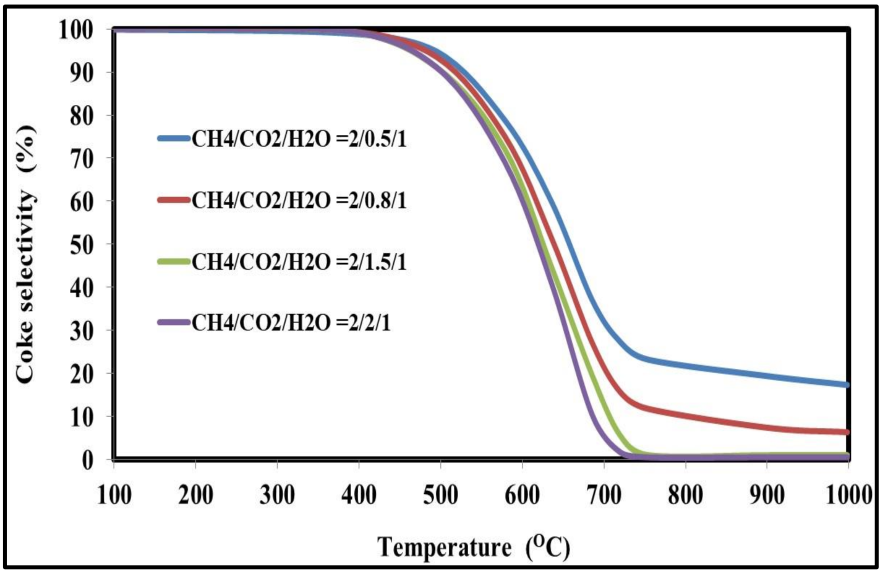


Fig. 2.7 (c) Effect of thermodynamic equilibrium analysis at 1 bar on coke selectivity [10]

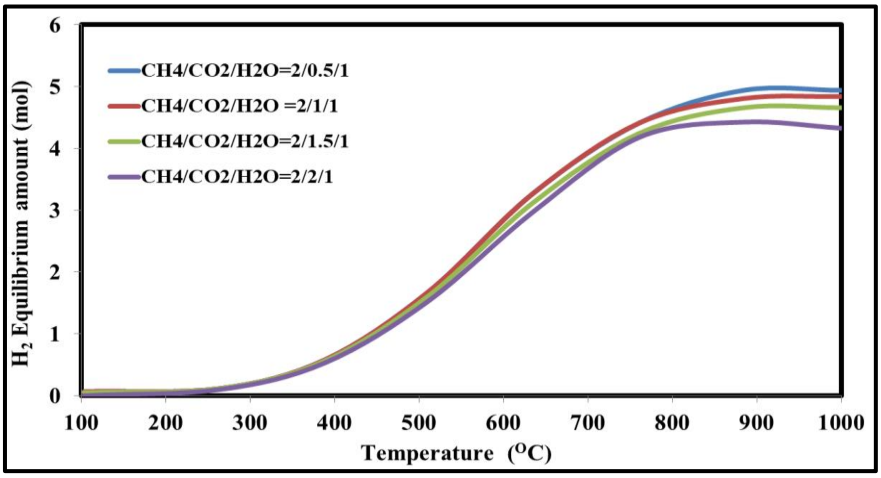


Fig. 2.7 (d): Effect of thermodynamic equilibrium analysis at 1 bar on H_2 yields [10]

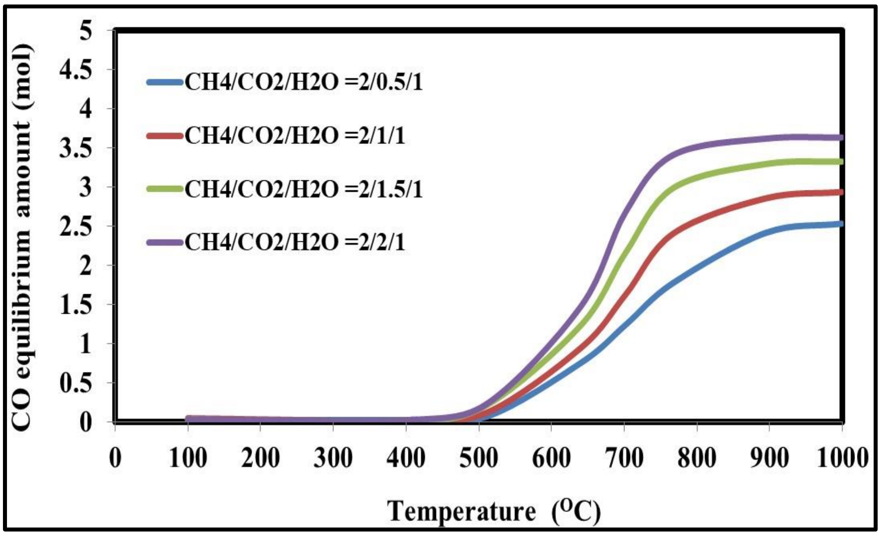


Fig. 2.7 (e): Effect of thermodynamic equilibrium analysis at 1 bar on CO equilibrium amounts [10]

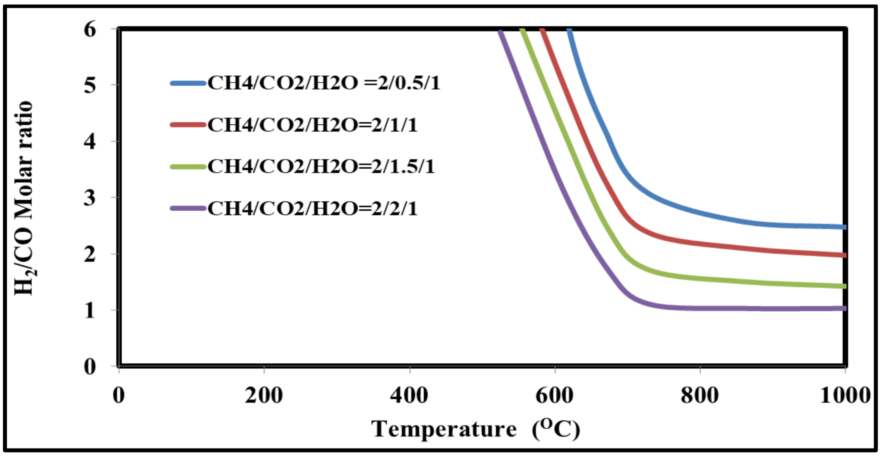


Fig. 2.7 (f) Effect of thermodynamic equilibrium analysis at 1 bar on H_2/CO molar ratios [10]

2.6 Research Gap

Numerous studies have examined the economically feasible production of hydrogen from various compositions of biogas using diverse methods and parameters. However, certain aspects of this area remain underexplored:

i.) The current study lacks simulation tools capable of predicting the optimization of key parameters for hydrogen production from biogas.

ii.) There is limited research on critical operating parameters such as catalyst characteristics, optimal temperature, the impact of impurities in biogas, and their concentrations, all of which are essential for achieving efficient hydrogen production.

iii.) Further investigation is needed in the field of simulation and modeling of biogas reforming, utilizing software tools like CFD, Aspen Plus, and COMSOL Multiphysics, which can validate existing experimental results and enhance our understanding of hydrogen production processes.

2.7 Research Objectives

Based on the research gap, certain research objectives have been framed. Simulation studies of the proposed system can achieve that:

i.) To optimize performance affecting parameters such as temperature, pressure, CH_4/CO_2, S/C ratio, Gas hourly space velocities (GHSV), HO_2/CH_4, H_2/CO, etc. in H_2 production methods from biogas.

ii.) To study simulation and modelling for hydrogen production to increase the yield of Hydrogen.

iii.) To validate the simulation and modelling results with previous experimental results.

2.8 Research Scope

The analysis of hydrogen production through biogas system is required to reveal the next level of development in the field of essential production techniques. Many more researchers have also worked in this area with certain research gaps, as represented in Table 2.1. Hence, by fulfilling the research gap (performance evaluation, optimization of process parameters), one can improve essential H_2 production through simulation study. In the investigation of hydrogen production from biogas, computational tools are employed through modeling and simulation to enhance the understanding, optimization, and improvement of the underlying processes. Given the interdisciplinary nature of hydrogen production, researchers exploring the intricate aspects of biogas-based hydrogen production may find it necessary to collaborate with experts in areas of chemistry, engineering, economics, environmental science, and policy to effectively address the complex issues involved. Therefore, this novel proposed model has better research scope to increase hydrogen production and better analyse tools for predicting industrial data.

2.9 Research Contribution

In the context of biogas-based hydrogen production, the use of simulation and modelling tools helps with process optimization, cost reduction, resource efficiency improvement, predictive insights, and environmental issues. Research contributions of present study are as follows:

i. The primary innovation of this research lies in the developed methodology for analyzing a chemical reaction system and offering recommendations to improve the operational parameters of mixed reforming involving methane and biogas.

ii. Traditionally, the optimization of operational parameters in chemical reactions involves extensive experimental trials and empirical analysis. However, the proposed methodology in this research introduces a new approach to examine the mixed reforming process more efficiently and effectively.

iii. The researchers may have developed a comprehensive computational model to simulate and predict the behavior of the mixed reforming process under different parameter conditions.

iv. The proposed model could incorporate reaction kinetics, thermodynamics, and transport phenomena to provide a detailed understanding of the system.

CHAPTER 3

METHODOLOGY

3.1 Introduction

The current study introduces a 0-D mathematical model to explore hydrogen production through steam reforming of methane and biogas with varying compositions. The model was performed by using a batch reactor and incorporated both heat and mass transfer with the chemical reactions occurring in the reactor and calculated product distribution and temperature through the application of energy and mass balances. Fig. 3.1 depicts a graphical representation of the current work's methodology.

The model was also presented to explain the reaction mechanism involved in the production of hydrogen, and the reaction performance was validated through a simulation analysis using the finite element analysis software (COMSOL Multiphysics 5.6). The presented reactor model closely predicts outcomes from both the 1-D and 2-D non-isothermal models of methane and biogas steam reforming. Therefore, a zero-dimensional model is favoured to simplify this study.

3.2 Literature Review

The literature reviews of this thesis have three parts, which include basic concepts of conventional as well as advanced methods, literature on their experimental approach, and literature on simulation modelling approach to evaluate experiment data with model and find the best optimum method. Various research papers, articles and related books have been studied. Literature review and the identified research gaps are given in Chapter 2.

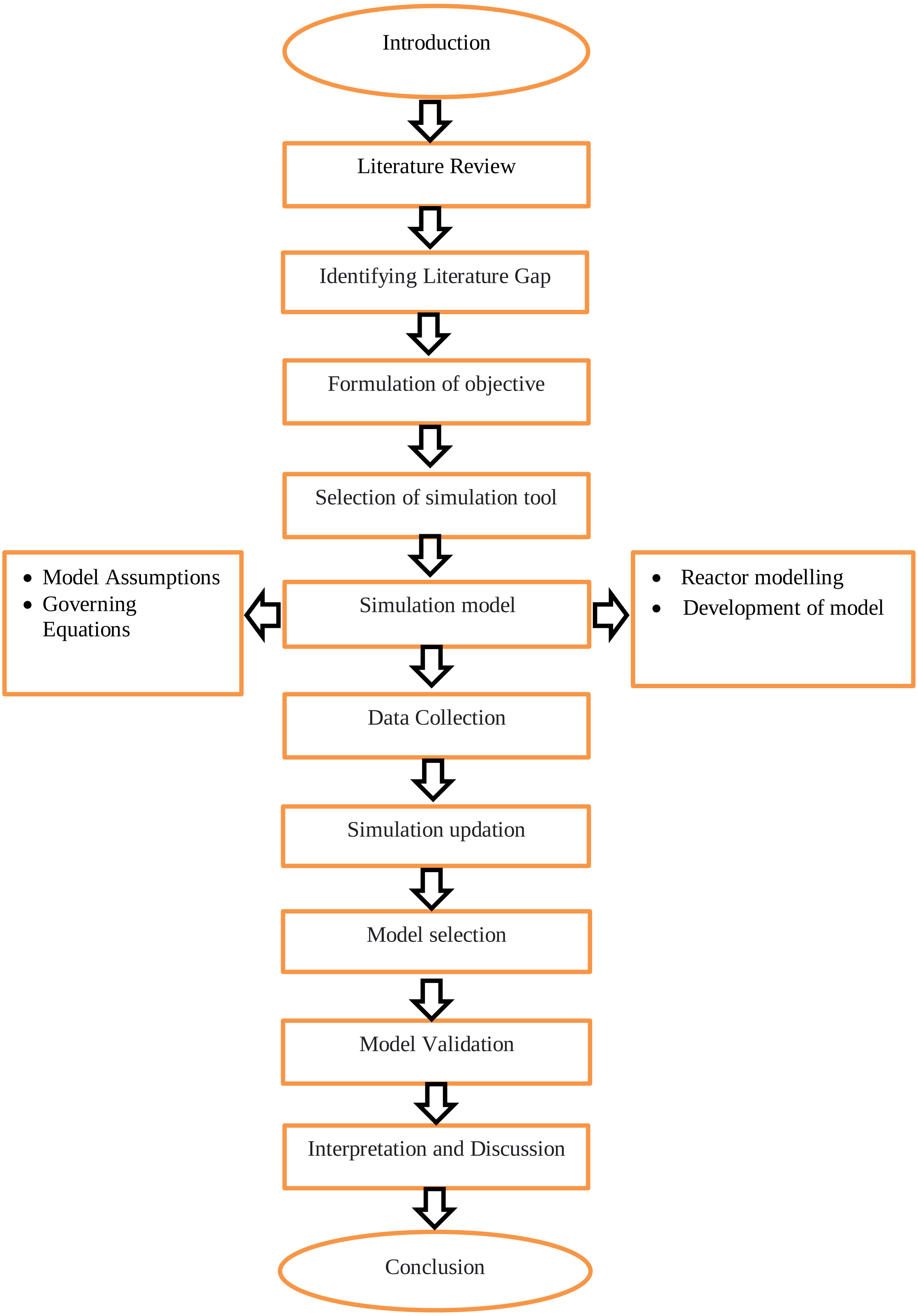


Fig. 3.1: Flow chart of present work

3.3 Formulation of Research Objectives

The research objectives of the present work are as follows:

- To optimize performance affecting parameters in H_2 production from biogas reforming methods.
- To study simulation and modelling for hydrogen production to increase the yield of Hydrogen.
- To validate the simulation and modelling results with previous experimental results.

3.4 Selection of simulation tool

The selection of a simulation tool typically involves several key steps to ensure that the chosen tool is the most appropriate for the specific research goals:

i.) **Simulation objectives:** Clearly express the objectives of the simulation. Understand what the aim is to achieve with the simulation, such as predicting system behaviour, optimizing processes, or testing hypotheses.

ii.) **Identify simulation requirements:** Determine the specific requirements and constraints of the simulation project. Consider factors such as the type of system being simulated (e.g., physical, biological, social), the level of detail needed, computational resources available, and any industry or domain-specific standards or regulations.

iii.) **Research available tools:** When surveying simulation tools, consider widely used options with strong reputations in related field. Look for features like compatibility, scalability, and ease of use, ensuring the support of the types of simulations needed.

iv.) **Evaluate tools:** Once a list of potential simulation tools, evaluate each one against the requirements. This evaluation may involve several steps, such as: Reviewing documentation, user manuals, and tutorials to understand the capabilities and limitations of each tool. Testing the tools with sample or simplified models relevant to project to assess their performance, usability, and accuracy.

v.) **Select the best fit:** Based on evaluation, choose the simulation tool that best meets requirements and objectives. Consider not only the technical capabilities of the tool but also practical considerations such as cost, support, and ease of integration with existing workflow or infrastructure.

vi.) **Plan implementation:** Once select a simulation tool, develop a plan for implementing it within project or research. This may involve tasks such as setting up the software, acquiring necessary licenses or permissions, training team members, and establishing workflows for model development, validation, and analysis.

vii.) **Iterate and refine:** As begin using the selected simulation tool, be prepared to iterate and refine your approach based on feedback, new insights, and evolving project requirements.

By following these steps, it can make an informed decision when selecting a simulation tool that aligns with the project goals and requirements.

3.4.1 Simulation tools based on hydrogen production methods

Simulation is a powerful and important tool because it provides a way in which alternative design and plan can be evaluated without having to experiment on a real system, which may be prohibitively costly, time-consuming or simply impractical.

There are some identified simulation tools for hydrogen production process such as

- ANSYS Fluent software
- MOSAIC modelling
- HYSYS
- MATLAB
- ASPEN Plus V11
- COMSOL Multiphysics

These tools are very useful for optimization of hydrogen production parameters like steam carbon ratio (S/C), O_2/CH_4, Gas hourly space velocities (GHSV), CH_4/CO_2 ratio, H_2/CO, mole fraction of CH_4, CO_2 and H_2O.

3.4.2 COMSOL Multiphysics

COMSOL Multiphysics is interactive software with Graphical User Interface (GUI) that employs the Finite Element Method, capable of handling PDEs and DAEs. The software has proven robust enough to apply various physical phenomena to geometries with appropriate boundary conditions and material properties. The relevant equations that the software utilizes to describe the varying phenomena are designed into modules that allow the user to easily enter inputs. The user also has the option of entering their equations if so desired [235].

COMSOL Multiphysics is a powerful finite element analysis and simulation software package used for modeling and simulating physics-based systems and processes [236]. It allows engineers and scientists to simulate coupled physics phenomena in a unified environment, including structural mechanics, heat transfer, fluid flow, electromagnetics, acoustics, chemical reactions, and more.

COMSOL Multiphysics is widely used across various industries and research fields, including mechanical engineering, electrical engineering, chemical engineering, biomedical engineering, and more, for applications such as heat exchanger design, electromagnetic device optimization, fluid-structure interaction analysis, and many others.

3.4.2.1 Key features of COMSOL Multiphysics

i. **Multiphysics Simulation:** Ability to couple multiple physical phenomena together, enabling realistic modeling of complex systems where different physics interact.

ii. **Geometry Modeling:** Provides tools for creating and importing complex 3D geometries, allowing users to accurately represent their physical systems.

iii. **Mesh Generation:** Automatic and manual meshing capabilities for generating high-quality finite element meshes are crucial for accurate simulation results.

iv. **Solver Technology:** Includes a variety of solvers tailored for different physics domains, optimized for efficiency and accuracy.

v. **Built-in Physics Interfaces:** Predefined physics interfaces cover a wide range of applications, making it easier to set up simulations for specific problems.

vi. **Customization and Extensibility:** COMSOL Multiphysics offers flexibility for users to customize and extend its capabilities through user-defined functions, custom equations, and scripting.

vii. **Post-Processing:** Advanced visualization and post-processing tools allow users to analyze simulation results in detail and extract meaningful insights from their data.

viii. **Application Builder:** Allows users to create custom simulation applications based on their models, which can be shared and deployed to colleagues or clients without requiring them to have COMSOL Multiphysics installed.

ix. Engineers and scientists use the COMSOL Multiphysics® software to simulate designs, devices, and processes in all fields of engineering, manufacturing, and scientific research. COMSOL Multiphysics® is a simulation platform that provides fully coupled multiphysics and single-physics modeling capabilities.

3.5 Simulation model

i. The utilization of Chemical Species Transport interfaces involves the computation of the concentration of chemical species fields in solutions, accounting for diverse transport mechanisms including diffusion, convection, and migration. Furthermore, these interfaces also account for chemical reactions occurring in dilute and concentrated solutions. This comprehensive modelling allows for a more accurate understanding of the complex behavior of chemical species in a range of different contexts.

ii. Reaction engineering interface facilitates the modeling of different types of chemical reactors and the temporal evolution of chemical reactions.

iii. Mass balance and energy balance equations in these systems assume the presence of ideal or clearly defined mixing within the reactor. The kinetic and thermodynamic expressions of the reaction(s) occurring in a reactor can be distributed to a space-dependent model.

iv. A time-dependent study is employed to analyze systems where the field variables are time-dependent.

v. Reaction engineering module is employed in a wide range of applications, such as calculating the time-dependent chemical composition in chemical species transport or analyzing reaction kinetics and the chemical composition of a system undergoing chemical reactions.

3.5.1 Simulation procedure

The following steps are considered for the simulation work.

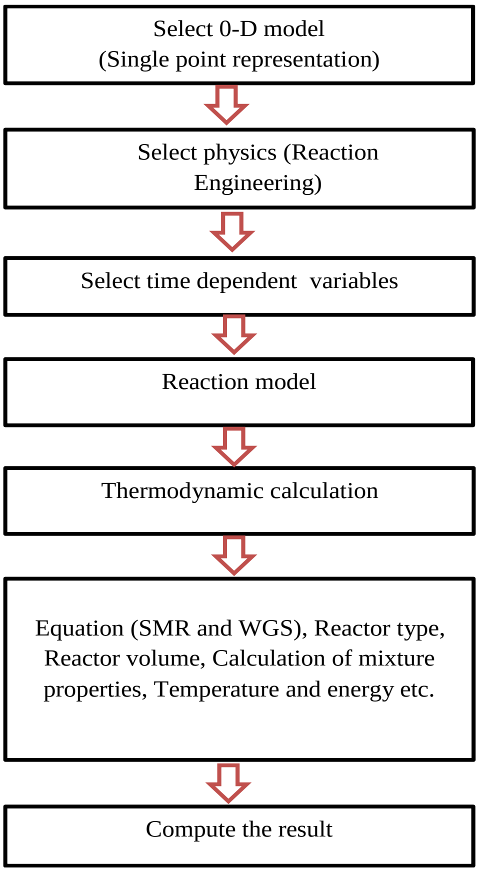


Fig. 3.2: Simulation procedure

3.5.2 Reactor modeling

To model a wide range of processes occurring in a reactor, transport phenomena are represented using Partial Differential Equations (PDEs) and solved through the application of Finite Element Methods. This comprehensive model effectively combines heat and mass transport with chemical reactions that occur within the reactor. By employing energy and mass balances, it becomes feasible to analyze the temperature and product distributions along the length of the reactor. The reactor is simplified and modeled as a batch-type reactor, with a focus on the transient state.

3.5.2.1 Concept of Zero dimensional (0-D) model

A zero-dimensional (0-D) model, often referred to as a lumped-parameter model or point model, is a simplified representation of a system where all the components or variables are assumed to be uniformly distributed or concentrated at a single point. In a 0-D model, the entire system is treated as a single entity without spatial distribution.

Here are some key concepts associated with 0-D models:

i.) **Point Representation:** In a 0-D model, the entire system or a component is represented by a single point or node. This point encapsulates the behavior of the system or component without considering spatial variations.

ii.) **Simplified Geometry:** Since the model does not account for spatial distribution, complex geometries are often simplified to a single point or volume.

iii.) **Idealizations:** 0-D models often make idealizations and assumptions to simplify the mathematical description of the system. These assumptions can include neglecting certain physical effects, such as gradients, spatial variations, or detailed geometrical features.

iv.) **Conservation Laws:** Despite its simplicity, a 0-D model still adheres to the fundamental principles of conservation laws relevant to the system being modeled. These could include conservation of mass, energy, momentum, or other relevant quantities.

v.) System Parameters: The behavior of the system in a 0-D model is typically described by a set of parameters or variables that represent its properties and interactions. These parameters could include mass, volume, temperature, pressure, flow rates, etc.

vi.) **Applications:** 0-D models are commonly used in various fields of engineering and science where a simplified representation of a system is sufficient for analysis or simulation. Examples include electrical circuits (where components are represented by nodes and branches), thermal systems (where components are represented by thermal capacitance and resistance), and chemical kinetics (where reactions are represented by rate equations).

vii.) **Simulation and Analysis:** 0-D models are often used for rapid prototyping, preliminary design analysis, and system-level optimization studies. They provide insights into the overall behavior and performance of the system without the computational expense of more detailed, spatially resolved models.

viii.) **Limitations:** While 0-D models offer simplicity and computational efficiency, they may lack the accuracy and detail provided by higher-dimensional models. They are most suitable for systems where spatial variations can be reasonably neglected or when detailed spatial information is not required for the analysis. Additionally, 0-D models may require calibration or validation against experimental data to ensure their accuracy and reliability.

Zero-dimensional (0-D) models are often utilized in the field of biogas reforming for their ability to provide a simplified yet insightful representation of complex reaction systems. In the context of biogas reforming, a 0-D model can be constructed to simulate the chemical reactions involved in the reforming process, typically steam reforming or dry reforming of methane present in biogas.

3.5.2.2 0-D model for biogas reforming

Biogas reforming is a promising technology for converting methane-rich biogas into valuable syngas, which can be further processed to produce hydrogen or synthesis gas for various industrial applications. In this study, we proposed a 0-D model to simulate the methane and biogas reforming process and analyze the key parameters influencing its performance. The reactor is assumed to have uniform temperature, pressure, and composition throughout, allowing for a simplified one-dimensional representation.

The 0-D model allows for the simulation of biogas reforming under various operating conditions, such as temperature, pressure, and feed composition. Sensitivity analysis can be conducted to investigate the effects of these parameters on reactor performance, including gas conversion, biogas composition, and heat transfer characteristics.

The proposed 0-D model provides a valuable tool for understanding and optimizing biogas reforming processes. Future research efforts will focus on refining the model predictions through experimental validation and extending its applicability to dynamic operating conditions and reactor configurations. Such a 0-D model serves as a starting point for studying biogas reforming systems, offering insights into the fundamental aspects of the process while balancing computational efficiency with predictive accuracy.

3.5.3 Model Assumptions

Following primary assumptions are considered for the model:

i.) The process follows the ideal gas law.

ii.) The catalyst particles exhibit uniformity in both shape and size.

iii.) Reformer operations under transient state conditions.

iv.) Chemical components such as CH_4, CO_2, CO, H_2, and H_2O are considered in the present reactor model.

v.) Carbon formation is neglected.

vi.) N_2, H_2S, and other traces of gases are neglected.

3.5.4 Governing equations

The primary equations that govern the model are given as:

Species mass balance:

$$\frac{dc_i}{dt} = R_i \tag{3.1}$$

Reactor energy balance:

$$V_r C_p \frac{dT}{dt} = Q + Q_{ext} + \frac{dp}{dt} V_r \tag{3.2}$$

$$Q = -V_r \sum_j H_j r_j \tag{3.3}$$

In the above equations, C_i represents the molar flow rate of the species in mol/s, V_r denotes the volume of the reactor in m^3, and R_i signifies the net reaction rate of the species in mol/(m^3s). The molar heat capacity of the species is represented by C_p in J/(mol·K), and Q_{ext} corresponds to the heat added to the system per unit volume in J/ (m^3·s). Q represents the heat resulting from the chemical reaction in J/(m^3·s), H_j represents the heat of the reaction in J/mol, and r_j denotes the reaction rate in mol/(m^3·s).

Arrhenius expression

$$k^f = A^f \left(\frac{T}{T_{ref}}\right)^{n^f} \exp\left(\frac{-E^f}{R_g T}\right), T_{ref} = 1K \tag{3.4}$$

$$k^r = A^r \left(\frac{T}{T_{ref}}\right)^{n^r} \exp\left(\frac{-E^r}{R_g T}\right), T_{ref} = 1K \tag{3.5}$$

Where,

A^f- Forward Frequency factor m^3/s.mol

n^f- Forward temperature exponent m^3/s.mol

E^f- Forward activation energy

A^r- Reverse Frequency factor

n^r- Reverse temperature exponent

E^r- Reverse activation energy

k^f- Forward Rate constant

3.6 Reaction kinetic model

The literature extensively examines various kinetic models for SMR and WGSR reactions. The model presented here can be applied to any suitable kinetic model for the specific catalyst employed. The model expressed by Xu and Froment [237] has experimented on a laboratory scale for SMR using Ni-based catalysts. The expression of kinetic rate for main reactions such as steam methane reforming (SMR-R_1), water gas shift (WGS- R_2) reaction, and reverse methanation reforming (RMR- R_3) have been developed based on Langmuir- Hinshelwood approach, have been extensively used to simulate the kinetics of SMR [34] and also used in the present work. The kinetic rate expression for the main three reactions R_1, R_2, and R_3 are expressed by Xu and Froment kinetic equations [238, 239].

3.6.1 Kinetic rate expressions

SMR: $$R_1 = \frac{\frac{k_1}{P_{H_2}^{2.5}}\left(P_{CH_4}P_{H_2O} - \frac{P_{H_2}^{3}P_{CO}}{K_{eq.1}}\right)}{[DEN]^2} \tag{3.6}$$

WGSR: $$R_2 = \frac{\frac{k_2}{P_{H_2}}\left(P_{CO}P_{H_2O} - \frac{P_{H_2}P_{CO_2}}{K_{eq.2}}\right)}{[DEN]^2} \tag{3.7}$$

RMR: $$R_3 = \frac{\frac{k_3}{P_{H_2}^{3.5}}\left(P_{CH_4}P_{H_2O}^{2} - \frac{P_{H_2}^{4}P_{CO_2}}{K_{eq.3}}\right)}{[DEN]^2} \tag{3.8}$$

$$DEN = 1 + \frac{F_{H_2O}^{in}}{F_{CH_4}^{in}} + \frac{F_{H_2}^{in}}{F_{CH_4}^{in}} + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4} + \frac{K_{H_2O}P_{H_2O}}{P_{H_2}} \tag{3.9}$$

Where, Ri represents the reaction rates for three different reactions (i = 1, 2, and 3), measured in kmol/kgh.

ki corresponds to the reaction rate constants for the three reactions (i = 1, 2, and 3).

Ki stands for the adsorption constants of chemical species, namely CH_4, H_2O, CO, and H_2.

K_{eq}.i denotes the equilibrium constants for the three reactions (i = 1, 2, and 3).

Pi represents the partial pressures of chemical species (CH_4, CO_2, H_2O, CO, and H_2) in the reaction zone.

F_i^{in} refers to the molar flow rate as i (i = H_2O, H_2, and CH_4).

The parameter DEN represents a dimensionless value, while P represents the partial pressure of the respective component within the catalyst.

3.6.2 Partial pressures

The calculated values of the partial pressures (Pi) for chemical constituents including CH_4, H_2O, CO_2, H_2, and CO in the feeding process are offered as follows [240, 241].

$$P_{CH_4} = \frac{(1 - X_{CH_4})}{\sigma} \tag{3.10}$$

$$P_{H_2O} = \frac{(\theta_{H_2O} - X_{CH_4} - X_{CO_2})}{\sigma} \tag{3.11}$$

$$P_{CO} = \frac{(\theta_{CO} + X_{CH_4} - X_{CO_2})}{\sigma} \tag{3.12}$$

$$P_{CO_2} = \frac{(\theta_{CO_2} + X_{CO_2})}{\sigma} \tag{3.13}$$

$$P_{H_2} = \frac{(\theta_{H_2} + 3X_{CH_4} - X_{CO_2} - \frac{F_{H_2}}{F_{CH_4}})}{\sigma} \tag{3.14}$$

$$\sigma = \frac{1 + \theta_{H_2O} + \theta_{CO} + \theta_{CO_2} + \theta_{H_2}}{P_{op.}} ; \theta_j = \frac{F_j^{in}}{F_{CH_4}^{in}} \tag{3.15}$$

Where,

X_{CH_4} : represents the total equilibrium conversion of methane, which is calculated as ($X_{CH_4} = X_{CO} + X_{CO_2}$).

X_{CO_2} : represents the equilibrium conversion to carbon dioxide.

X_{CO} : denotes the equilibrium conversion to carbon monoxide.

σ : refers to a stated parameter.

θ_j : represents the ratio of the inlet molar flow rates of chemical components j (such as H_2O, CO, CO_2, and H_2) to the inlet molar flow rate of methane.

F_j^{in} : represents the inlet molar flow rates of chemical components j in kmol/h.

$F_{CH_4}^{in}$: denotes the inlet molar flow rate of methane in kmol/h.

Kinetic rates, adsorption, equilibrium constants, and net rate of chemical species are computed by using expressions as follows [238-240].

3.6.3 Rate constants

The inlet operating temperature is a determining factor in the value of the kinetic constants of the rate equations, which are represented by Arrhenius-type functions.

$$k_1 = 9.490 \times 10^{16} \exp\left(-\frac{240.10}{RT_{op.}^{in}}\right) [\frac{kmol(kPa)^{0.5}}{kg_{cat.}h}] \tag{3.16}$$

$$k_2 = 4.390 \times 10^{4} \exp\left(-\frac{67.13}{RT_{op.}^{in}}\right) [\frac{kmol(kPa)^{0.5}}{kg_{cat.}h}] \tag{3.17}$$

$$k_3 = 2.290 \times 10^{16} \exp\left(-\frac{243.90}{RT_{op.}^{in}}\right) [\frac{kmol(kPa)^{0.5}}{kg_{cat.}h}] \tag{3.18}$$

3.6.4 Adsorption constants:

The constants $K_{CH_4}, K_{H_2O}, K_{H_2}, K_{co}$ are associated with the equilibrium of surface adsorption and their behavior is influenced by the operating temperature at the inlet.

$$K_{CH_4} = 6.650 \times 10^{-6} \exp\left(-\frac{38.28}{RT_{op.}^{in}}\right) [kP_a^{-1}] \tag{3.19}$$

$$K_{H_2O} = 1.770 \times 10^{5} \exp\left(-\frac{88.68}{RT_{op.}^{in}}\right) [-] \tag{3.20}$$

$$K_{H_2} = 6.120 \times 10^{-11} \exp\left(-\frac{82.90}{RT_{op.}^{in}}\right) [kP_a^{-1}] \tag{3.21}$$

$$K_{co} = 8.230 \times 10^{-7} \exp\left(-\frac{70.65}{RT_{op.}^{in}}\right) [kPa^{-1}] \tag{3.22}$$

3.6.5 Equilibrium constants

Through the calculation of the standard Gibbs energy intended for every reaction at the inlet operating temperature, the equilibrium factors in order to reactions R_1, R_2, and R_3 have been determined. This method involves assessing the thermodynamic behavior of the reactions at specific temperature conditions to establish their equilibrium constants.

$$\mathrm{K_{eq.1}} = 10266.76\exp\left(-\frac{26830}{\mathrm{RT_{op.}^{in}}} + 30.114\right)[\mathrm{kP_a^2}] \tag{3.23}$$

$$\mathrm{K_{eq.2}} = \exp\left(\frac{4400}{\mathrm{RT_{op.}^{in}}} - 4.063\right)[-] \tag{3.24}$$

$$\mathrm{K_{eq.3}} = \mathrm{T_{op.}^{in}.K_{eq.1}T_{op.}^{in}.K_{eq.2}}[\mathrm{kP_a^2}] \tag{3.25}$$

Where, R is the gas constant (J/kmol K) and $\mathrm{T_{op.}^{in}}$ is the inlet temperature (^{o}C).

3.6.6 Net rates:

The formula is utilized to calculate the net rates (r_i) of chemical constituents, including both consumption and formation for reactions like R_1, R_2, and R_3 as indicated above.

$$\mathrm{r_i} = \sum_{j=1}^{3}\sum_{i=1}^{5}\eta_i\,\sigma_{ij}\mathrm{R_j} \tag{3.26}$$

Where, η_i denotes the reaction effectiveness factor, σ_{ij} denotes the stoichiometric coefficients of chemical components involved in the reactions, R_j presents reaction rates, respectively.

3.6.7 Net rates of chemical components

The net rate (consumption and formation) of each i element kmol per kg-h was then expressed by using the net rate expression. These net rates ($r_{CH_4}, r_{H_2O}, r_{H_2}, r_{co}, r_{CO_2}$) are obtained by summing the reaction rates of each chemical species across all reactions (R_1 to R_3). The effectiveness factors ($\eta_i T_{op.}$) are employed to consider the impact of intraparticle transport limitation. These factors take into account the influence of intraparticle transport on the overall reaction rates.

$$r_{CH_4} = -[\eta_1(T_{op.})R_1 + \eta_3(T_{op.})R_3] \tag{3.27}$$

$$r_{H_2O} = -[\eta_1(T_{op.})R_1 + \eta_2(T_{op.})R_2 + 2\eta_3(T_{op.})R_3] \tag{3.28}$$

$$r_{H_2} = [3\eta_1(T_{op.})R_1 + \eta_2(T_{op.})R_2 + 4\eta_3(T_{op.})R_3] \tag{3.29}$$

$$r_{co} = [\eta_1(T_{op.})R_1 - \eta_2(T_{op.})R_2] \tag{3.30}$$

$$r_{CO_2} = [\eta_2(T_{op.})R_2 + \eta_3(T_{op.})R_3] \tag{3.31}$$

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the results of the developed model for simulating the performance of steam reforming of methane and biogas with varying compositions for hydrogen production and the analysis of the outcomes are presented. The results are presented in terms of the concentrations and different steam carbon ratios for all reaction species (CH_4, CO_2, CO, H_2O, and H_2).

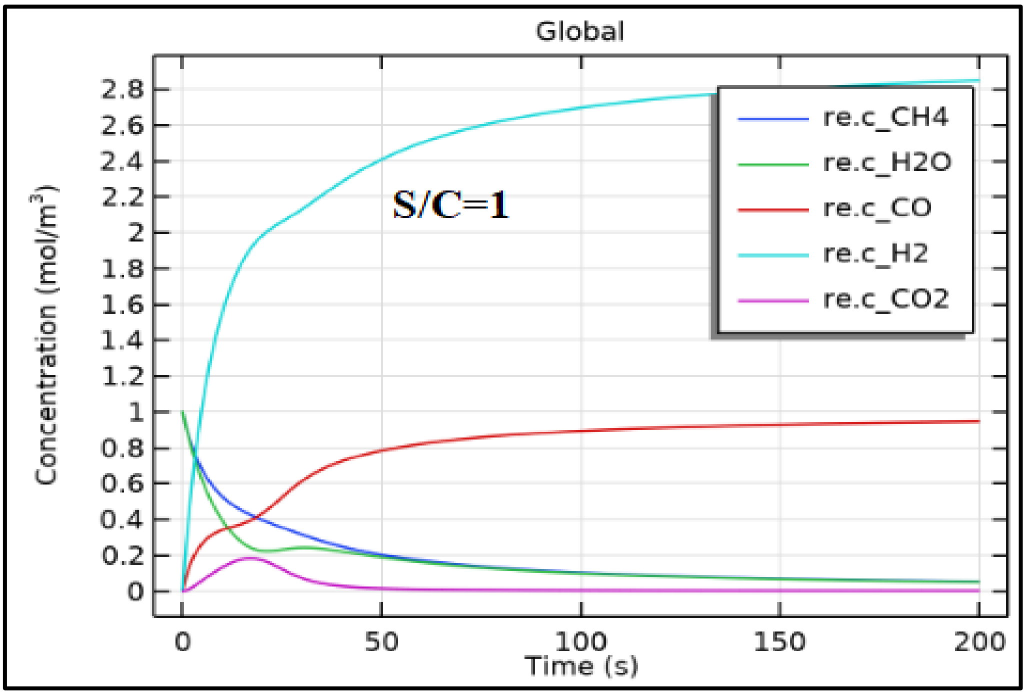
4.1 Simulation analysis of steam methane reforming (SRM)

The evaluation of species concentration (mol/m^3) to reach steady levels straightaway after the feed gas is offered as displayed in Fig. 4.1. Generally, all curves define the distribution of product gas that attains a steady state after running the reactor at a certain temperature. As could be seen after 140 sec. (Fig.4.1a), 80 sec. (Fig 4.1b and 4.1c), and the curves of chemical reaction achieved a constant condition with time along the reactor volume. It is observed that methane amount is consumed with the amount of water in the inlet condition of a gas mixture, also known as the steam methane reforming process during transient periods as well as operation proceeds. The by-product gas on wet basis contains 2.8 of H_2 mol/m^3, 0.9 of CO mol/m^3, 0.05 of CO_2 mol/m^3, 0.1of CH_4 mol/m^3, and 0.1of H_2O mol/m^3 under the prescribed condition with temperature 900^{o}C at S/C are equal to 1, (Fig.4.1a). In a similar way, the by-product gas concentration species at temperature 900^{o}C for S/C = 2 and 3 as mentioned in Fig. 4.1(b) and 4.1(c).

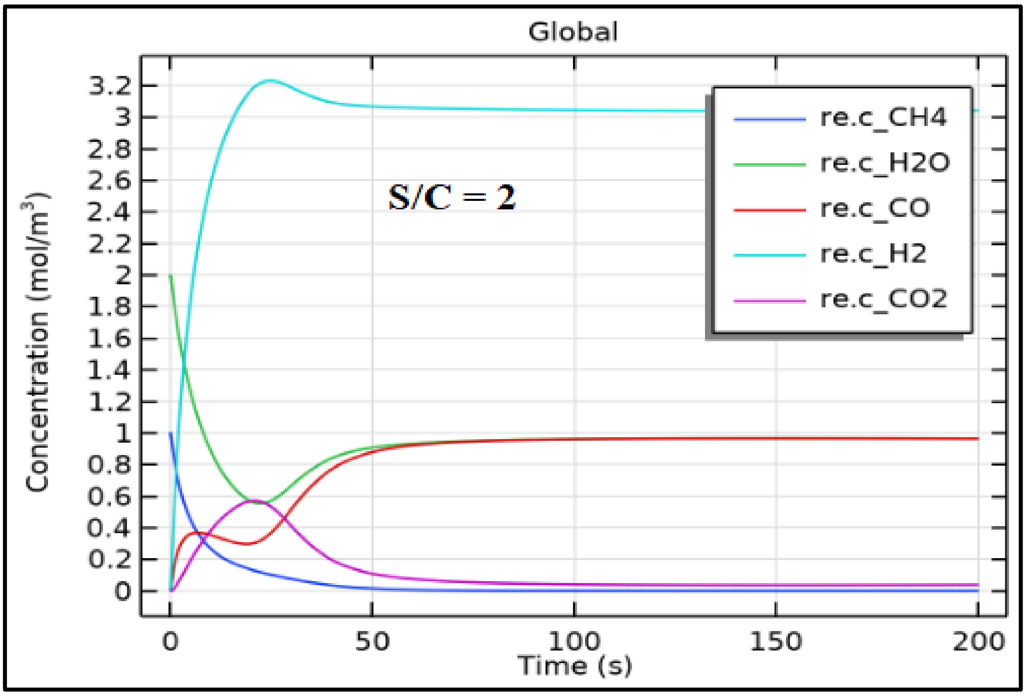
Fig 4.1(d) shows the influence of H_2 yield along with time and various temperatures at steam carbon ratio 1. It is noted that the optimum temperature is 900^{o}C for S/C =1 for the yield of hydrogen but there are no more variations after 900^{o}C in H_2 yield from the initial temperature 700-1100 ^{o}C. The concentrations of species evaluation are generated by Comsol multiphysics 5.6 software as similar trends of the curve are also explained by Silva et al. [241].

Fig 4.1(a, b, and c) shows the H_2 yield through the steam methane reforming to syngas amount and Fig 4.1(e, f, and g) represents the total reaction (combine SMR and WGS). It is observed that after 400s (Fig. 4.1e, 4.1f, and 4.1g), the curves of chemical reaction achieved a constant condition with time along the reactor volume. It is observed that methane amount is consumed with the amount of water in the inlet condition of a gas mixture, also known as the steam methane reforming process during transient periods as well as operation proceeds. By including water gas shift reaction in SMR process, the concentration of CO decreases and CO_2 amount increases.

The water-gas shift (WGS) reaction is crucial in enhancing hydrogen production during the steam methane reforming process. SMR converts methane (CH_4) and steam (H_2O) into hydrogen (H_2) and carbon monoxide (CO). The WGS reaction then converts CO into additional hydrogen and carbon dioxide (CO_2), significantly increasing hydrogen yield and reducing CO concentration. This makes the reformate gas safer and more suitable for purification. Effective integration of the WGS reaction improves the efficiency and environmental sustainability of the SMR process, making it vital for industrial hydrogen production.

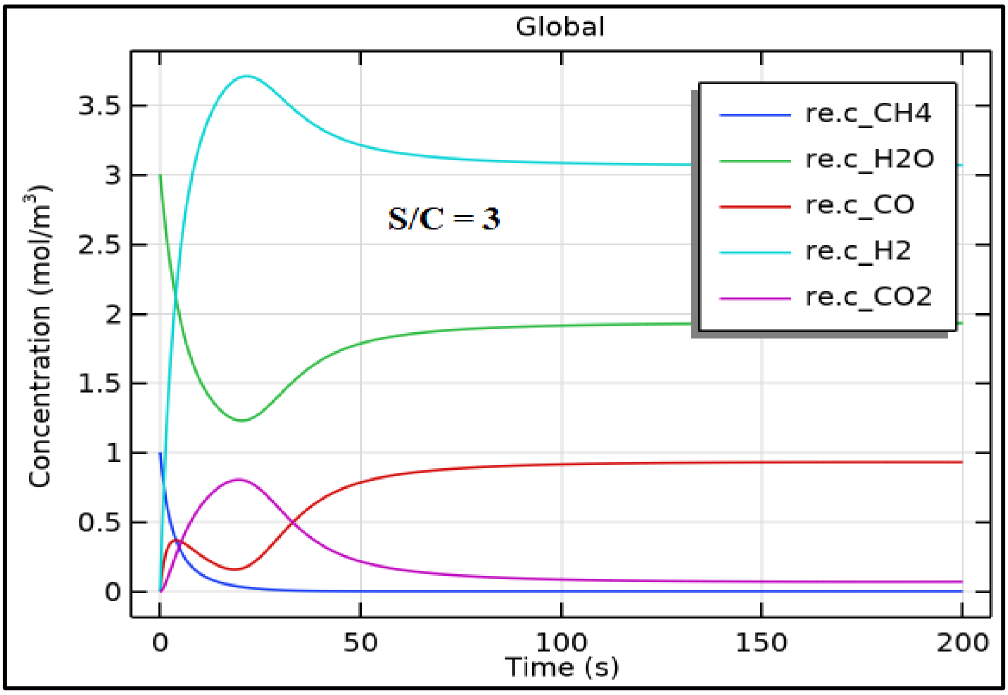


(a)

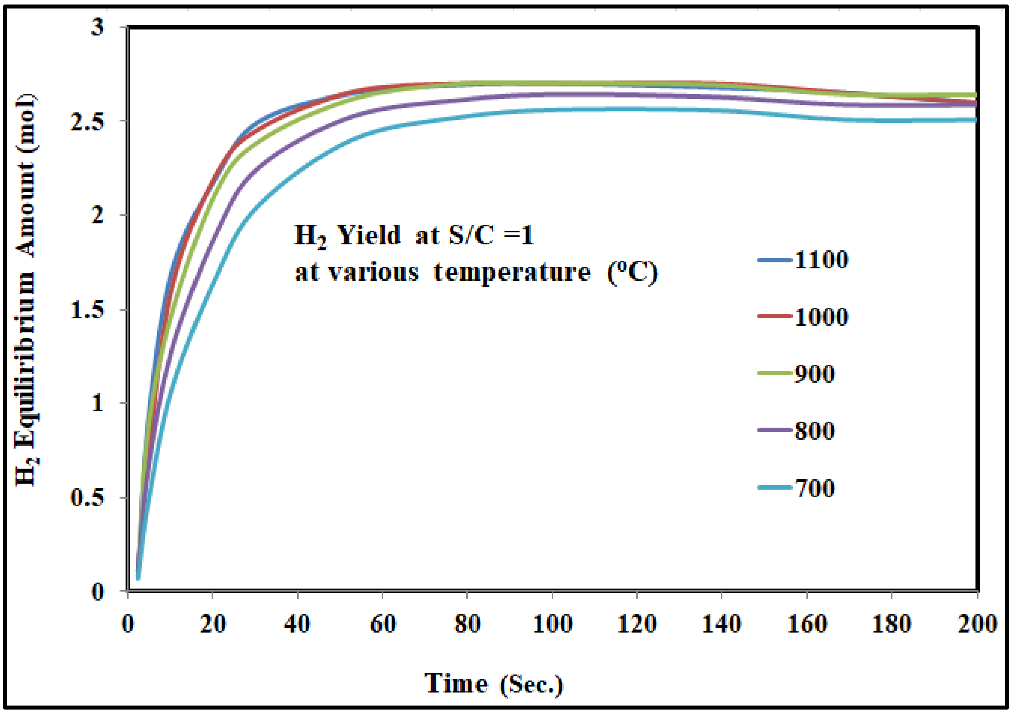

Global
S/C = 2
re.c_CH4
re.c_H2O
re.c_CO
re.c_H2
re.c_CO2
Concentration (mol/m³)
3.2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
50
100
150
200
Time (s)

(b)

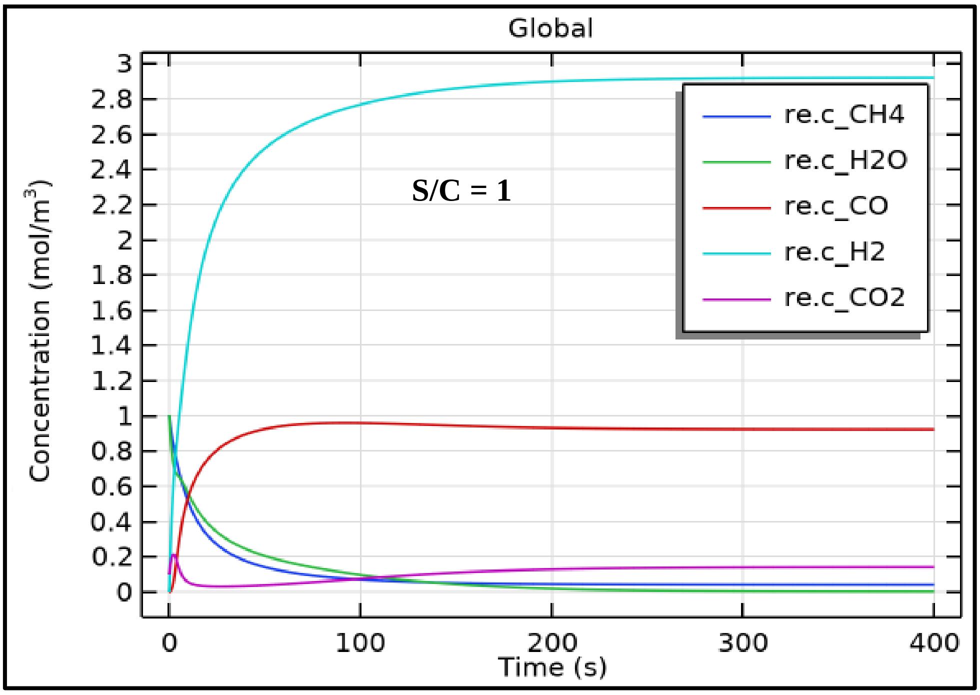
\


Global
S/C = 3
re.c_CH4
re.c_H2O
re.c_CO
re.c_H2
re.c_CO2
Concentration (mol/m³)
3.5
3
2.5
2
1.5
1
0.5
0
0
50
100
150
200
Time (s)

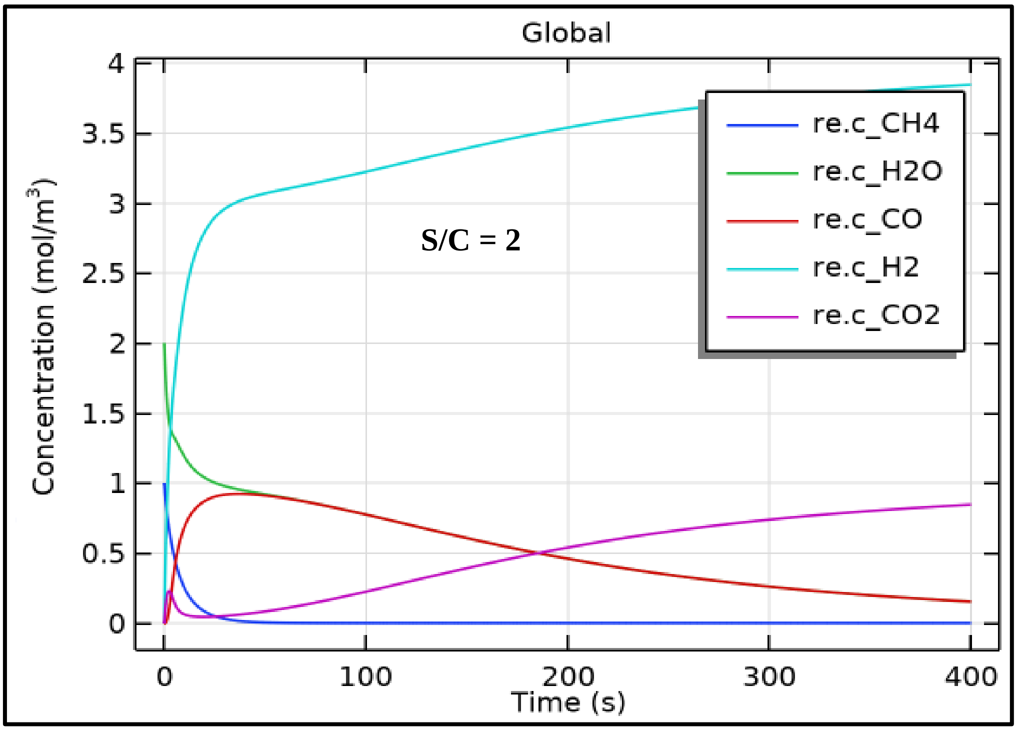
(c)


H_2 Equilibrium Amount (mol)
3
2.5
2
1.5
1
0.5
0
0
20
40
60
80
100
120
140
160
180
200
Time (Sec.)
H_2 Yield at S/C =1
at various temperature (°C)
1100
1000
900
800
700

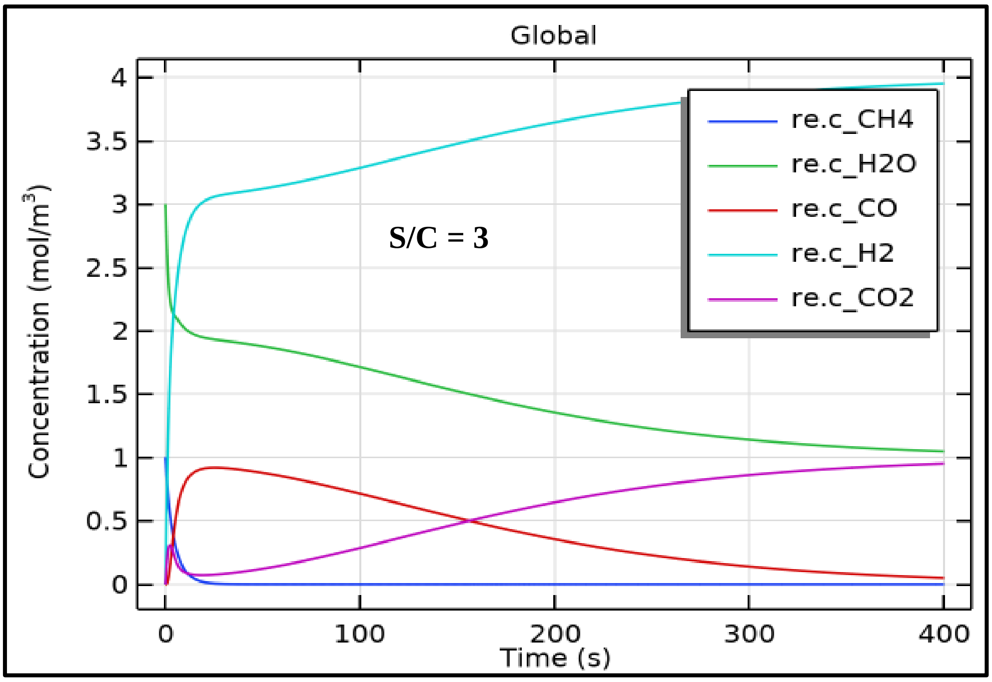
(d)


Global
Concentration (mol/m^3)
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
100
200
300
400
Time (s)
S/C = 1
re.c_CH4
re.c_H2O
re.c_CO
re.c_H2
re.c_CO2

(e)



(f)



(g)

Fig. 4.1: Simulation analysis of the product gas distribution in the batch reactor at 1 bar and 900°C (a) S/C = 1, (b) S/C = 2, (c) S/C = 3, (d) effect of various temperatures on H_2 yields along with the time (sec.) at steam carbon (S/C) ratio 1, (e) Water gas shift reaction effect at S/C = 1, (f) S/C = 2, and (g) S/C = 3.

4.1.1 Temperature effect of chemical equilibrium amounts

The results presented in Fig. 4.2 illustrate the relationship between temperature and the gaseous product's mole fractions as a function of time. As temperature progressively increases, H_2 mole fraction exhibits a gradual rise starting from zero value and eventually stabilizes approximately at temperature 850ºC. On the other hand, CH_4 mole fraction consistently decreases until it reaches zero. This indicates a simultaneous occurrence where H_2 formation and CH_4 consumption take place in parallel at high temperatures. Fig.4.2 presents the simulation results of equilibrium amount of chemical species at various operating temperature and time at atmospheric pressure.

4.1.1.1 H_2 yield

Fig. 4.2 (a) depicts the comparison of H_2 mole with different S/C ratios from 1-3 at optimum temperature through the simulation process. Hydrogen amount touches the maximum yield during steam methane reforming process (Syngas) as well as increasing the S/C ratio from 2:1 to 3:1.

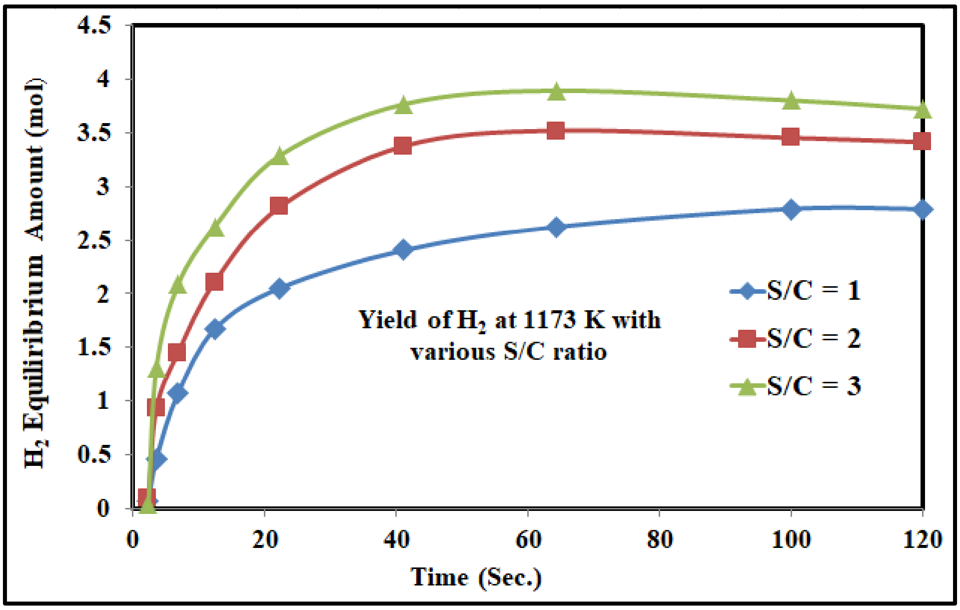


Fig. 4.2 (a): Simulation results of equilibrium amount compared to yield of H_2 mol at 900ºC

The exclusion or inclusion of the water-gas shift (WGS) reaction in steam methane reforming (SMR) significantly affects hydrogen production. Without the WGS reaction, the hydrogen yield is limited to that produced by the primary SMR reaction.

This process produces 3 moles of H_2 for each mole of CH_4 and H_2O reacted, resulting in a lower total hydrogen output compared to when the WGS reaction is included as shown in Fig.4.2 (b). It also shows the comparative yield of hydrogen with (represented by S/C*) and without (represented by S/C) using WGSR.

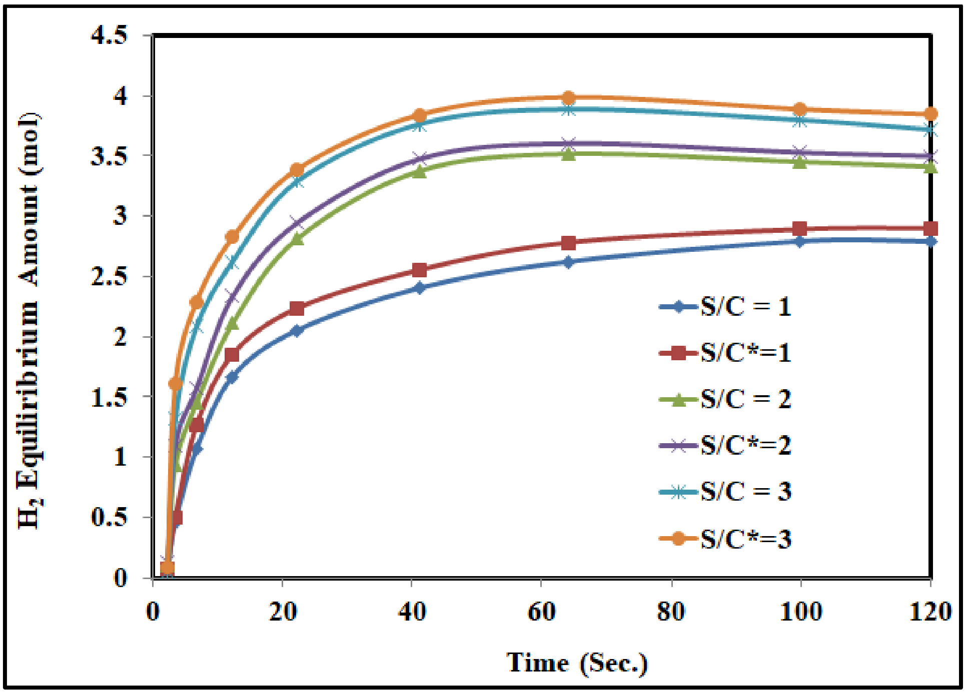


Fig. 4.2 (b): Comparison of yield of H_2 with and without water gas shift reaction at 900°C.

The syngas contain a lower proportion of hydrogen and a higher proportion of carbon monoxide, which may not be suitable for applications requiring high-purity hydrogen without further processing. The H_2/CO ratio remains around 3:1, determined solely by the SMR reaction. The absence of the WGS reaction means less CO_2 is produced directly from the reaction, although the syngas still contain CO, which may be converted to CO_2 in subsequent processes. Additionally, the process is more endothermic, requiring higher energy input to maintain the reaction temperatures for SMR without the exothermic contribution of the WGS reaction.

Fig. 4.2 (c) describes the comparison assessment of hydrogen yield with different s/c ratio during both the including equation steam methane and water shift reaction. This process took 400 s to attain equilibrium and enhanced the yield of H_2 amount compared to without using WGSR.

The inclusion of the WGS reaction boosts the H_2/CO ratio. After SMR alone, the typical H_2/CO ratio is around 3:1. With the WGS reaction, this ratio can increase to approximately 5:1 or higher, depending on how completely the WGS reaction proceeds. The WGS reaction increases the CO_2 content in the syngas because CO is converted into CO_2.

Incorporating the water-gas shift reaction into the steam methane reforming process significantly enhances the hydrogen yield, increasing it by 33.3% compared to the SMR process without WGSR. This improvement makes the combined process more efficient and effective for industrial hydrogen production.

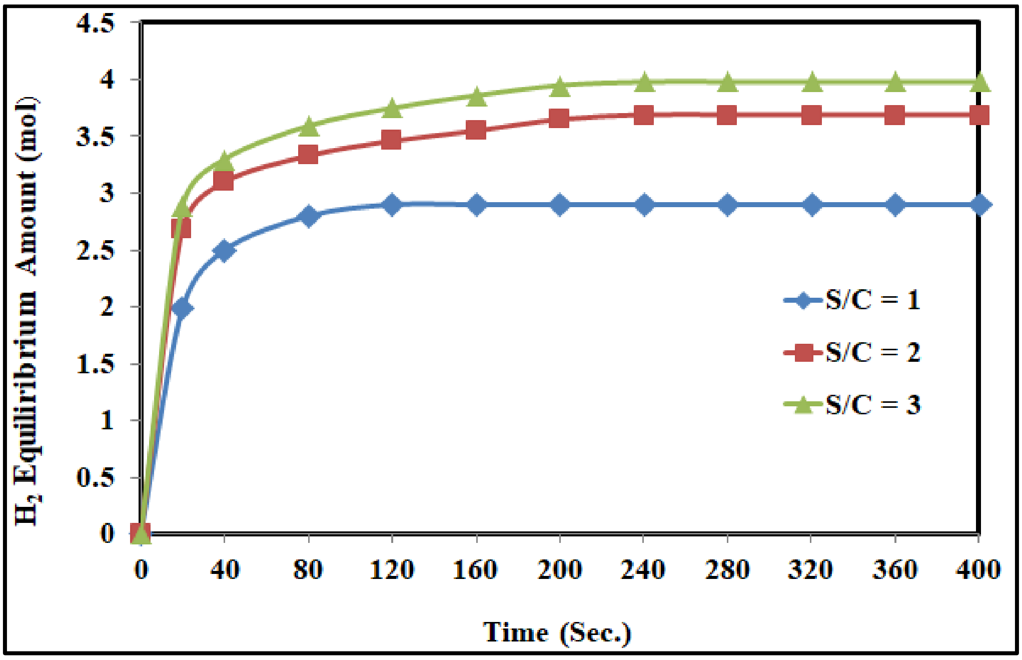


Fig. 4.2 (c): Simulation results of equilibrium H_2 Yield at 900°C with WGS Reaction

4.1.1.2 CO_2 amount

The water-gas shift reaction (WGSR) is closely integrated with the steam methane reforming (SMR) process, which is a primary method for hydrogen production. The WGSR is crucial for maximizing hydrogen production. In the primary reforming reaction, each mole of methane produces 3 moles of hydrogen. The WGSR then further converts CO produced in the SMR into additional hydrogen, thereby increasing the overall hydrogen yield.

The water gas shift (WGS) reaction is accountable in order to produce CO_2 amount and it is also an assessment of CO_2 amount in Fig. 4.2 (d). The quantity of CO_2 rises as well as increases the S/C molar ratio at a certain temperature and it touches a maximum mole of CO_2 at optimum temperature 900°C with S/C ratio 1-3. Fig. 4.2(d) shows the effect of CO_2 equilibrium with SMR (R1) and WGSR (R2) with time. R1 produces less producing upto 40 seconds after that increasing amount of CO2 due to effect of WGSR up to 120 sec., but Fig.4.2 (e) depicts the performance of CO_2 due to WGSR up to equilibrium point (400s.).

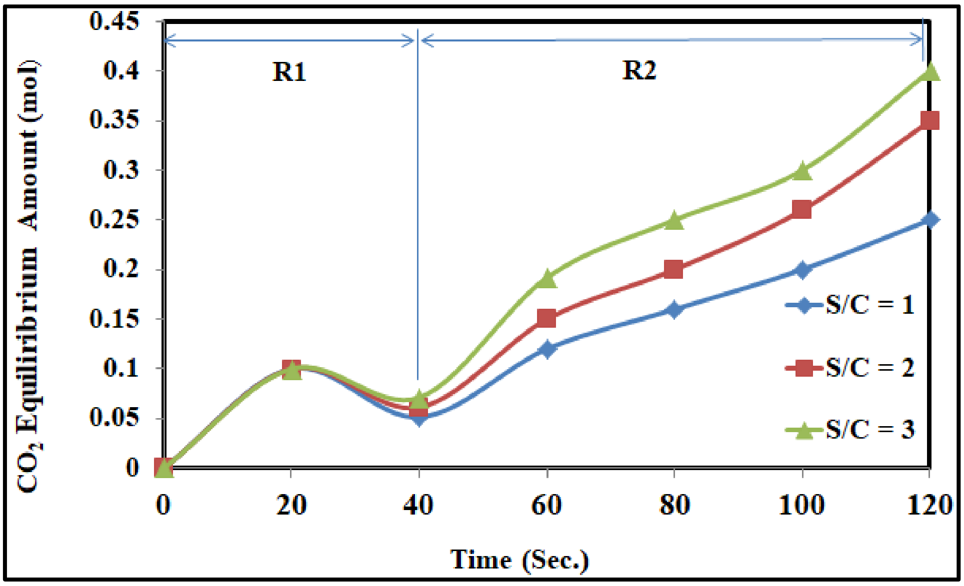


Fig. 4.2 (d): CO_2 equilibrium effect in both SMR and WGSR

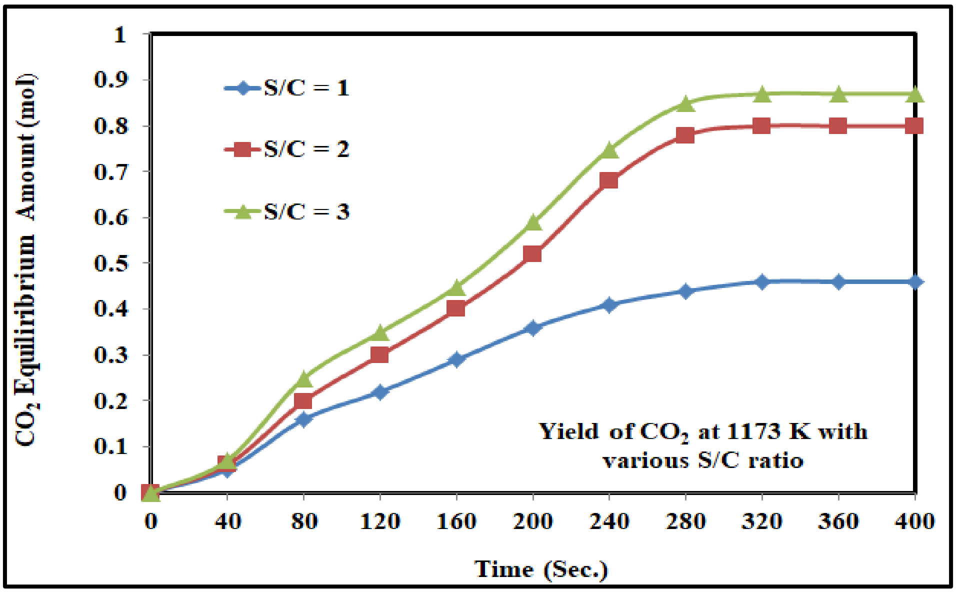


Fig. 4.2 (e): Simulation results of equilibrium amount compared to CO_2 amount at 900°C

4.1.1.3 CH_4 conversion

Fig. 4.2 (f) presents the effect of methane conversion at various temperatures with steam carbon ratio 1. CH_4 mole fraction steadily decreases when the temperature increases. Meanwhile, more consumption of methane mole as well as the H_2 moles increases.

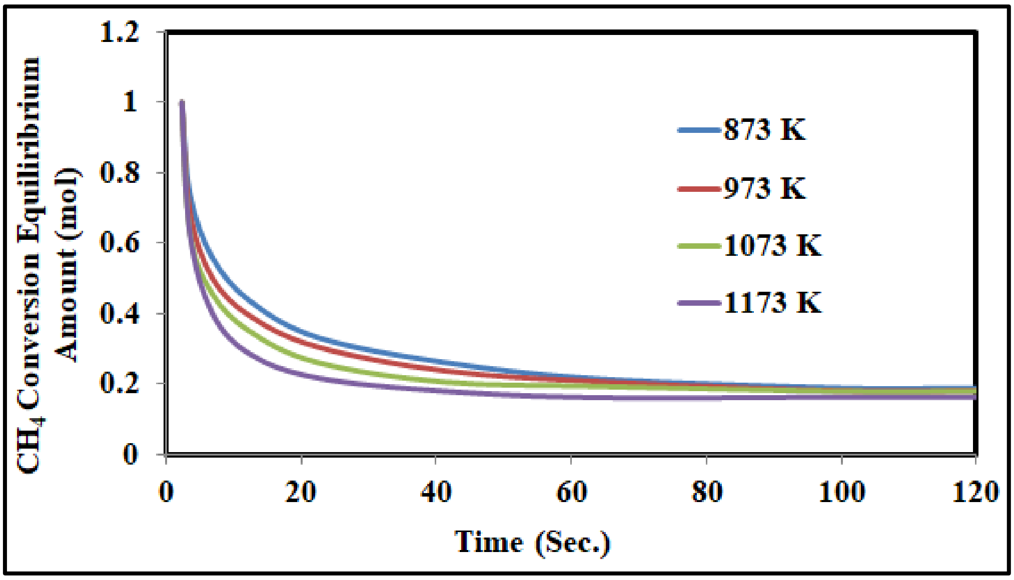


Fig. 4.2 (f): Simulation results of equilibrium amount of CH_4 conversion with various temperatures at S/C =1

4.1.1.4 CO amount

The amount of CO attained after 600°C, also increases its amount with a certain temperature as presented in Fig.4.2 (g). The amount of CO is slightly affected by the molar ratio of S/C at nearly 900°C, after that temperature, the increasing molar ratio is favored by WGS and thus starts to reduce the CO amount as shown in Fig.4.2 (h).

The WGS reaction converts carbon monoxide and water into additional hydrogen and carbon dioxide. For every mole of CO converted, one additional mole of H_2 is produced. This significantly increases the total hydrogen yield from the process. The additional hydrogen produced by the WGS reaction increases the hydrogen content in the syngas, which is beneficial for applications requiring high-purity hydrogen.

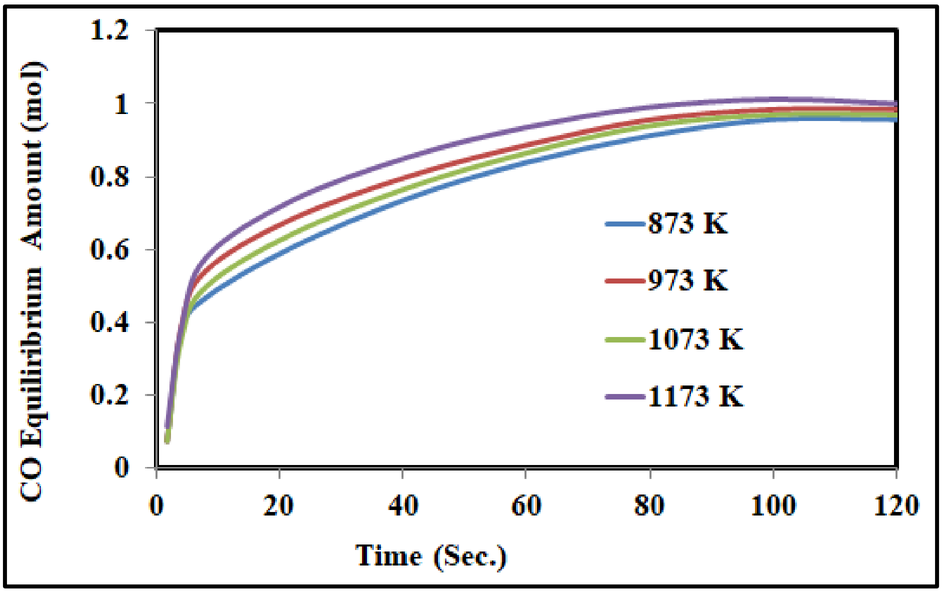


Fig. 4.2 (g): Simulation results of equilibrium amount of CO at different temperature at S/C =1

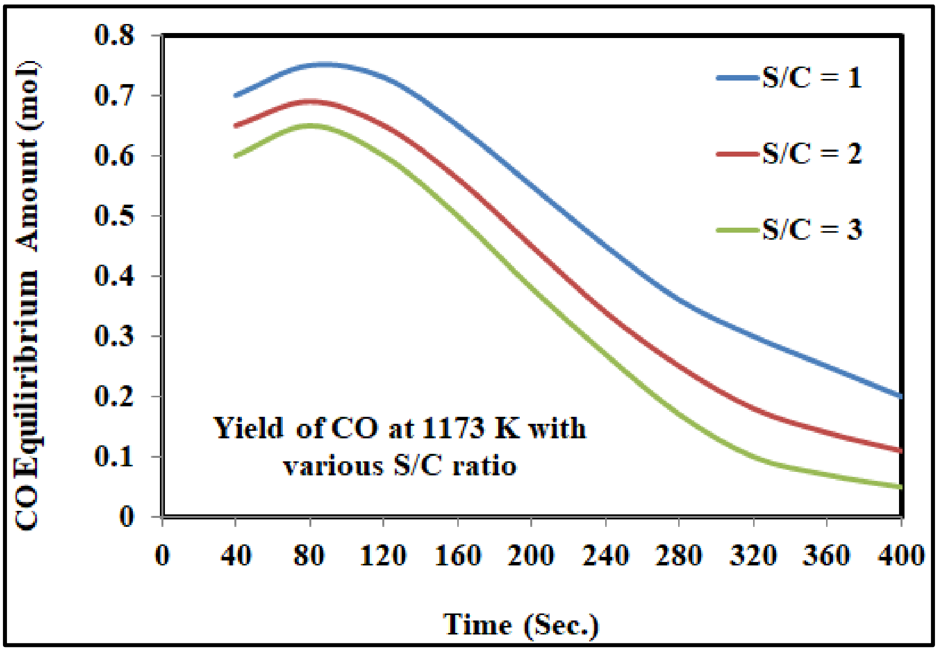


Fig. 4.2 (h): Effect of WGSR at different steam carbon ratios (S/C)

Table 4.1 shows the relationship between a diverse set of operating temperatures and the equilibrium conversions of reactants, as well as S/C ratio in the resulting product. Notably, the optimal quantities of H_2, CH_4, CO, CO_2, and H_2O were observed at 1173K. At a specific temperature, higher molar ratio of S/C can lead to higher yield of H_2. The equilibrium amounts of these components depend on the stoichiometric ratio.

The outcomes presented here exhibit strong concurrence with the previously reported results by Khzouz and Gkanas [242], whose study employed the CAE software program for their calculations.

Table 4.1: Optimal simulation results (Equilibrium conversions of reactants) of SRM at various temperature and the corresponding operating conditions. P =1 bar, S/C = 1-3.

S/C ratio	**Operating Temperature (K)**	**Equilibrium Amount (mol)**			
		H_2	CH_4	**CO**	H_2**O**
1	873	2.20	0.19	0.899	0.212
	973	2.52	0.17	0.932	0.183
	1073	2.68	0.153	1.00	0161
	1173	2.77	0.139	1.02	0.131
2	873	2.39	0.22	0.714	1.04
	973	2.99	0.141	0.98	1.06
	1073	3.25	0.114	1.08	1.10
	1173	3.35	0.081	1.14	1.12
3	873	3.10	0.03	0.977	1.98
	973	3.38	0.011	0.978	2.09
	1073	3.40	0.011	1.00	2.095
	1173	3.42	0.01	0.809	1.78

4.2 Validation of the numerical model with the experimental results

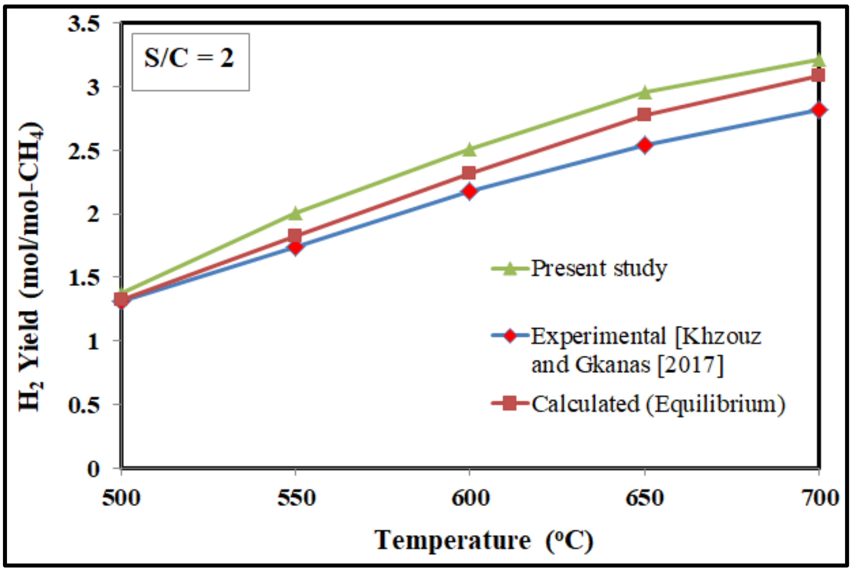
To compare the results of the model with experimental data published by Khzouz and Gkanas [242], similar initial operating parameters were selected as temperatures, mass fraction, and pressure and steam carbon ratio for the current study. The model suggested and discussed in the current study provides the concentration of species and temperature profiles during the chemical reaction. The simulation work has been done on the steam reforming process at various temperatures such as 500°C, 550°C, 600°C, 650°C, and 700°C to validate the proposed mathematical model. The simulation study and mathematical equations were performed by COMSOL Multiphysics 5.6.

Steam carbon ratio (S/C 2 and 3) was considered for calculations to validate the process. The formation of hydrogen yield increases with increased temperatures as depicted in Fig.4.3 (a) and (b). The present study of results follows a similar trend of

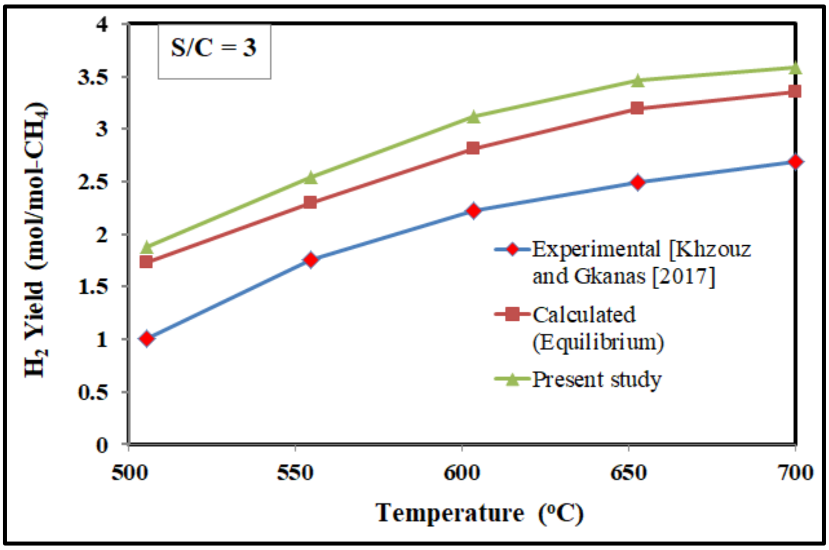
H_2 yields obtained from chemical reactions using COMSOL software and compared with the experiment and chemical equilibrium data (analysis from CAE software) [242]. The system approach is calculated from 500 to 700°C for steam carbon ratios 2 and 3. Although, hydrogen yield form experimentally at S/C = 2 and 3 are less than the present work and calculated (Equilibrium) results since the water amount is more consumed.

The present study data showed a maximum and minimum yield of hydrogen 3.1 mol/mol-CH_4 at 700°C and 1.4 mol/mol-CH_4 at 500°C respectively, at S/C = 2, with a higher value than the experiment data. Similarly, at S/C = 3, maximum and minimum hydrogen yields 3.3 mol/mol-CH_4 at 700°C and 1.8 mol/mol-CH_4 at 500°C respectively.

Fig. 4.3 (a) and (b) present the comparative assessment between the present work and the previous study as experiment and simulation work. The results for H_2 yield; experiment and present simulation work as well as previous simulation work (Comsol software) follow an almost similar trend and hydrogen yields are increasing with increasing temperature at S/C = 2. The results of the present study show higher yields of hydrogen, achieving 6% and 8.2% respectively, compared to the previous simulation study at a steam-to-carbon (S/C) ratio of 2 and 3, and a temperature of 700°C.



(a)



(b)

Fig. 4.3: Validation of experiment work with present simulation work and previous simulation data within temperature between 500°C-700°C at atmospheric pressure using Ni/Al_2O_3 based catalyst; (a) H_2 yield at S/C = 2, (b) H_2 yield at S/C = 3 [242]

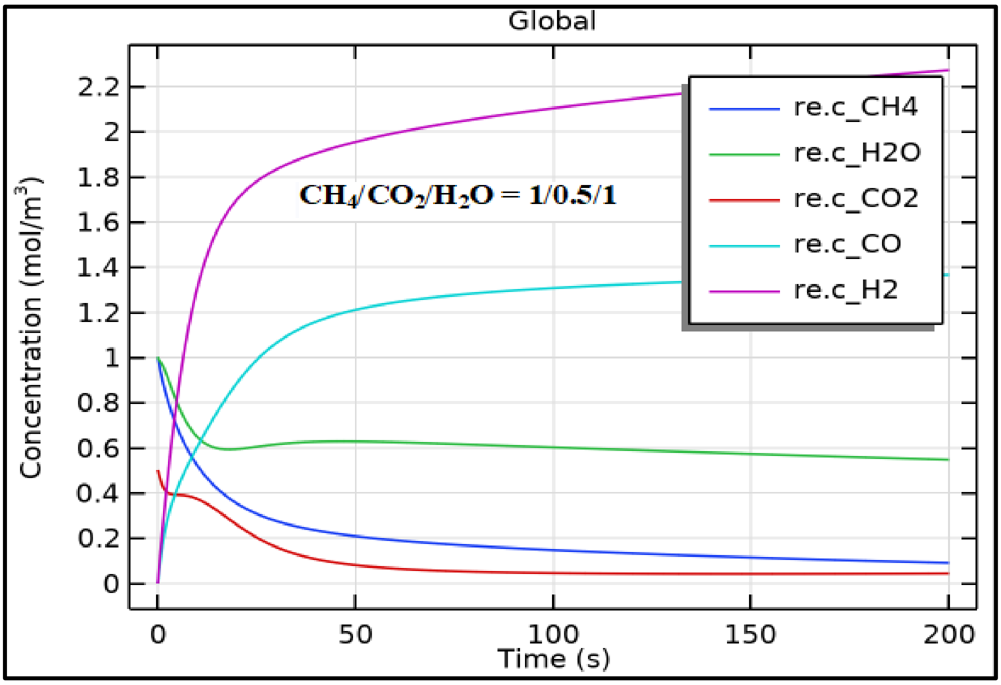
Table 4.2: Calculated data from current and previous research on SRM at various temperatures with operating conditions: P = 1 bar, S/C = 2-3.

S/C	Temperature (°C)	Experimental Data	CAE software	Present study	Enhanced H_2 yield (%)
2	500	1.3	1.3	1.4	3.5
	550	1.7	1.8	2.0	9.1
	600	2.2	2.3	2.5	7.7
	650	2.5	2.8	3.0	5.9
	700	2.8	3.1	3.2	3.9
3	500	1	1.7	1.8	7.6
	550	1.7	2.2	2.5	9.8
	600	2.2	2.8	3.1	9.6
	650	2.4	3.1	3.4	7.7
	700	2.6	3.3	3.5	6.4

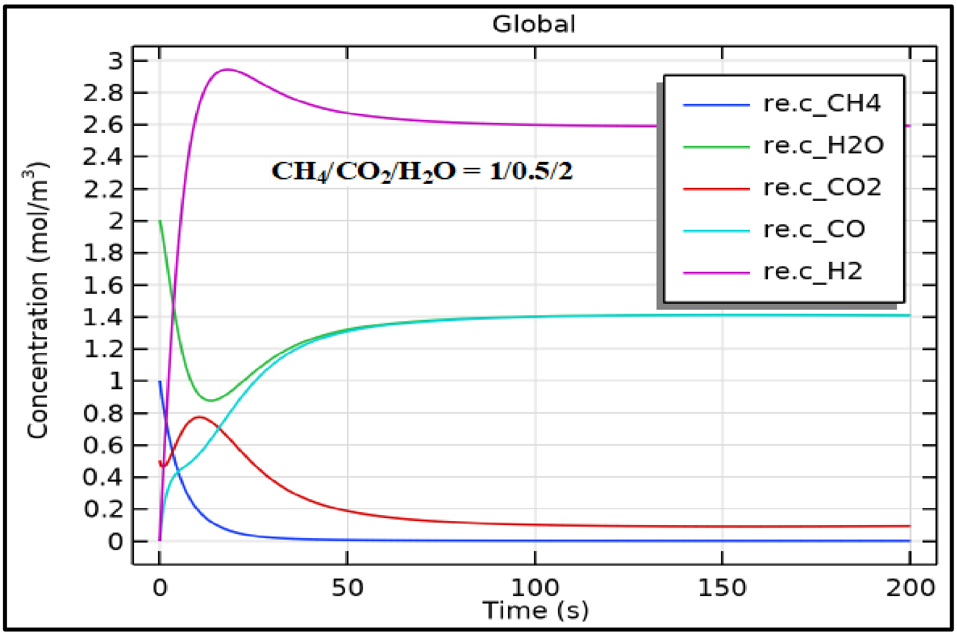
4.3 Simulation analysis of steam biogas reforming (SBR)

The evaluation of species concentration (mol/m^3) to reach steady levels straightaway after the feed gas is offered as shown in Fig. 4.4. Generally, all curves define the distribution of product gas that attains a steady state after running the reactor at a certain temperature. As it could be seen after 200 sec. (Fig. 4.4a), 100 sec. (Fig. 4.4b and 4.4c), the curves of chemical reaction achieve a constant condition with time along with the reactor volume. The inlet parameters are the same for the simulation study [219].

It is observed that methane and CO_2 amounts are consumed with the amount of water in the inlet condition of the gas mixture, also known as the steam biogas reforming process during transient periods as well as operation proceeds. The by-product gas as dry basis contains 2.2 of H_2 mol/m^3, 1.2 mol/m^3 of CO, 0.05 mol/m^{3}of CO_2, 0.1 mol/m^3 of CH_4, and 0.1 mol/m^3 of H_2O under the prescribed condition with temperature 1000ºC at S/C equal to 1, (Fig. 4.4 a). In a similar way, the by-product gas concentration species at temperature 1100 ºC for S/C = 2 and S/C = 3 as mentioned in Fig. 4.4b and 4.4c.



(a)



(b)

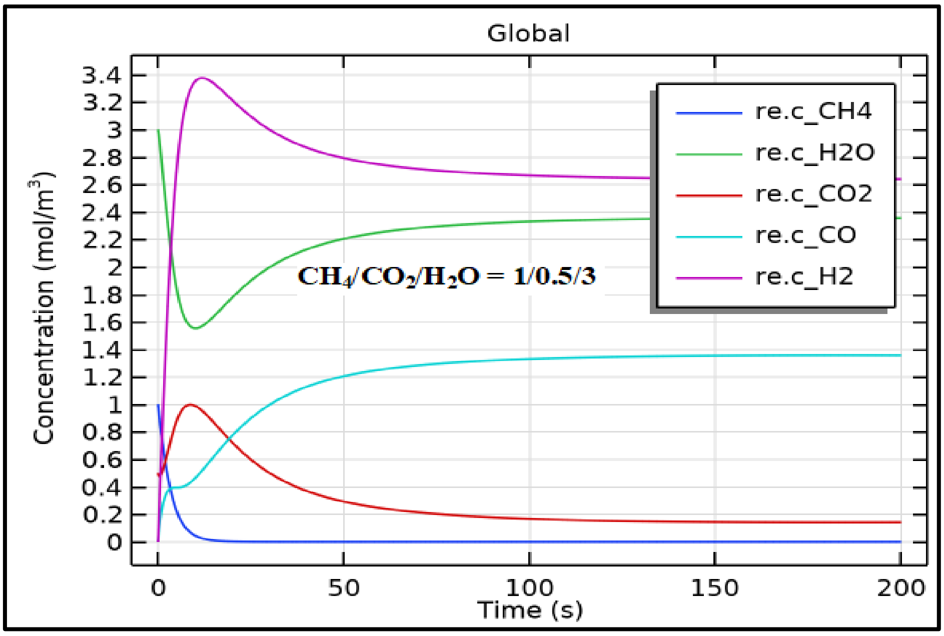


Fig. 4.4: Simulation analysis of the product gas distribution in the batch reactor at 10 bar and 1100 °C along with the time (sec.) at various steam carbon ratios (a) S/C = 1, (b) S/C = 2, and (c) S/C = 3

4.3.1 Effect of temperature on equilibrium conversion

Temperature is the main parameter for producing a mole fraction of hydrogen. As the temperature progresses, the H_2 mole fraction begins to form and stabilizes at around 850-1000°C. At the same time, the mole fraction of CH_4 steadily decreases until it reaches zero, indicating a simultaneous occurrence of H_2 formation and CH_4

consumption at high temperatures. At temperatures below 600°C, the mole fraction of CO_2 increases. This observation strongly indicates a preference for the water-gas shift reaction over the reaction of CO_2 reforming at comparatively low temperatures. The reducing H_2O mole fraction further reinforces this conclusion as supporting evidence. As the CO_2 reforming reaction is endothermic in nature, it becomes more favourable as the operating temperatures increase. As a consequence, CO_2 mole fraction shows a gradual rise before displaying a significant reduction as the temperature exceeds 600°C. With the prevalence of the reaction of CO_2 reforming, there is also an enhancement in the mole fraction of CO.

- **Effect of temperature and steam-carbon (S/C) ratio**

At lower temperatures, an increase in H_2O content leads to a significant decrease in CH_4 conversion. However, as the temperature rises and surpasses an inflection point at relatively higher temperatures, CH_4 conversion shows a transition towards an increasing trend. Impressively, regardless of the H_2O content, CH_4 conversion reaches nearly 100% above 850 °C. An increase in the H_2O content leads to a considerable reduction in CO_2 conversion. In the biogas process, both CO_2 and H_2O are well-known oxidants. However, CH_4 shows a higher tendency to react with H_2O rather than CO_2, mainly since H_2O exhibits higher chemical reactivity compared to CO_2.

- **Effect of CO_2/CH_4 ratio**

The relationship between the CO_2/CH_4 ratio and temperature is studied to understand its effects. It is perceived that as the ratio of CO_2/CH_4 and temperature increases, CH_4 conversion also increases. On the other hand, CO_2 conversion shows an inverse relationship with the CO_2/CH_4 ratio at high temperatures, leading to a decrease as the ratio increases. Unlike the trends observed in the conversion of CH_4 and CO_2, the effect of the ratio of CO_2/CH_4 on the yield of H_2 and CO amounts appears to be insignificant when varying the CO_2/CH_4 ratios at low temperatures. It is noteworthy that there is a significant decrease in H_2 and CO yields when CO_2 is added at temperatures between 800-1200°C. Due to the endothermic nature of both CO_2 reforming and RWGS, an increase in temperature will promote and favor the existence of these reactions.

Due to the continuous presence of a net positive amount of H_2O as a feedstock throughout the process, RWGS has a greater probability of occurring compared to CO_2 reforming. The CO_2 reforming reaction continuously consumes CH_4 as a reactant, resulting in a net negative amount of CH_4. The superior performance of RWGS over the reaction of CO_2 reforming is evident as it leads to a noticeable reduction in the H_2 yield [38]. An increase in the ratio of CO_2/CH_4 leads to a decrease in the conversion of H_2O amount in higher temperature zones. The presence of an increasing content of CO_2 is the outcome of a minor drop in the ratio of H_2/CO, which can be endorsed to the entire reaction selectivity favoring reverse water-gas shift over CO_2 reforming.

Table 4.3: Optimal simulation results (Equilibrium conversions of reactants) of SRB at various temperature and the corresponding operating conditions. P =10 bar, CO_2 =0.583 and S/C = 1-3

S/C ratio	**Operating Temperature (^oC)**	**Conversions Amount (mol)**				
		H_2	**CH_4**	**CO_2**	**CO**	**H_2O**
1	600	1.40	0.45	0.82	0.6	0.3
	800	2.50	0.40	0.70	0.8	0.4
	1000	2.70	0.1	0.40	1.45	0.6
	1200	2.69	0.1	0.30	1.45	0.5
2	600	1.60	0.15	0.9	1.30	0.4
	800	2.80	0.14	1.1	0.6	0.8
	1000	2.90	0.06	0.9	1.41	1.4
	1200	2.80	0.07	0.7	1.42	1.45
3	600	1.90	0.11	1.5	0.66	1.1
	800	3.21	0.09	1.3	0.60	1.2
	1000	3.20	0.04	1.2	0.40	1.5
	1200	2.95	0.04	0.7	1.23	2.0

4.3.2 Effect of water gas shift reaction

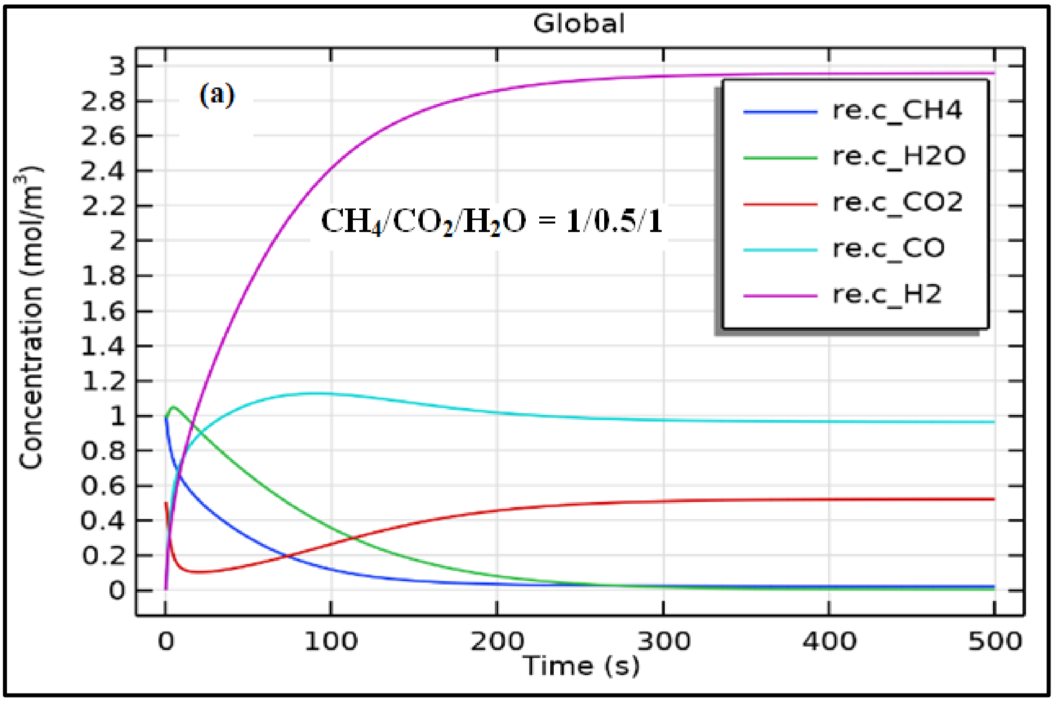
The WGS reaction is normally used after reforming or gasification processes. The common products of gasification and reforming include CO, which the WGS reaction converts while producing additional hydrogen, making WGS very important for increased hydrogen production. The WGS reaction is reversible and thermal equilibrium is reached faster at higher temperatures. Low-temperature catalysts provide high conversions but are kinetically limited so the reaction proceeds slowly.

Incorporating the water-gas shift (WGS) reaction in biogas reforming is essential for maximizing hydrogen production and minimizing carbon monoxide levels. The WGS reaction boosts the efficiency and sustainability of the process by increasing hydrogen yield, streamlining purification, and aiding in CO_2 management. These advantages make the WGS reaction a vital part of hydrogen production from biogas, promoting a more sustainable and efficient energy system.

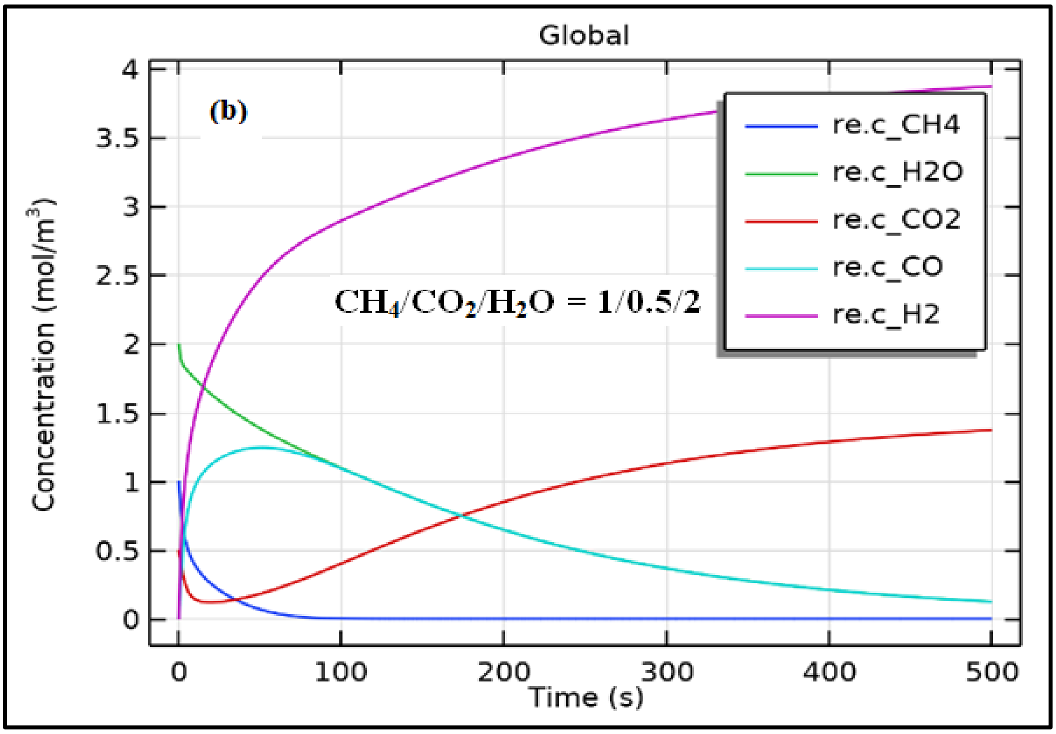
Fig 4.4 (a, b, and c) shows the H_2 yield through the steam methane reforming to syngas amount and Fig 4.5(a, b, and c) represents the total reaction (combine SBR and WGS). It is observed that after 500s (Fig. 4.5a, 4.5b, and 4.5c), the curves of the chemical reaction achieved a constant condition with time along the reactor volume. It is observed that methane amount is consumed with the amount of water in the inlet condition of a gas mixture, also known as the steam methane reforming process during transient periods as well as operation proceeds. As a water gas shift reaction in the SBR process, the concentration of CO decreases and the CO_2 amount increases.

Fig. 4.5 illustrates the combined effect of the steam reforming and water-gas shift (WGS) reactions during the process. It is observed that the hydrogen (H_2) yield is enhanced at different steam-to-carbon (S/C) ratios compared to the data provided in Table 4.2. At an S/C ratio of 1 with a fixed temperature, the amount of carbon monoxide (CO) slightly decreases while the amount of carbon dioxide (CO_2) increases. Concurrently, methane (CH_4) and water (H_2O) are fully converted, reaching a value of zero, i.e., 100% conversion. As the S/C ratio increases from 1 to 2, the amount of H_2 and CO_2 both increase, while the CO concentration decreases to 0.2 mol/m^3. Similarly, at S/C ratio of 3, the maximum mol of H_2 and CO_2 yield are achieved as 3.6 and 1.5. Both CH_4 and H_2O have achieved 100% conversion.

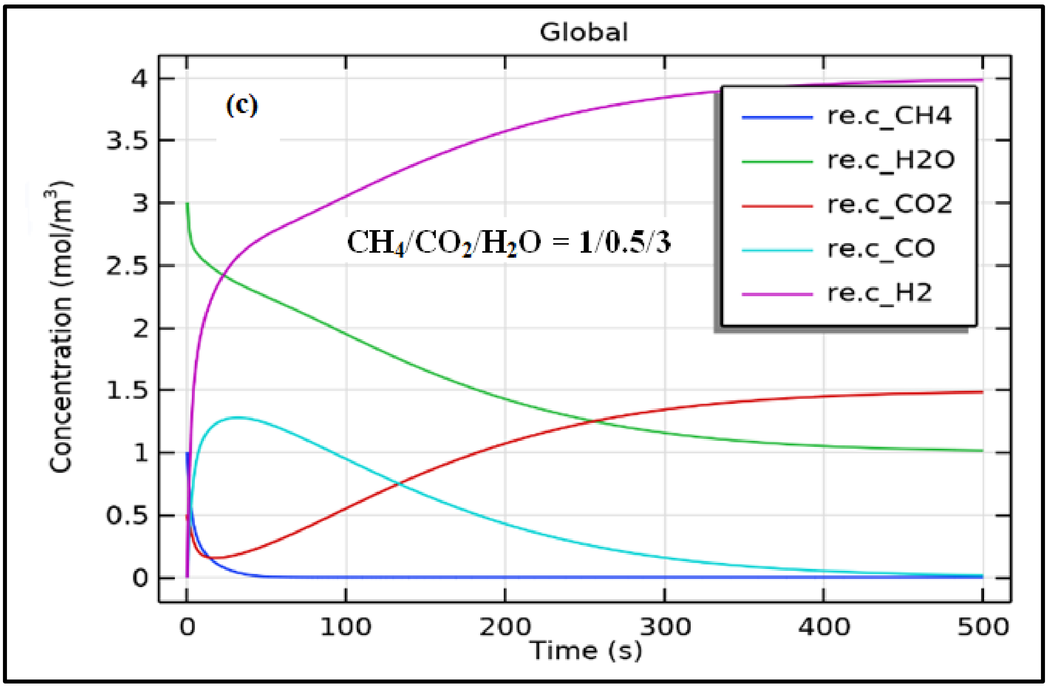
Table 4.3 illustrates the conversion amounts (in mol) at different temperatures and steam-to-carbon ratios. CH_4, H_2O, and CO_2 are the reactants, while CO and H_2 are the main products of the gas during the process. The amounts of reactant gases are decreasing, as initially provided, indicating an increase in the amount of product gases as well as efficient conversion of gases.


Global
(a)
$CH_4/CO_2/H_2O$ = 1/0.5/1
Concentration (mol/m^3)
Time (s)
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
100
200
300
400
500
re.c_CH4
re.c_H2O
re.c_CO2
re.c_CO
re.c_H2

(a)


Global
(b)
$CH_4/CO_2/H_2O$ = 1/0.5/2
Concentration (mol/m^3)
Time (s)
4
3.5
3
2.5
2
1.5
1
0.5
0
0
100
200
300
400
500
re.c_CH4
re.c_H2O
re.c_CO2
re.c_CO
re.c_H2

(b)



(c)

Fig. 4.5: Simulation analysis of the product gas distribution in the batch reactor at 10 bar and 1100 °C °C along with the time (sec.) at various steam carbon ratios including water gas shift reaction (a) S/C = 1, (b) S/C = 2, and (c) S/C = 3

Table 4.4: Optimal simulation results including water gas shift reaction for SRB at various temperature and the corresponding operating conditions. P =10 bar, CO_2 = 0.583 and S/C = 1-3

S/C ratio	Operating Temperature (°C)	Conversions Amount (mol)				
		H_2	CH_4	CO_2	CO	H_2O
1	600	1.6	0.25	0.32	0.20	0.4
	800	2.2	0.10	0.40	0.18	0.3
	1000	2.6	0.08	0.45	0.08	0.2
	1200	2.9	0.01	0.50	0.06	0.1
2	600	2.3	0.15	0.9	0.30	1.4
	800	2.8	0.10	1.1	0.20	1.0
	1000	3.2	0.02	1.2	0.10	0.60
	1200	3.4	0	1.3	0	0.20
3	600	2.7	0.15	1.0	0.18	1.3
	800	3.1	0.08	1.3	0.11	1.2
	1000	3.4	0.05	1.2	0.03	1.1
	1200	3.6	0	1.5	0	1

4.4 Validation of the Numerical Model with the previous simulation Results

To compare the results of the model with simulation data published by Hajjaji et al, [219], the main operating parameters were selected as S/C ratio, mass fraction, pressure, CO_2 composition, and operating temperature in order to present the study. The model suggested and discussed in the present study offers the concentration of species and temperature profiles during the chemical reaction process. The simulation work has been done on the biogas steam reforming process at various temperatures such as 600, 800, 1000, and 1200^{o}C to validate the proposed mathematical model. The simulation study and mathematical equations were performed by COMSOL, whereas the previous simulation result was performed by Aspen plus™ in order to the simulation of the reforming process.

Fig. 4.6 shows the comparative assessment between the present work and the previous study as simulation work. The results for H_2 yield; present simulation work (COMSOL software), as well as previous simulation work (Aspen plus™), follow almost similar trends and hydrogen yields are increasing with an increase in temperature at S/C 1 to 3.

The results of the current study show higher H_2 yields, with percentages reaching 5.33% at 800°C, 3.87% at 1000°C, and 2.9% at 1200°C (averaging percentages across steam-to-carbon ratios from 1 to 3), compared to a previous simulation study at the same operating temperatures. It is observed and confirmed that the values obtained from the current simulation enhance the productivity rate by almost 4% compared to the previous data.

According to Fig.4.6 the yield of H_2 amount as a function of steam/Carbon ratio (S/C) and operating temperature. The amount of H_2 increases as the S/C ratio (1/1 to 3/1) increases for temperature. This trend can be explained by Le Chatelier's Principle, which states that an increase in steam on the reactant side favors the H_2 production on the product side. However, the H_2 productivity gain becomes less significant when the S/C ratio exceeds 3, as the reaction starts to consume excessive amounts of water. As for the effect of temperature, the H_2 yield rises with increasing reforming temperature, reaching a maximum before slightly decreasing. This behavior is attributed to the inhibition of the exothermic WGS reaction. To summarize, increasing the steam-carbon ratio up to a certain point and raising the reforming temperature can enhance H_2 productivity, but the excessive use of water and the inhibition of the WGS reaction can limit this enhancement.

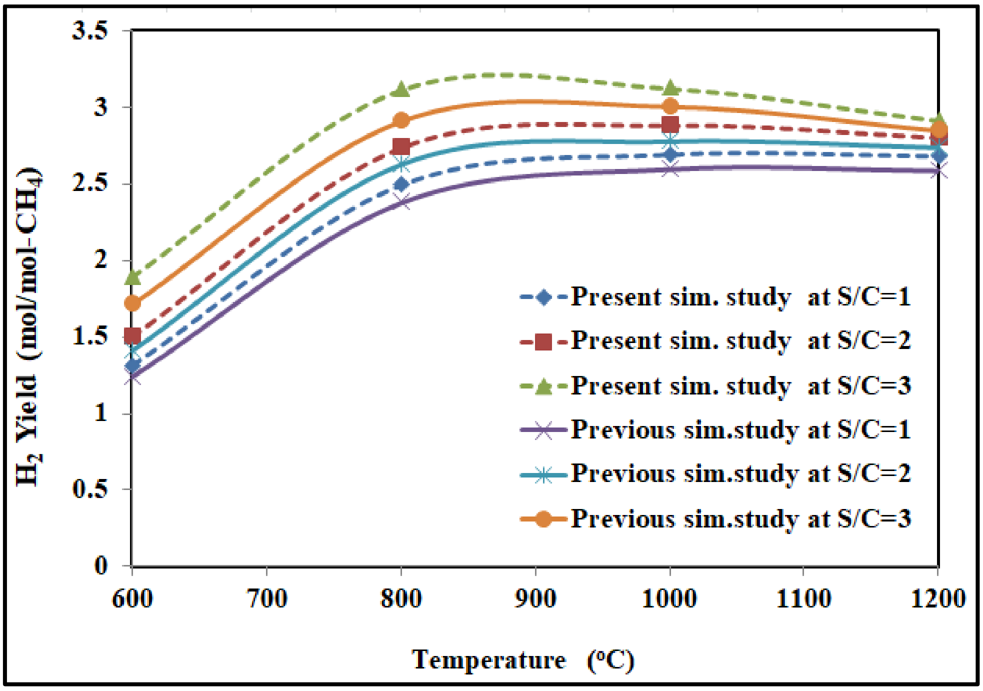


Fig. 4.6: Comparison assessment of yield of hydrogen between present and previous studies at S/C (1 to 3) via biogas reforming

The data presented in Fig.4.7 demonstrates a clear correlation between temperature and CO yields. As the temperature increases, there is a noticeable rise in the CO content of the synthesis gas (SG). The observed phenomenon can be attributed to the inhibitory impact of high temperatures on the exothermic WGSR, ultimately leading to a higher concentration of CO in the syngas. It is important to note that achieving high production of H_2 while maintaining a low CO content in the synthesis gas simultaneously is challenging. This is because the reforming temperature needs to be sufficiently high to ensure a reasonable yield of H_2. However, in order to minimize the CO content, it is preferable to keep the temperature as low as possible. The results obtained from the thermodynamic calculations lead us to recommend a reforming temperature of 800°C and an S/C ratio of approximately 3 for the biogas reforming system. These optimal conditions will be further employed to simulate the entire process of converting biogas (BG) into hydrogen (H_2).

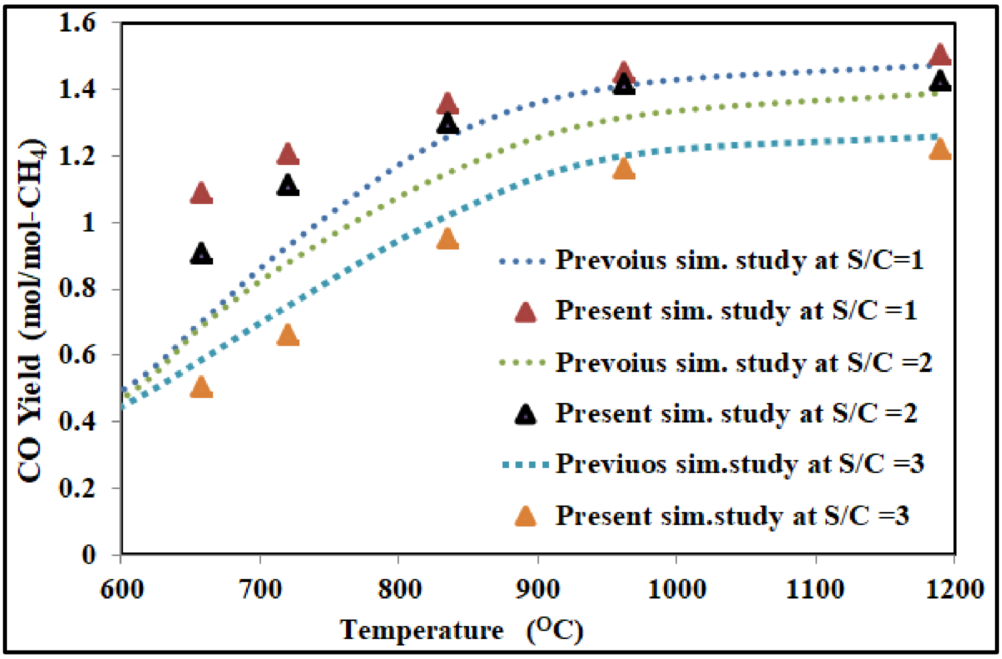


Fig. 4.7: Comparison assessment of CO yield between present and previous studies at S/C (1 to 3) from biogas reforming

Table 4.5: Estimated data from present and previous research for SRB at various temperature and the corresponding operating conditions. P =10 bar, CO_2 = 0.583 and S/C = 1-3

S/C	Temperature (°C)	Previous sim. study	Present sim. study	Enhanced H_2 yield (%)
1	600	1.23	1.31	5.57
	800	2.37	2.49	4.68
	1000	2.59	2.69	3.54
	1200	2.58	2.68	3.55
2	600	1.40	1.5	6.15
	800	2.62	2.733	3.95
	1000	2.77	2.88	3.62
	1200	2.73	2.8	2.29
3	600	1.70	1.89	9.54
	800	2.90	3.11	6.54
	1000	3.0	3.12	3.76
	1200	2.84	2.91	2.19

4.5 Estimation of simulation analysis results with thermodynamic analysis

The simulation analysis of the SRM has been conducted at a fixed pressure of 1 bar, spanning a temperature range from 500 to 1000 °C. Various Steam-to-Carbon (S/C) ratios, ranging from 1 to 3, were considered. Additionally, biogas simulation was performed under conditions of S/C ratio =1-3, pressure (P) =10 bar, and temperature ranging from 600 to 1200°C. According to simulation results, it is observed that the CH_4 mole fraction steadily decreases with an increase in temperature for both SRM and BSR processes. Meanwhile, the increased consumption of methane molecules increases the production of hydrogen moles. Hydrogen amount touches the maximum yield due to the existence of WGSR as well as increasing S/C ratio from 2:1 to 3:1. The performance of the reformer has been assessed based on several criteria, including hydrogen yield (Y_{H2}), carbon monoxide yield (Y_{CO}), total methane conversion (X_{CH4}) and the molar compositions of the products.

Furthermore, the simulation results of the reactor were compared with the outcomes of thermodynamic equilibrium analysis at exit conditions, which include temperature and pressure. The simulation results of the reactor indicate that methane conversion can be achieved within the range of 96% to 86.10% for S/C ratios ranging from 1 to 3, with varying optimum temperature and pressure conditions. The simulation results closely align with the thermodynamic analysis, as depicted in Table 4.6.

Table 4.6: Evaluation of simulation results of reactor with thermodynamic equilibrium at optimum pressure and temperature

Gas Composition	**S/C ratio**	X_{CH_4}(%)		Y_{H_2}**(mol)**	
CH_4/CO_2/H_2O		**Simulation**	**Thermodynamic [234]**	**Simulation**	**Thermo-dynamic[10]**
1/0/1	1	86.1	92.06	2.77	2.98
1/0/2	2	91.9	97.05	3.35	3.43
1/0/3	3	96	98.10	3.42	3.65
1/0.58/1	1	92	96.08	2.1	2.30
1/0.58/2	2	93	98.90	2.90	2.70

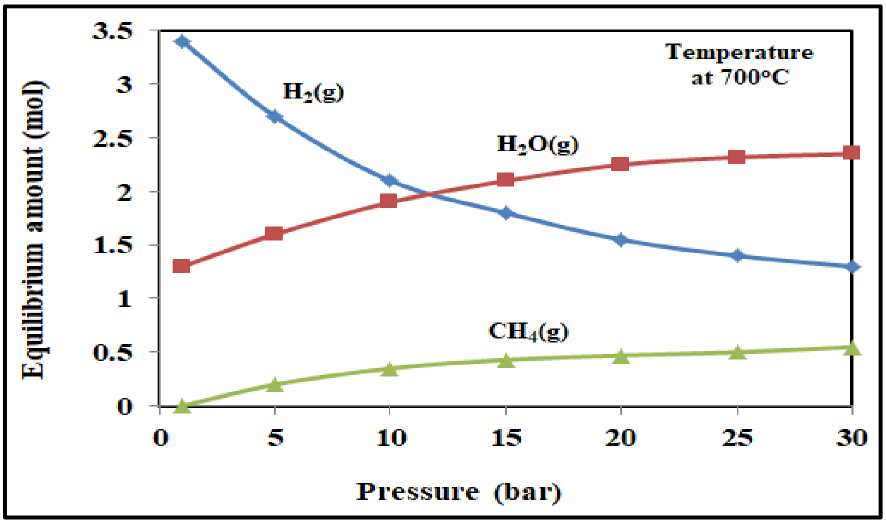
4.6 Pressure effect on methane and biogas reforming

4.6.1 Pressure effect on SMR

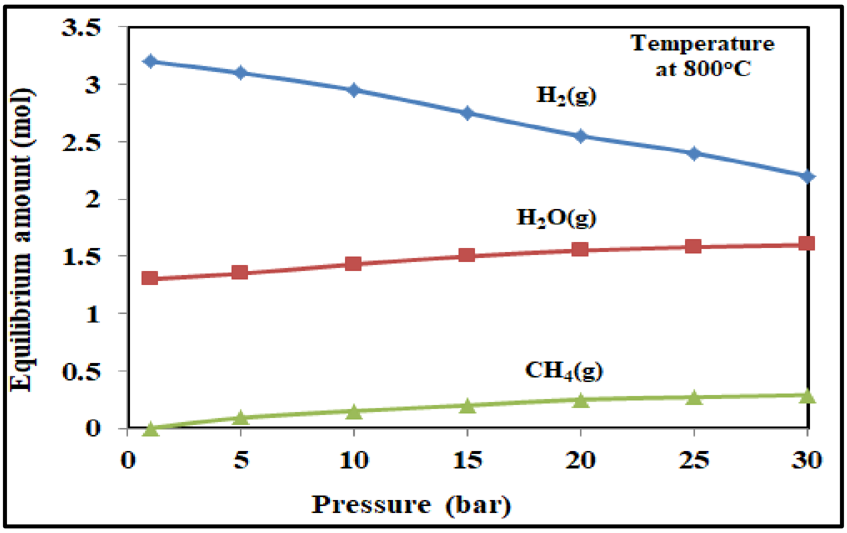
From the simulation results, SMR is favoured at temperatures above 700°C with an H_2O/CH_4 (S/C) molar ratio of 1.5 or greater at atmospheric pressure. SMR is not favoured at high pressures. However, for various reasons, it can be conducted at 30 bar or higher in large-scale units. Fig. 4.8 illustrates the effect of pressure on the quantities of key species such as H_2, H_2O, and CH_4 in the SMR process at temperatures of 700, 800, and 900°C, using a mixture of 1 mol CH_4 and 3 mol H_2O also known as steam carbon ratio (S/C = 3). Under these conditions, the system's behavior is similar at each temperature. Fig.4.8 (a) shows the equilibrium amount of hydrogen gas decreases as pressure increases at a particular temperature, whereas gaseous water and methane content slightly increase with the pressure variation. Fig.4.8 (b) shows the amount of hydrogen slightly decreases as pressure increases at 800^{o}C but there is not much more variation in water vapor for pressure increases. Even at 900°C, complete methane conversion is not achieved above 5 bar as shown in Fig.4.8 (c) As expected, increasing the reaction pressure strongly burdens methane conversion. At each reaction temperature, the amount of CH_4 conversion decreases as pressure increases as shown in Fig. 4.8(d). This results in a substantial decrease in hydrogen production with higher pressure.

SMR is an endothermic reaction (absorbs heat). According to Le Chatelier's principle, increasing the pressure shifts the equilibrium towards the side with fewer moles of gas. Since the reactants (methane and steam) have 2 moles of gas, and the products (CO and hydrogen) have 4 moles of gas, higher pressure favors the reverse reaction, reducing hydrogen yield. The reaction has no change in the number of gas moles (1 mole CO + 1 mole $H_2O \rightarrow$ 1 mole CO_2 + 1 mole H_2), so pressure has little effect on its equilibrium in order to water as shift reaction. High pressure generally increases the rate of reaction due to more frequent collisions between reactant molecules. However, for SMR, the effect of increased pressure on reaction rate is less significant than its effect on equilibrium.

In industry, steam methane reforming (SMR) is typically carried out at moderate pressures (15-30 bar). These pressures strike a balance between maintaining reasonable hydrogen yields and facilitating downstream processes such as pressure swing adsorption (PSA) for hydrogen purification, which is more efficient at higher pressures. While higher pressures can improve heat transfer within the reactor, aiding the endothermic SMR reaction, they can also lead to increased catalyst deactivation due to sintering (aggregation of catalyst particles) and coking (carbon deposition). Therefore, finding the optimal pressure is crucial for sustaining catalyst longevity and activity. Overall, while higher pressures generally reduce hydrogen yield due to equilibrium shifts, they can enhance reaction kinetics and heat transfer. Industrial operations use moderate pressures to effectively balance these factors and achieve optimal efficiency. The effect of pressure though simulation process is almost similar trending with thermodynamic analysis on SMR performance [10].



(a)



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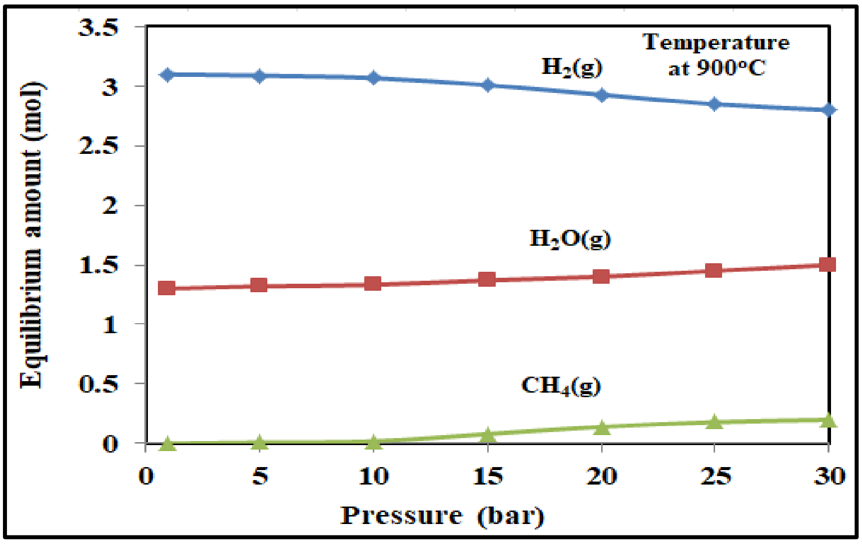

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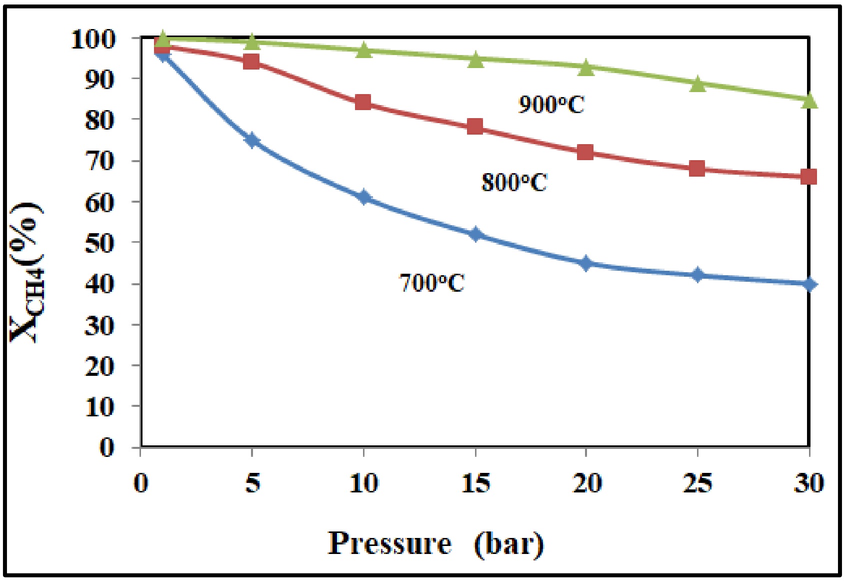

(d)

Fig. 4.8: Effect of reaction pressure on SMR at 700–900°C for S/C =3 : (a) 700°C, (b) 800°C, (c) 900°C, and (d) CH_4 conversion at various temperatures

4.6.2 Pressure effect on SRB

Steam biogas reforming is a process similar to steam methane reforming, but it involves the conversion of biogas (a mixture primarily of methane and carbon dioxide) into hydrogen, carbon monoxide, and other by-products. The pressure effect on steam biogas reforming can be understood through the 3 equations such as SMR, WGSR, and DR. The effect of pressure on the equilibrium of a chemical reaction can be explained using Le Chatelier's principle. This principle states that if a system at equilibrium is subjected to a change in pressure, temperature, or concentration, the system will adjust itself to partially counteract the change and re-establish equilibrium. Le Chatelier's Principle states that in steam and dry reforming reactions, rising pressure changes the equilibrium to the side with fewer moles of gas. Because both reforming reactions produce more moles of gas than they consume, increasing pressure tends to move the equilibrium towards the reactants, lowering the yield of hydrogen and carbon monoxide. There is no change in the number of gas moles between reactants and products, so changes in pressure have little effect on the equilibrium position of the water-gas shift reaction.

Overall, high pressure shifts the equilibrium of steam methane reforming and steam biogas reforming reactions towards the reactant side because these reactions produce more moles of gas as products than they consume as reactants. Increasing pressure favors the side with fewer moles of gas to counteract the applied pressure change, thus reducing the yield of hydrogen and other products.

The effects due to the variation of pressure are shown in Fig. 4.9. Fig. 4.9 (a) and (b) displays the equilibrium conversions of methane and carbon dioxide over a range of temperatures from 400 to 1200^{o}C with a fixed pressure of 1, 10, 20, and 30 bar for steam biogas reforming. Producing syngas at high pressure is desired for applications like Fischer-Tropsch synthesis for high-chain fuels. In Fig. 4.9 (a) and (b), both CH_4 and CO_2 conversions decrease with increasing pressure, indicating biogas reforming is unfavorable at high pressures. The figures also show that the difference in CH_4 and CO_2 conversions becomes smaller as pressure increases, meaning both conversions approach limiting values as pressure rises.

As pressure increases, there is a consistent decrease in methane conversion across the entire temperature range. As shown in Fig. 4.9 (a), methane conversion initially decreases up to 500°C, then increases with rising temperature; however, with increased pressure (1–30 bar), conversion decreases throughout the entire range. Regarding CO_2, maximum conversion is achieved at high temperatures above 900°C for the selected input feed molar ratios. Unlike CH_4, CO_2 conversion shows a different trend with pressure. There is a minor increase in CO_2 conversion up to 600°C, followed by a significant decrease as pressure continues to rise.

Higher pressures cause reactions to favor the side with fewer moles. Consequently, increased pressures favor the reverse of the SMR process. This effect on methane conversion is particularly noticeable in Fig. 4.9 (a). Generally, increasing pressure reduces CH_4 conversion, and higher temperatures are needed to achieve the same methane conversion as at lower pressures. The increased number of moles on the product side compared to the reactants causes this shift, favouring carbon monoxide methanation. As a result, at lower temperatures (where carbon monoxide methanation is preferred), methane conversion decreases significantly as pressure rises. Even though SMR is more efficient at higher temperatures, increasing pressure limits methane conversion.

Regarding carbon dioxide conversion (Fig. 4.9 (b)), pressure has a negligible thermodynamic influence, as the WGS reaction has the same number of moles on both the reactant and product sides. However, as CO production decreases from the SMR reaction with increasing pressure, the WGS reaction equilibrium (where CO is a reactant) shifts towards the reactant side, impacting CO_2 conversion. Thus, under conditions where the WGS reaction dominates (low temperatures), carbon dioxide conversion slightly increases with total pressure. Consequently, the lowest CO_2 conversion shifts to higher temperatures as pressure rises. The effect of pressure though simulation process is almost similar trending on SBR performance [244, 245].

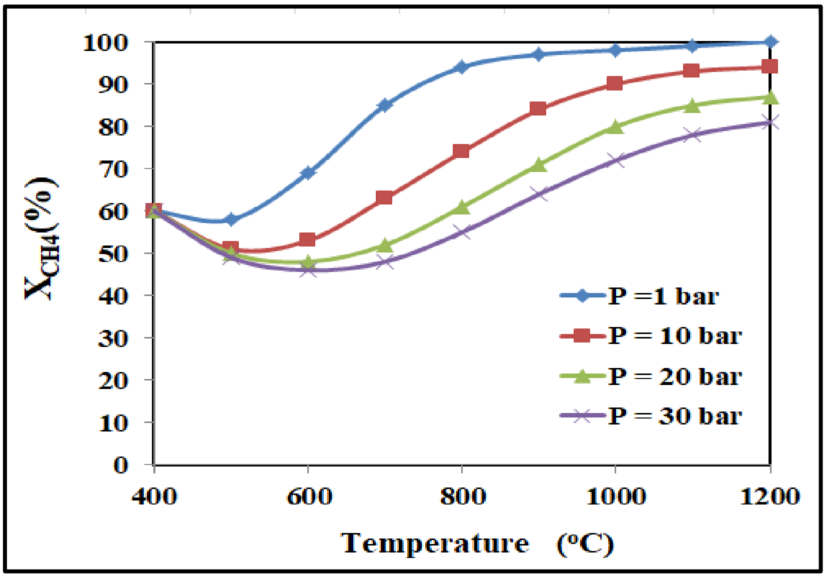

Fig. 4.9 (a): Pressure effect on CH_4 conversion at S/C = 3 and CO_2 = 0.5

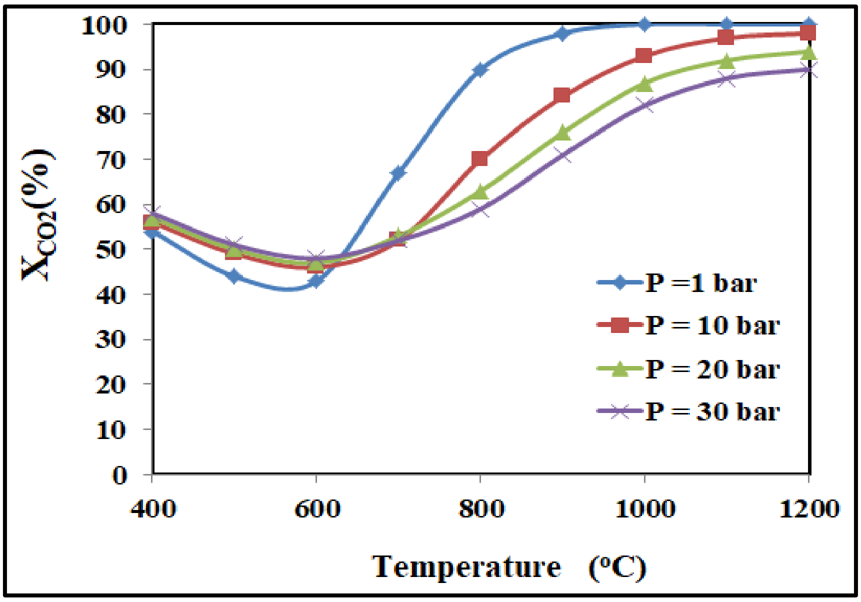

Fig. 4.9 (b): Pressure effect on CO_2 conversion at S/C = 3 and CO_2 = 0.5

Fig. 4.9 (c) shows the H_2O amount as a function of pressure. Water always forms in the reaction system and its amount increases with the increase in pressure but decreases with increased temperature. Water formation may be due to reactions such as RWGSR, CO/CO_2 methanation and CO/CO_2 hydrogenation.

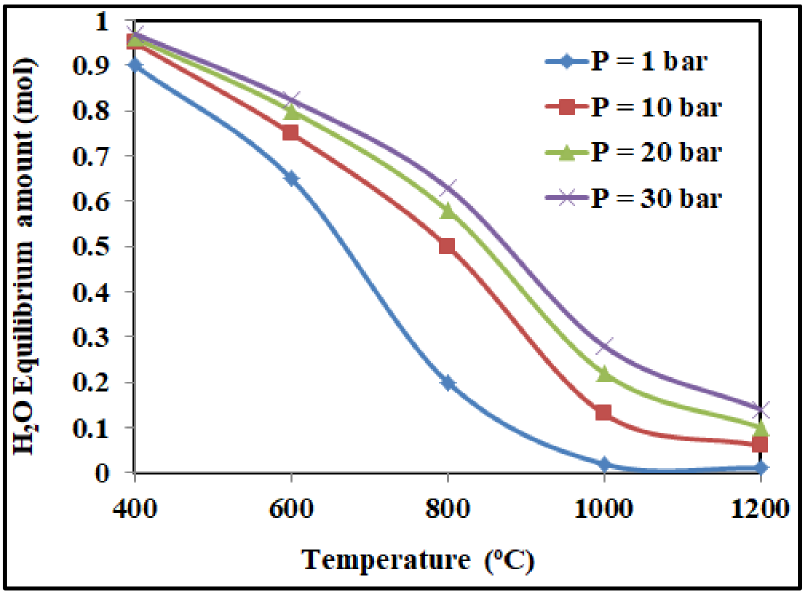

Fig.4.9 (c): Pressure effect on H_2O conversion at S/C = 1 and CO_2 = 0.5

The more significant influence of the pressure on the water conversion is observed at temperatures between 400 and 1000 ◦C in Fig. 4.9 (c), as the pressure shifts the SMR reaction towards the reactants side, and thus less water is converted. Below 400ºC, as the reverse of SMR reaction is prevalent, an increase in pressure produces more water (more negative conversion). Over 1000ºC, the SBR process is predominant; thus, water conversion is not affected since it is not involved in this reaction. At the industrial scale, it is common to use high pressures (20 bar) to improve the reaction kinetics.

Beyond the effect of operating temperature, the impact of pressure on product distribution from biogas reforming reactions is also important. The equilibrium product compositions as a function of pressure are shown in Fig. 4.9 (d). As depicted in 4.9 (d), increasing the pressure from 1 to 30 bar decreases the H_2 composition from 2.91 to 1.4 moles at 950°C. Additionally, at 1 bar and temperatures below 400°C and 600°C, the yields of hydrogen and carbon monoxide are negative, indicating their consumption. This occurs because lower temperatures favor the exothermic CO methanation and the WGS reaction. At higher temperatures, however, the yields of hydrogen and carbon monoxide become positive (outlet molar flow rate higher than the inlet) because the SMR and reverse WGS reactions dominate.

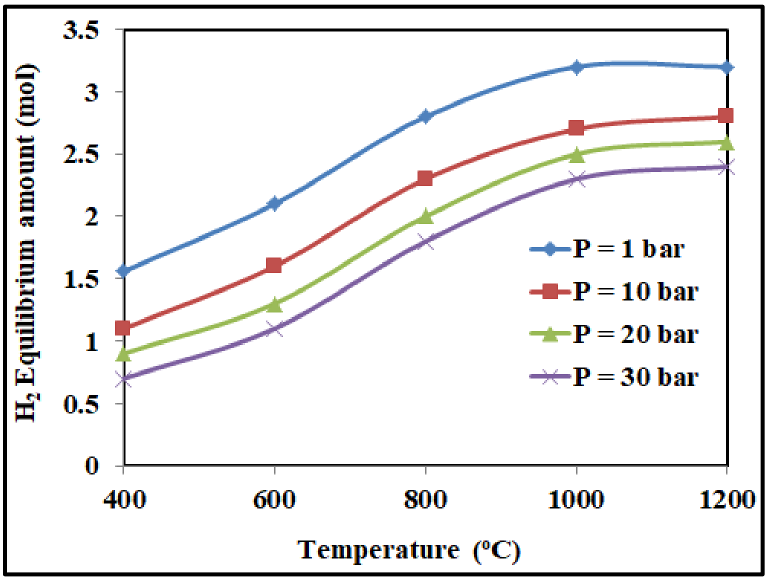

Fig.4.9 (d): Pressure effect on H_2 equilibrium amount at S/C = 3 and CO_2 = 0.5

The H_2 yield increases to a maximum and then slightly decreases, as the SMR produces hydrogen while the reverse WGS reaction consumes it. Conversely, the CO yield consistently increases with temperature as it is produced by both the SMR and the reverse WGS reaction. The same trending graph shows the validation of work for hydrogen equilibrium amount with different pressure and temperature [154, 246].

Table 4.7: Methane conversion (%) with CO_2 = 0.5 calculation of simulation results at different temperature and pressure (bar) for S/C = 3

T(^{O}C)	**P =1**	**P = 3**	**P = 5**	**P = 7**	**P = 9**	**P = 10**	**P =15**
400	60	60	60	60	60	60	60
500	58	56	55	54	53	51	50
600	69	63	59	57	55	53	50
700	85	76	72	68	66	63	60
800	94	87	82	79	76	74	72
900	97	93	90	88	86	84	82
1000	98	96	94	93	92	90	87
1100	99	98	97	96	95	93	90
1200	100	99	99	98	96	94	90

CHAPTER 5

CONCLUSION, FUTURE SCOPE AND SOCIAL IMPACT

5.1 Conclusion

In this work, the modeling and simulation of biogas-to-hydrogen production under different operating conditions were investigated and optimized. A zero-dimension (0-D) mathematical model is also presented in the present study to examine the production of hydrogen by steam reforming methane and biogas of different compositions. The findings of the previous experimental study were compared with the simulation analysis. Based on the results of this study, the following conclusions can be drawn.

5.1.1 Simulation analysis of SRM

- The present study data showed a maximum and minimum yield of hydrogen 3.1 mol/mol-CH_4 at 700°C and 1.4 mol/mol-CH_4 at 500°C respectively, at S/C = 2, with a higher value than the experiment data. Similarly, at S/C = 3, maximum and minimum hydrogen yields 3.3 mol/mol-CH_4 at 700°C and 1.8 mol/mol-CH_4 at 500°C respectively.
- The higher yields of hydrogen are achieved at 6% and 8.2% when compared with a previous simulation study at a temperature of 700°C with an S/C ratio of 2 and 3.
- At a specific temperature, a higher molar ratio of S/C can lead to a higher yield of H_2. The equilibrium amounts of these components depend on the stoichiometric ratio.

5.1.2 Simulation analysis of SRB

- The higher H_2 yields are achieved as 5.33% at 800 °C, 3.87% at 1000 °C, and 2.9% at 1200 °C (average percentage of mol for steam carbon ratio from 1-3) and compared with previous simulation studies at the same operating temperatures.

- It is observed and confirmed that the values obtained from the current simulation enhance the productivity rate by almost 4% compared to the previous data.
- H_2 productivity gain becomes less significant when the S/C ratio exceeds 3, as the reaction starts to consume excessive amounts of water. The effect of temperature on the H_2 yield rises with increasing reforming temperature, reaching a maximum and then slightly decreasing.
- It can be observed that increasing the temperature leads to an increase in the CO yields. This outcome is attributed to the high temperature inhibiting the exothermic WGS reaction and resulting in a higher CO content in the SG.
- Higher temperatures result in more CO yields. This can be attributed to the inhibitory effect of high temperatures on the exothermic water-gas shift reaction, leading to an increased concentration of CO in the synthesis gas.
- The results obtained from the thermodynamic calculations show for suggest a reforming temperature of 800°C and an S/C ratio of approximately 3 for the biogas reforming system. These optimal conditions will be further employed to simulate the entire process of converting biogas (BG) into hydrogen (H_2).

5.1.3 Thermodynamic equilibrium study

- At a specific temperature, it has been observed that an increase in the steam-to-carbon (S/C) molar ratio leads to a higher yield of hydrogen when methane is transformed into hydrogen.
- The presence of the water gas shift reaction facilitates the attainment of the maximum hydrogen yield, and this is achieved by increasing the S/C ratio from 2:1 to 3:1.
- The production of CO_2 is associated with the water gas shift (WGS) process. At a given temperature, the quantity of CO_2 increases in tandem with the S/C molar ratio, reaching a peak at around 600°C for each molar ratio.
- Methane (CH_4) conversion decreases with increasing water content below 600°C due to the formation of water content from a mixture of methane and CO_2

through a water gas shift reaction. But, adding water content leads to a slight improvement in methane conversion above 700°C. Therefore, it is possible to touch approx.100% methane conversion.

- The effect of decreased CO_2 conversion with an increasing amount of water content added to the mixture is due to the reason WGS. Conversely, this also strongly affects the various amounts of solid carbon (Coke), hydrogen yield, and content of CO by adding the quantity of H_2O to the system.
- The formation of hydrogen is strongly influenced and favorable by adding water to the system due to coke gasification, and due to the presence of WGS touches the maximum hydrogen yield amount.
- Coke selectivity is sharply limited with increasing CO_2 amount, which is explained by coke gasification through CO_2 to form CO amount at temperatures above 550°C. This observation further highlights the beneficial effect of the initial quantity of CO_2 on CO production.
- As the initial amount of CO_2 increases, the molar ratio of H_2/CO decreases. This phenomenon can be attributed to the significant impact of the initial CO_2 amount on CO formation, whereas the yield of H_2 is comparatively less influenced.

5.1.4 Analysis of pressure effect on SMR

- The equilibrium amount of hydrogen decreases as pressure increases at a particular temperature, whereas gaseous water and methane content slightly increase with the pressure variation.
- Increasing the reaction pressure strongly burdens methane conversion. At each reaction temperature, the amount of CH_4 conversion decreases as pressure increases. This results in a substantial decrease in hydrogen production with higher pressure.
- In industry, steam methane reforming (SMR) is typically carried out at moderate pressures (15-30 bar). These pressures strike a balance between maintaining reasonable hydrogen yields and facilitating downstream processes such as

pressure swing adsorption (PSA) for hydrogen purification, which is more efficient at higher pressures.

- Overall, while higher pressures generally reduce hydrogen yield due to equilibrium shifts, they can enhance reaction kinetics and heat transfer. Industrial operations use moderate pressures to effectively balance these factors and achieve optimal efficiency.

5.1.5 Analysis of pressure effect on SBR

- Methane conversion initially decreases up to 500°C, then increases with rising temperature; however, with increased pressure (1-30 bar), conversion decreases throughout the entire range.
- Generally, increasing pressure reduces CH_4 conversion, and higher temperatures are needed to achieve the same methane conversion as at lower pressures.
- The increased number of moles on the product side compared to the reactants causes this shift, favouring carbon monoxide methanation.
- Over 1000°C, the SBR process is predominant; thus, water conversion is not affected since it is not involved in this reaction. At the industrial scale, it is common to use high pressures (20 bar) to improve the reaction kinetics.
- Increasing the pressure from 1 to 30 bar decreases the H_2 composition from 2.91 to 1.4 moles at 950°C. Additionally, at 1 bar and temperatures below 400°C and 600°C, the yields of hydrogen and carbon monoxide are negative, indicating their consumption. This occurs because lower temperatures favour the exothermic CO methanation and the WGS reaction.

5.2 Future Scope

A 0-D mathematical model has been analysed for hydrogen production through steam reforming of methane and biogas with varying compositions in the present study. The proposed mathematical model can be analysed at different variable parameters such as steam carbon ratio, CO_2/CH_4, different chemical species, etc. to predict the outcome of experimental data as well as help optimize the parameters for hydrogen production.

Furthermore, experimental practices are always recommended along with the CFD analysis for the proposed model to design and check its validity, competency, and sustainability for the continuous existence in the competitive market for the production of essential fuel and also the corresponding responses under the variable meteorological conditions.

As per the findings of the present study, the following are recommended for future work.

- To achieve an optimized syngas synthesis from biogas, a systematic experimental process development is necessary. Key factors such as the composition of the biogas, catalyst properties, reaction pressure, reaction temperature, space velocity, and time on stream can influence the reactant conversions and produced molar ratio H_2/CO throughout the biogas reforming process.
- To advance the modeling work presented in this study, a more comprehensive experimental setup needs to be established.
- Single-step reforming of CH_4 and CO_2 into chemicals and fuels is a promising pathway. Designing highly effective catalysts is essential for desired product outcomes.
- Integrating reforming with Fischer-Tropsch synthesis enhances biogas fuel production, increasing reactant conversions, enabling by-product recovery, and improving energy efficiency. This hybrid system may ultimately reduce total processing costs.
- The design and development of reactors along with the biogas reforming process contribute to effective hydrogen production with reduced energy consumption.
- Investigating simulation and modeling tools like CFD, HYSYS, MATLAB, ASPEN Plus V11, and COMSOL Multiphysics offers open research areas that can be used to validate existing experimental results.

5.3 Challenges

The primary technical hurdle is achieving cost-competitiveness in the conversion of biogas to H_2 production as well as syngas. Notably, one of the most costly factors is the amount of energy required at high temperatures, and the price of catalysts also has a big impact. Deactivation of catalysts can occur after a specific duration of use. Therefore, it becomes essential to address the regeneration of used catalysts or explore the development of catalysts with extended lifetimes. The process requires H_2S removal and the introduction of oxidizing agents. Challenges involve carbon formation, side reactions consuming hydrogen, moderate selectivity, high operating temperatures, energy demands, and potential catalyst expenses.

Challenges associated with the simulation and modelling of hydrogen production from biogas are as follows.

- **Reaction kinetics:** The chemical reactions involved in biogas reforming processes are complex and may include steam reforming, dry reforming, and water-gas shift reactions. Accurately modeling these reactions and their kinetics is challenging due to the presence of multiple reactants and products, as well as catalyst effects.
- **Biogas composition variability:** Biogas composition can vary depending on the feedstock and digestion process, leading to fluctuations in methane, carbon dioxide, hydrogen sulfide, and trace contaminants. Modeling the impact of these variations on hydrogen production efficiency requires robust simulation techniques that can account for compositional changes.
- **Catalyst modeling:** Catalysts play a crucial role in biogas reforming processes by facilitating reaction kinetics and enhancing selectivity. However, accurately modeling catalyst behavior under realistic operating conditions, including deactivation mechanisms and regeneration strategies, remains a challenge.
- **Transport phenomena:** Transport phenomena such as heat and mass transfer are critical in determining the performance of biogas reforming reactors. Modeling these phenomena accurately, particularly in complex reactor

geometries and multi-phase systems, requires advanced simulation techniques and computational resources.

- **Scale-up considerations:** Scaling up biogas-to-hydrogen production processes from laboratory-scale to industrial scale presents challenges in terms of reactor design, process optimization, and economics. Simulation models must account for scale-up effects and address issues such as reactor dynamics, heat management, and safety considerations.
- **Data availability and validation:** Validating simulation models for biogas reforming processes requires experimental data from laboratory-scale or pilot-scale studies. However, such data may be limited or unavailable, making model validation challenging.
- **Parameter sensitivity and uncertainty:** Simulation models are sensitive to input parameters such as reaction kinetics, thermodynamic properties, and transport coefficients. Uncertainty in these parameters can lead to variability in simulation results and affect the reliability of predictions.
- **Interdisciplinary collaboration:** Addressing the challenges of simulating hydrogen production from biogas requires interdisciplinary collaboration between researchers in chemical engineering, materials science, environmental science, and computational modeling. Integrating expertise from different disciplines is essential for developing comprehensive simulation models and addressing complex research questions.

By addressing these challenges, simulation, and modeling of hydrogen production from biogas can contribute to developing efficient and sustainable energy technologies, helping to reduce greenhouse gas emissions and dependence on fossil fuels.

5.4 Social Impact

Simulation modelling of hydrogen production from biogas holds the potential to generate positive social impacts by promoting environmental sustainability, energy security, economic development, and community well-being. By addressing societal challenges related to energy access, climate change, and pollution, these efforts contribute to a more equitable and sustainable future for all.

- **Environmental sustainability:** By providing insights into more efficient and cleaner energy production methods, simulation modeling of hydrogen production from biogas contributes to reducing greenhouse gas emissions and mitigating climate change. This can lead to improved air quality and overall environmental health, benefiting communities and ecosystems.
- **Energy security and independence:** Biogas-based hydrogen production offers a renewable energy source that can help reduce dependency on fossil fuels and imported energy. This enhances energy security and resilience, particularly in regions prone to energy supply disruptions or geopolitical tensions.
- **Rural development and job creation**: Biogas production from organic waste sources such as agricultural residues, municipal waste, and wastewater can stimulate rural development by providing additional income opportunities for farmers and waste management professionals. The establishment of biogas-to-hydrogen production facilities can create jobs in construction, operation, and maintenance, thereby boosting local economies.
- **Access to clean energy:** Simulation modeling of biogas-to-hydrogen production can pave the way for decentralized energy systems, bringing clean and affordable energy to remote or underserved communities. This can improve living standards, support economic development, and reduce energy poverty.
- **Technological innovation and knowledge transfer:** Research and development in simulation modeling foster technological innovation and knowledge transfer, driving advancements in renewable energy technologies, chemical engineering, and environmental science. This can lead to spin-off benefits in other sectors and contribute to national competitiveness and innovation.
- **Community engagement and education:** Simulation modeling projects involving hydrogen production from biogas can raise awareness about renewable energy and sustainable practices, fostering community engagement

and participation in energy transition efforts. Educational initiatives related to simulation modeling can also inspire future generations of scientists, engineers, and policymakers to address pressing environmental and energy challenges.

- **Health and well-being:** By reducing pollution and reliance on fossil fuels, biogas-based hydrogen production can improve public health outcomes, particularly in urban areas where air quality is a concern. Cleaner energy sources contribute to lower rates of respiratory diseases and other health issues associated with air pollution, enhancing overall well-being and quality of life.

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APPENDICES

1. Effect of chemical component at 873K and steam carbon ratio (S/C) 1 by simulation results.

S.No.	**Time(s)**	**H_2**	**CH_4**	**H_2O**	**CO**	**CO_2**
1	2.39	0.106656	1.08473	1.09295	0.0984371	0.106709
2	4.26	0.714668	0.771974	0.698036	0.361065	0.204601
3	6.21763	1.30612	0.59886	0.459185	0.442641	0.286124
4	14.1095	1.92187	0.491235	0.261009	0.466577	0.310183
5	22.6373	2.15949	0.408022	0.301243	0.564715	0.210884
6	31.1773	2.21629	0.341247	0.28322	0.744588	0.136189
7	47.2336	2.4286	0.249146	0.214932	0.842163	0.110141
8	69.5967	2.63214	0.213999	0.188479	0.930656	0.101112
9	90.339	2.7372	0.170597	0.160407	0.993382	0.0993523
10	122.068	2.81664	0.152434	0.149829	1.00729	0.0881763
11	153.393	2.86325	0.150551	0.123324	1.0138	0.0861171
12	170.479	2.88643	0.139533	0.106568	1.00389	0.0925411

2. Effect of chemical component at 973K and steam carbon ratio (S/C) 1 by simulation results.

S.No.	**Time(s)**	**H_2**	**CH_4**	**H_2O**	**CO**	**CO_2**
1	2.39244	0.106737	1	1	0.426906	0.10672
2	4.78489	0.698415	0.690006	0.665408	0.516834	0.196803
3	10.3673	1.51187	0.492193	0.369173	0.713611	0.295037
4	20.7345	2.08677	0.343437	0.278331	0.893363	0.154586
5	30.9024	2.21783	0.235398	0.327206	0.950044	0.112852
6	53.0325	2.51277	0.176639	0.27721	0.981791	0.111619
7	78.3526	2.67605	0.175768	0.226894	1.02121	0.0938263
8	101.48	2.7819	0.149498	0.201098	1.01998	0.0844945
9	138.562	2.85427	0.15688	0.174949	1.03576	0.0746539

3. Effect of chemical component at 1073K and steam carbon ratio (S/C) 1 by simulation results.

S.No.	**Time(s)**	**H_2**	**CH_4**	**H_2O**	**CO**	**CO_2**
1	2.03475	0.107026	1.07691	1.06045	0.10706	0.0906043
2	4.56026	0.641491	0.740384	0.53511	0.411768	0.289141
3	8.5177	1.28293	0.560152	0.30591	0.478359	0.16721
4	15.2827	1.85886	0.44611	0.331893	0.726107	0.103827
5	26.8272	2.15575	0.332503	0.243886	0.909303	0.11541
6	55.3115	2.52807	0.260325	0.204934	0.977533	0.110364
7	88.8016	2.74467	0.21345	0.182978	0.995802	0.11188
8	116.422	2.82925	0.167916	0.154128	1.02436	0.106694

4. Effect of chemical component at 1173K and steam carbon ratio (S/C) 1 by simulation results.

S.No.	**Time(s)**	**H_2**	**CH_4**	**H_2O**	**CO**	**CO_2**
1	2.2234	0.0751773	1.0752	1.06684	0.0752128	0.075266
2	5.05319	0.725426	0.57617	0.550816	0.37578	0.234592
3	8.48936	1.27573	0.452004	0.351454	0.468156	0.226826
4	17.5851	1.96819	0.344929	0.310355	0.635691	0.169096
5	28.7021	2.1775	0.246613	0.319521	0.761489	0.0953014
6	42.4468	2.42037	0.198635	0.23828	0.888138	0.0801418
7	65.0851	2.63902	0.160266	0.18195	0.940301	0.0836702
8	98.6383	2.79197	0.162021	0.159663	0.96695	0.0787057

5. Effect of chemical component at 1273K and steam carbon ratio (S/C) 1 by simulation results.

S.No.	**Time (s)**	**H_2**	**CH_4**	**H_2O**	**CO**	**CO_2**
1	2.27896	0.0667177	1	1	0.0749916	0.075027
2	3.49725	0.465716	0.566347	0.507849	0.391469	0.208936
3	6.77764	1.07265	0.417762	0.367138	0.541979	0.201261
4	12.3427	1.67148	0.311092	0.317895	0.684034	0.151909
5	22.2834	2.05462	0.229716	0.302546	0.801212	0.094736
6	41.1553	2.4053	0.19009	0.221405	0.885695	0.087806
7	64.1894	2.62338	0.168484	0.173488	0.954483	0.081222
8	99.8936	2.79271	0.147041	0.151918	0.964555	0.083547
9	139.964	2.87932	0.140438	0.171608	0.982847	0.077707

6. Effect of chemical component at 1373K and steam carbon ratio (S/C) 1 by simulation results.

S.No.	**Time (s)**	H_2	CH_4	H_2O	**CO**	CO_2
1	2.44277	0.0829973	1.06918	1.06089	0.0747189	0.0747189
2	4.64707	0.679779	0.630322	0.547387	0.356682	0.356682
3	6.66139	1.06937	0.456752	0.381962	0.497913	0.497913
4	12.7415	1.69118	0.349543	0.340935	0.622524	0.622524
5	21.2887	2.04791	0.308409	0.300149	0.78057	0.78057
6	34.5359	2.31368	0.234696	0.226427	0.863888	0.863888
7	60.4339	2.61315	0.202393	0.194132	0.948069	0.948069
8	78.9974	2.72998	0.178377	0.186726	0.999671	0.999671
9	99.6062	2.78061	0.162674	0.154912	1.01789	1.01789
10	137.559	2.88171	0.139513	0.131484	1.02745	1.02745

7. Effect of chemical component at 1473K and steam carbon ratio (S/C) 1 by simulation results.

S.No.	**Time (s)**	H_2	CH_4	H_2O	**CO**	CO_2
1	1.84315	0.0908192	1.08812	1.07164	0.115562	0.0908016
2	4.16022	0.676185	0.586337	0.56124	0.388108	0.174085
3	8.10808	1.28642	0.446931	0.421711	0.677826	0.125834
4	22.0463	2.06235	0.316703	0.348346	0.794324	0.102608
5	41.0143	2.42664	0.244238	0.283823	0.894497	0.0877661
6	59.7555	2.61782	0.204687	0.211323	0.954696	0.0976316
7	79.298	2.71842	0.166831	0.18831	0.989446	0.0761357
8	99.8555	2.80262	0.153701	0.175285	1.0009	0.120557

8. Effect of chemical component at 873K and steam carbon ratio (S/C) 2 by simulation results.

S.No.	**Time (s)**	H_2	CH_4	H_2O	**CO**	CO_2
1	2.64501	0.0877456	1.07382	2.0987	0.0876896	0.301911
2	3.52668	0.66808	0.668585	1.2687	0.427097	0.702414
3	4.62877	1.09378	0.21882	0.67245	0.410396	0.530792
4	6.61253	1.69373	0.0886205	0.5773	0.354852	0.262654
5	15.4292	2.90453	0.0555547	0.8901	0.676717	0.142347
6	28.4339	3.41061	0.0606581	1.030	1.03006	0.138062
7	44.5244	3.19232	0.0713697	1.037	1.04679	0.138825
8	65.6845	3.15903	0.0916938	1.06	1.04267	0.149761

9. Effect of chemical component at 973K and steam carbon ratio (S/C) 2 by simulation results.

S.No.	**Time (s)**	**H_2**	**CH_4**	**H_2O**	**CO**	**CO_2**
1	2.42905	0.0959926	1.12203	2	0.0768043	0.0864035
2	3.25993	0.498774	0.709856	1.3045	0.47015	0.470384
3	3.67593	0.709754	0.336259	0.653167	0.422724	0.691503
4	4.50793	1.13171	0.231218	0.931862	0.403841	0.481043
5	7.17816	1.91815	0.126727	0.989763	0.711181	0.241806
6	21.597	3.35723	0.0893179	1.0578	1.00919	0.156462
7	25.2336	3.39577	0.0998751	1.06838	1.05779	0.147871
8	33.5055	3.28112	0.0912541	1.0885	1.06841	0.13923
9	44.4049	3.21455	0.114294	1.0895	1.07933	0.143041

10. Effect of chemical component at 1073K and steam carbon ratio (S/C) 2 by simulation results.

S.No.	**Time (s)**	**H_2**	**CH_4**	**H_2O**	**CO**	**CO_2**
1	2.46497	0.104905	1.13488	2.17439	0.0953678	0.104905
2	3.99194	0.934605	0.53406	1.56403	0.457766	0.591281
3	5.06244	1.35422	0.247956	0.705722	0.429155	0.658038
4	7.17781	1.97411	0.123978	0.944142	0.724796	0.467302
5	12.7919	2.81335	0.0953678	1.06812	0.982289	0.219346
6	21.6426	3.37602	0.104905	1.09673	1.1158	0.152589
7	31.8509	3.3188	0.104905	1.1158	1.12534	0.133515
8	41.6496	3.25204	0.114441	1.10627	1.08719	0.133515

11. Effect of chemical component at 1173K and steam carbon ratio (S/C) 2 by simulation results.

S.No.	**Time (s)**	**H_2**	**CH_4**	**H_2O**	**CO**	**CO_2**
1	1.62283	0.0860656	1	2	0.105191	0.114754
2	2.74051	0.717213	0.506831	0.803279	0.506831	0.382514
3	3.47893	1.17623	0.229508	1.07104	0.468579	0.64071
4	7.18441	2.22814	0.143443	1.13798	0.84153	0.602459
5	17.0288	3.29918	0.124317	1.10929	1.03279	0.439891
6	21.1085	3.38525	0.0860656	1.13798	1.09973	0.229508
7	29.9224	3.32787	0.0956284	1.145	1.13798	0.162568

12. Effect of chemical component at 1273K and steam carbon ratio (S/C) 2 by simulation results

S.No.	Time (s)	H_2	CH_4	H_2O	CO	CO_2
1	2.63607	0.114489	1	2	0.114509	0.124072
2	3.2444	0.764701	0.754934	1.64418	0.506177	0.343385
3	5.67769	1.60599	0.314022	0.868422	0.514781	0.581782
4	7.90822	2.27516	0.227304	1.04889	0.714805	0.523793
5	21.6969	3.3735	0.129777	1.12423	1.08602	0.389321
6	40.1494	3.37164	0.0799829	1.09364	1.09356	0.196635
7	79.0822	3.35816	0.0971899	1.1396	1.13936	0.165967
8	118.826	3.35416	0.0818302	1.12608	1.14555	0.125878
9	171.75	3.36796	0.06799	1.11274	1.09335	0.123817

13. Effect of chemical component at 1373K and steam carbon ratio (S/C) 2 by simulation results.

S.No.	Time (s)	H_2	CH_4	H_2O	CO	CO_2
1	2.08336	0.1123	1.08406	2.23748	0.0097035	0.00968164
2	4.2993	1.10414	0.35891	1.33323	0.378543	0.209682
3	8.81166	2.25802	0.091888	0.857043	0.469123	0.41932
4	22.4766	3.29355	0.02244	0.967728	0.7285	0.261164
5	41.6542	3.38504	0.03112	1.01029	0.978674	0.0740078
6	82.2797	3.38929	0.01118	1.06468	1.02082	0.0271915
7	131.031	3.40434	0.00111	1.03925	1.06304	0.0208897
8	170.614	3.39854	0.011114	1.09261	1.05702	0.0356084
9	192.489	3.40083	0.011114	1.05261	1.05089	0.0580898

14. Effect of chemical component at 973K and steam carbon ratio (S/C) 3 by simulation results.

S.No.	Time (s)	H_2	CH_4	H_2O	CO	CO_2
1	1.98815	0.0783694	1.04466	3.07838	0.089558	0.100747
2	2.80571	0.550183	0.549972	2.08908	0.403881	0.661556
3	4.44531	1.5837	0.212378	1.33507	0.290607	0.918267
4	10.0802	3.11112	0.0761387	1.19921	0.131872	0.748789
5	21.6309	3.82886	0.0406464	1.61337	0.51253	0.410445
6	25.6056	3.90704	0.038087	1.84758	0.680176	0.229473
7	40.0797	3.5233	0.0242916	1.93498	0.869378	0.125602
8	58.7293	3.26267	0.0320757	1.98691	0.945799	0.134537
9	78.1813	3.17048	0.0378404	1.98343	0.953935	0.108966

15. Effect of chemical component at 1073K and steam carbon ratio (S/C) 3 by simulation results.

S.No.	**Time (s)**	**H_2**	**CH_4**	**H_2O**	**CO**	**CO_2**
1	2.37748	0.0341811	1.01723	3	0.068221	0.0568742
2	2.97185	0.610523	0.452614	2.36222	0.362124	0.520905
3	4.35871	1.44685	0.136913	1.70739	0.31768	0.804428
4	6.73618	2.32848	0.0364198	1.23423	0.149461	0.861467
5	11.4911	3.2895	0.0178152	1.63145	0.467212	0.73781
6	21.9917	3.87832	0.00420636	1.90523	0.773805	0.467566
7	27.7372	3.82251	0.0109106	1.97649	0.91192	0.209729
8	32.2941	3.67616	0.0160714	2.01379	0.937888	0.121195
9	40.0209	3.45109	0.0108988	2.00715	0.951662	0.0679733

16. Effect of chemical component at 1173K and steam carbon ratio (S/C) 3 by simulation results.

S.No.	**Time (s)**	**H_2**	**CH_4**	**H_2O**	**CO**	**CO_2**
1	0.202128	0.0228317	1.04265	3.22961	0.01117	0.0114882
2	1.21277	1.09938	0.532879	2.33465	0.385595	0.544488
3	3.6383	2.28933	0.159231	1.93817	0.284046	0.748996
4	8.08511	3.27543	0.0127057	1.53065	0.227738	0.568163
5	12.5319	3.76294	0.00846242	1.4289	0.409415	0.342065
6	18.1915	3.88793	0.00659394	1.81518	0.738666	0.172841
7	22.6383	3.80887	0.00822132	1.96349	0.852595	0.128371
8	33.3511	3.60555	0.0105599	2.06626	0.95559	0.0733892
9	49.9255	3.42523	0.0115243	2.09035	0.97923	0.0750648

17. Effect of chemical component at 1273K and steam carbon ratio (S/C) 3 by simulation results.

S.No.	**Time (s)**	**H_2**	**CH_4**	**H_2O**	**CO**	**CO_2**
1	2.59182	0.0452241	1.04804	3.21142	0.04526	0.0339683
2	3.98741	1.31855	0.608711	2.52424	0.372138	0.654207
3	5.78174	2.08485	0.135944	1.8034	0.304923	0.767261
4	6.97796	2.62577	0.0130411	1.4321	0.328002	0.609964
5	10.5666	3.29077	0.0270754	1.66936	0.802246	0.340192
6	14.7534	3.76426	0.0173803	1.98621	0.915975	0.160891
7	20.9339	3.88857	0.0153466	2.07893	1.0202	0.11672
8	25.9182	3.79872	0.0134667	2.08082	1.00004	0.0733872
9	37.0829	3.56276	0.010239	2.11617	1.02491	0.10855

18. Effect of chemical component at 1373K and steam carbon ratio (S/C) 3 by simulation results.

S.No.	**Time (s)**	**H_2**	**CH_4**	**H_2O**	**CO**	**CO_2**
1	2.40281	0.0334926	1.09866	3.35367	0.033529	0.0559405
2	3.73935	1.35903	0.611079	2.86616	0.429666	0.598743
3	5.09803	2.24264	0.156705	2.07217	0.394704	0.711198
4	8.45924	3.15989	0.0289385	1.61747	0.427049	0.607923
5	11.6422	3.63524	-0.010184	1.78569	0.809811	0.402557
6	19.6444	3.92842	0.00598851	2.02089	0.99775	0.230647
7	25.4618	3.8254	0.0129811	2.09709	0.993734	0.113782
8	33.0852	3.67673	0.00272531	2.13668	1.02239	0.0976449
9	53.9373	3.51436	0.00853452	2.12961	1.04953	0.0925171

LIST OF PUBLICATIONS

International Journal (03)

1. **Ravindra Kumar,** Anil Kumar, and Amit Pal. Simulation modelling of hydrogen production from steam reforming of methane and biogas. Fuel 362 (2024): 130742.https://doi.org/10.1016/j.fuel.2023.130742.**SCI Impact Factor 7.4**

2. **Ravindra Kumar** and Anil Kumar. Recent Advances of Biogas Reforming for Hydrogen Production: Methods, Purification, Utility and Techno-Economics. International Journal of Hydrogen Energy. International Journal of Hydrogen Energy. 2024 Feb 23. https://doi.org/10.1016/j.ijhydene.2024.02.143, **SCI Impact Factor 7.13**

3. **Ravindra Kumar,** Anil Kumar, and Amit Pal. Overview of hydrogen production from biogas reforming: Technological advancement. International Journal of Hydrogen Energy 47, no. 82 (2022): 34831-34855. https://doi.org/10.1016/j. ijhydene.2022.08.059. **SCI Impact Factor 7.13**

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1. **Ravindra Kumar,** Anil Kumar, and Amit Pal. (2021). An overview of conventional and non-conventional hydrogen production methods. Materials Today: Proceedings, 46, 5353-5359.

2. **Ravindra Kumar** and Anil Kumar (2023). Advancement in steam reforming of methanol to produce hydrogen: A review. Applied Chemical Engineering, 6(2), p.2123.

3. **Ravindra Kumar,** Anil Kumar, & D. N. Thoai (2021). Solar Thermal Application for Crop Residue Management. In Recent Advances in Mechanical Engineering (pp. 303-315). Springer, Singapore DOI: 10.1007/978-981-15-9678-0_27.(Book Chapter)

4. **Ravindra Kumar,** Anil Kumar, and Atul Sharma (2023). Overview of Hydrogen Production Methods from Solar Energy. Thermal Energy: Applications, Innovations, and Future Directions. CRC Press. DOI: 10.1201/9781003345558-14. (Book Chapter)

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Full Length Article

Simulation modelling of hydrogen production from steam reforming of methane and biogas

Ravindra Kumar[a], Anil Kumar[a,b,*], Amit Pal[a]

[a] *Department of Mechanical Engineering, Delhi Technological University, Delhi 110042, India*
[b] *Centre for Energy and Environment, Delhi Technological University, Delhi 110042, India*

ARTICLE INFO

Keywords:
Steam reforming
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ABSTRACT

The use of fossil fuels in energy systems has environmental consequences, which are driving investigations into H_2 production. While steam methane reforming is the most well-known method for producing H_2, other thermochemical pathways are becoming more prevalent. Steam-reforming of biogas is also a beneficial procedure for producing eco-friendly hydrogen gas and minimizing the burden on fossil fuels. In this study, a simulation modelling of steam methane reforming (SMR) and steam biogas reforming (SBR) are presented. The model reveals the hydrogen production reaction mechanism and validates its performance through simulation analysis using COMSOL Multiphysics 5.6 software (finite element analysis). The developed model has been validated by available previous experiments and simulation work for biogas reforming with various compositions as well as the methane reforming process. The core aim of this study is to estimate the yield of H_2 for SMR, and H_2 and CO for SBR at steam carbon ratio (S/C) from 1 to 3 with various temperatures, and find the optimum temperature for the reforming process. The yields of hydrogen (mol/mol-CH_4) are achieved higher from SMR as 12% and 22 % for comparison with the experiment and previous simulation study at $S/C = 2$, at a temperature of 700 °C. The H_2 yields (mol/mol-CH_4) are achieved higher as 30% at 800 °C, 21% at 1000 °C, and 20% at 1200 °C (average percentage of mol for steam carbon ratio from 1 to 3) and compared with previous simulation study at the same operating temperatures, stated by SBR. The findings indicate that the proposed work offers a viable method for utilizing distributed renewable methane resources to fuel cells and generate local electricity.

1. Introduction

Hydrogen is recognized as a highly auspicious energy carrier because its combustion does not generate greenhouse gases or pollutants [1]. However, the majority of hydrogen is currently produced from fossil fuels through the steam reforming of natural gas accounting for nearly half of its overall production [2,3]. As the demand for energy increases, while the fossil fuel reserves continue to diminish, the production of sustainable hydrogen must rely on renewable sources. Biogas is commonly generated through biodegradable substrates made of organic material under anaerobic conditions which provides an attractive renewable alternative for replacing or supplementing fossil fuels in hydrogen production. The composition of biogas primarily depends on the specific substrate utilized in the biogas digester, which may include agro-industrial waste, animal farm manure, sewage sludge, municipal solid waste, energy crops, and other organic waste materials [4,5].

The two main constituents of biogas are CH_4 (40–80%) and CO_2 (20–60%), it also presents small amounts of H_2S, N_2, H_2O, O_2, and siloxanes [6–10]. It has been reported that the presence of H_2S and siloxanes can significantly decrease the catalyst (Ni-based) activity during the reforming of the biogas process. Therefore, it is necessary to eliminate these components before conducting the biogas reforming operation [8–10]. The process of steam reforming of biogas (SRB) incorporates the group of dual reforming reactions, namely the dry reforming of methane (DRM) and the steam reforming of methane (SRM), both of which exhibit significant endothermic characteristics. Table 1 presents a compilation of chemical reactions that typically take place during the steam reforming process of biogas or methane. The primary outcomes of significance in the reforming of biogas are hydrogen and syngas.

To achieve a significant conversion of methane, it is obligatory to operate the steam reformer at high temperatures between 973 and 1273 K. Considering the endothermic nature of the process, it is crucial to have an efficient heat source to provide the necessary energy to drive the reactions [16]. Due to the presence of CH_4 and CO_2 as the primary

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[*] Corresponding author at: Department of Mechanical Engineering, Delhi Technological University, Delhi 110042, India.
E-mail address: anilkumar76@dtu.ac.in (A. Kumar).

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Recent advances of biogas reforming for hydrogen production: Methods, purification, utility and techno-economics analysis

Ravindra Kumar[a], Anil Kumar[a,b,*]

[a] *Department of Mechanical Engineering, Delhi Technological University, Delhi, 110042, India*
[b] *Centre for Energy and Environment, Delhi Technological University, Delhi, 110042, India*

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ABSTRACT

In recent times, there has been an amplified interest in exploring fresh applications of biogas, attributed to the rising concerns surrounding climate change and an enhanced emphasis on the utilization of renewable energy sources. This manuscript undertakes a comprehensive assessment of recent advancements in the domains of dry, bi-, and tri-reforming. Notably, it emphasizes situations in which the CO_2 present in biogas assumes the role of an oxidant or partial oxidant. A comparative evaluation of various techniques and the exploration of recent catalysts employed in the reforming process and techno-economic biogas conversion applications are also deliberated in this analysis. Biogas conversion exhibits economic feasibility, typically with a payback period ranging from 4 to 8 years. Opting for a higher reaction temperature within the range of 830–900 °C is typically favored as it results in increased CH_4 and CO_2 conversions within the bi-reforming of the biogas process. Similarly, the temperature range is maintained between 750 and 850 °C and 850–1000 °C or above (depending on various factors) for dry reforming and tri reforming respectively. In general, biogas can undergo conversion processes to produce hydrogen, methanol, compressed natural gas, liquid fuel, wax, and form of heat. The inclusive conversion of biogas efficiency ranges from around 35%–80%, depending on the specific type of product being generated.

1. Introduction

The never-ending rise in worldwide energy demand can be attributed to the fact that human activities are driven by energy-intensive appliances. Consequently, the per capita energy consumption of a country is widely recognized as a significant indicator of its economic enlargement [1]. In the present era, energy is not solely perceived as a mere factor of production; it is also widely recognized as a strategic resource that serves as a fundamental commodity influencing international relations and exerting a major effect on the global economy and political dynamics [2]. The patterns of global energy and electricity demand are present in conjunction with the corresponding worldwide CO_2 emissions [3,4] as shown in Fig. 1.

The worldwide consumption of fossil fuels experienced a notable increase during the 19th century due to the rapid processes of urbanization and industrialization [5]. It is noteworthy to highlight that conventional-based fossil fuels have established themselves as the dominant source of energy, accounting for 81% of global power generation. Specifically, natural gas, coal, and oil contribute 21.6%, 28.1%, and 31.7% respectively [6]. However, the steep increase in fossil fuel prices poses an additional economic burden on countries that rely on oil imports [7]. Due to the surge in fuel prices, the transportation costs of essential goods escalate, resulting in increased inflation rates on a global scale. This has sparked critical debates regarding the management of conventional fuel scarcity. Conversely, in the present context, environmental degradation has emerged as one of the most pressing global challenges for the scientific community operating in affected areas [8]. There is no doubt that modern advanced technology has unequivocally demonstrated its ability to introduce numerous efficient and innovative approaches to address this issue [9]. In conclusion, a substantial number of researchers argue that fostering greater attention to unconventional fuels can serve as a viable resolution to this concern [10]. Therefore, research initiatives have been concentrated on identifying suitable and economically efficient energy resources for the production of renewable fuels in both gaseous and liquid forms [11,12].

The motivation behind examining renewable energies stems from concerns regarding the exhaustion of petroleum-derived resources and global warming. The adoption of sustainable energy options within energy markets is driven by their mitigating environmental pollution, potential for viable energy development, and improving domestic

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[*] Corresponding author. Department of Mechanical Engineering, Delhi Technological University, Delhi, 110042, India.
E-mail address: anilkumar76@dtu.ac.in (A. Kumar).

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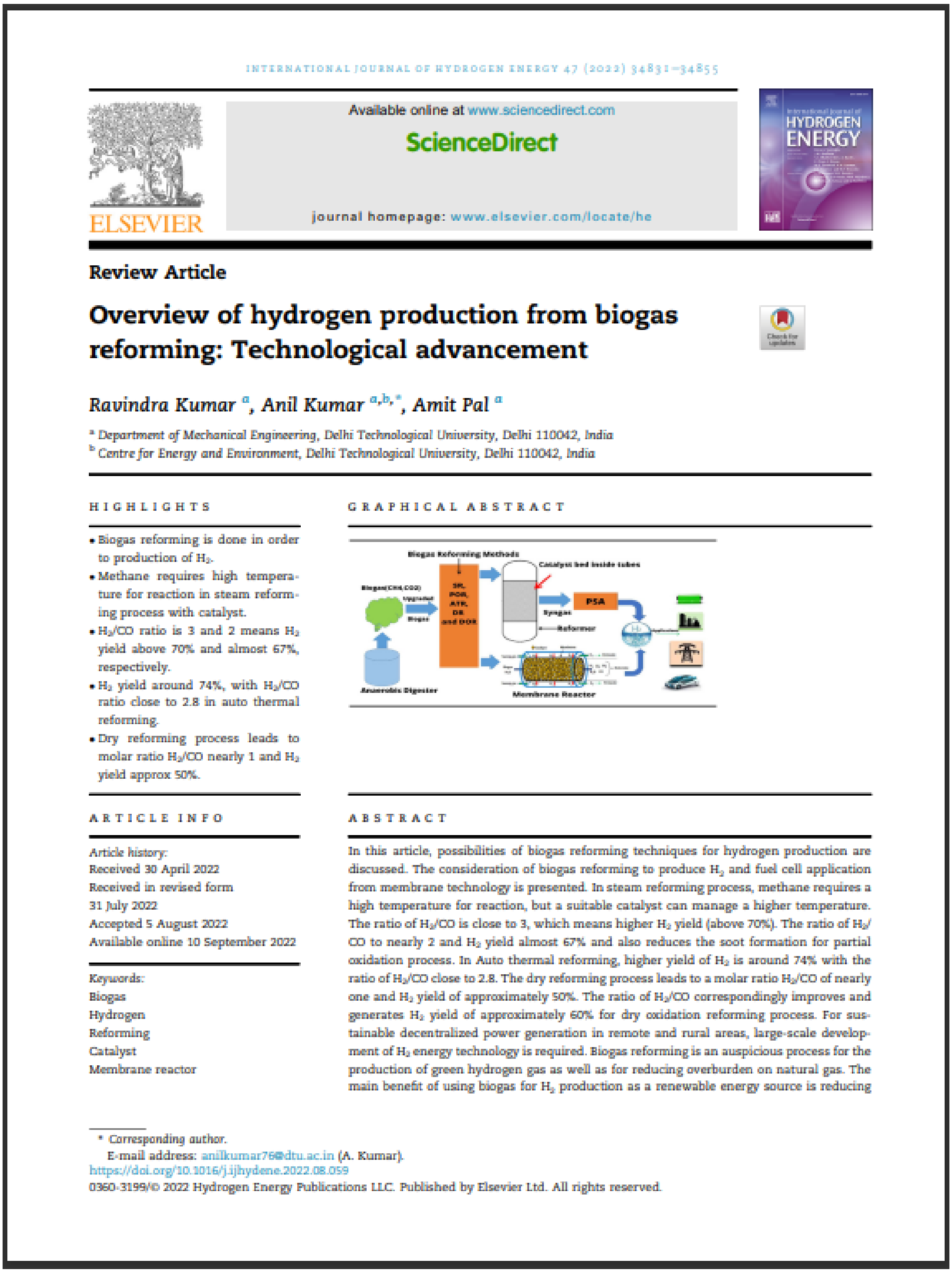

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Review Article

Overview of hydrogen production from biogas reforming: Technological advancement

Ravindra Kumar [a], *Anil Kumar* [a,b,*], *Amit Pal* [a]

[a] *Department of Mechanical Engineering, Delhi Technological University, Delhi 110042, India*
[b] *Centre for Energy and Environment, Delhi Technological University, Delhi 110042, India*

HIGHLIGHTS

- Biogas reforming is done in order to production of H_2.
- Methane requires high temperature for reaction in steam reforming process with catalyst.
- H_2/CO ratio is 3 and 2 means H_2 yield above 70% and almost 67%, respectively.
- H_2 yield around 74%, with H_2/CO ratio close to 2.8 in auto thermal reforming.
- Dry reforming process leads to molar ratio H_2/CO nearly 1 and H_2 yield approx 50%.

GRAPHICAL ABSTRACT

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ABSTRACT

In this article, possibilities of biogas reforming techniques for hydrogen production are discussed. The consideration of biogas reforming to produce H_2 and fuel cell application from membrane technology is presented. In steam reforming process, methane requires a high temperature for reaction, but a suitable catalyst can manage a higher temperature. The ratio of H_2/CO is close to 3, which means higher H_2 yield (above 70%). The ratio of H_2/CO to nearly 2 and H_2 yield almost 67% and also reduces the soot formation for partial oxidation process. In Auto thermal reforming, higher yield of H_2 is around 74% with the ratio of H_2/CO close to 2.8. The dry reforming process leads to a molar ratio H_2/CO of nearly one and H_2 yield of approximately 50%. The ratio of H_2/CO correspondingly improves and generates H_2 yield of approximately 60% for dry oxidation reforming process. For sustainable decentralized power generation in remote and rural areas, large-scale development of H_2 energy technology is required. Biogas reforming is an auspicious process for the production of green hydrogen gas as well as for reducing overburden on natural gas. The main benefit of using biogas for H_2 production as a renewable energy source is reducing

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* *Corresponding author.*
E-mail address: anilkumar76@dtu.ac.in (A. Kumar).

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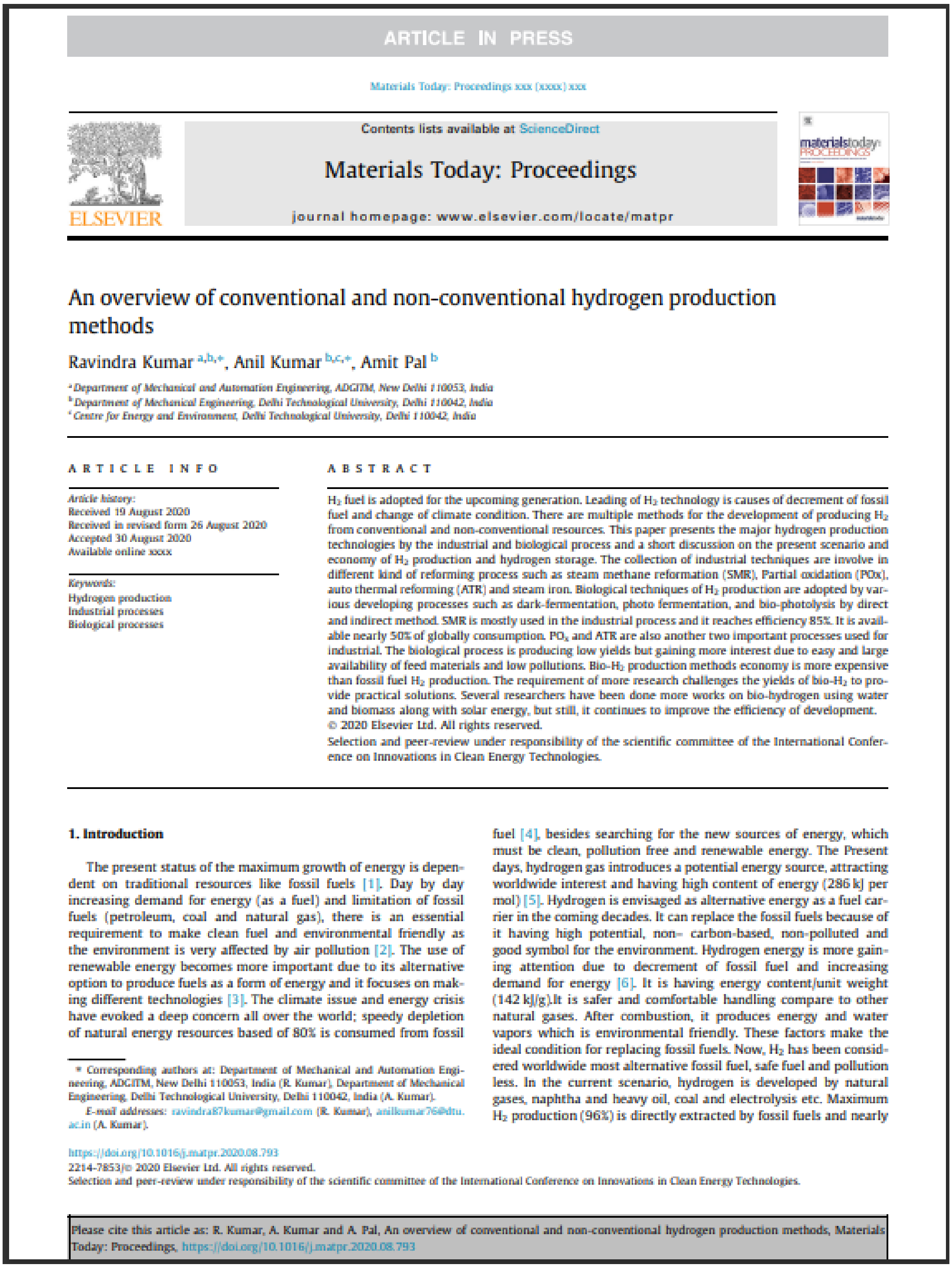

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An overview of conventional and non-conventional hydrogen production methods

Ravindra Kumar [a,b,*], Anil Kumar [b,c,*], Amit Pal [b]

[a] *Department of Mechanical and Automation Engineering, ADGITM, New Delhi 110053, India*
[b] *Department of Mechanical Engineering, Delhi Technological University, Delhi 110042, India*
[c] *Centre for Energy and Environment, Delhi Technological University, Delhi 110042, India*

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ABSTRACT

H_2 fuel is adopted for the upcoming generation. Leading of H_2 technology is causes of decrement of fossil fuel and change of climate condition. There are multiple methods for the development of producing H_2 from conventional and non-conventional resources. This paper presents the major hydrogen production technologies by the industrial and biological process and a short discussion on the present scenario and economy of H_2 production and hydrogen storage. The collection of industrial techniques are involve in different kind of reforming process such as steam methane reformation (SMR), Partial oxidation (POx), auto thermal reforming (ATR) and steam iron. Biological techniques of H_2 production are adopted by various developing processes such as dark-fermentation, photo fermentation, and bio-photolysis by direct and indirect method. SMR is mostly used in the industrial process and it reaches efficiency 85%. It is available nearly 50% of globally consumption. PO_x and ATR are also another two important processes used for industrial. The biological process is producing low yields but gaining more interest due to easy and large availability of feed materials and low pollutions. Bio-H_2 production methods economy is more expensive than fossil fuel H_2 production. The requirement of more research challenges the yields of bio-H_2 to provide practical solutions. Several researchers have been done more works on bio-hydrogen using water and biomass along with solar energy, but still, it continues to improve the efficiency of development.

Selection and peer-review under responsibility of the scientific committee of the International Conference on Innovations in Clean Energy Technologies.

1. Introduction

The present status of the maximum growth of energy is dependent on traditional resources like fossil fuels [1]. Day by day increasing demand for energy (as a fuel) and limitation of fossil fuels (petroleum, coal and natural gas), there is an essential requirement to make clean fuel and environmental friendly as the environment is very affected by air pollution [2]. The use of renewable energy becomes more important due to its alternative option to produce fuels as a form of energy and it focuses on making different technologies [3]. The climate issue and energy crisis have evoked a deep concern all over the world; speedy depletion of natural energy resources based of 80% is consumed from fossil fuel [4], besides searching for the new sources of energy, which must be clean, pollution free and renewable energy. The Present days, hydrogen gas introduces a potential energy source, attracting worldwide interest and having high content of energy (286 kJ per mol) [5]. Hydrogen is envisaged as alternative energy as a fuel carrier in the coming decades. It can replace the fossil fuels because of it having high potential, non- carbon-based, non-polluted and good symbol for the environment. Hydrogen energy is more gaining attention due to decrement of fossil fuel and increasing demand for energy [6]. It is having energy content/unit weight (142 kJ/g).It is safer and comfortable handling compare to other natural gases. After combustion, it produces energy and water vapors which is environmental friendly. These factors make the ideal condition for replacing fossil fuels. Now, H_2 has been considered worldwide most alternative fossil fuel, safe fuel and pollution less. In the current scenario, hydrogen is developed by natural gases, naphtha and heavy oil, coal and electrolysis etc. Maximum H_2 production (96%) is directly extracted by fossil fuels and nearly

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[*] Corresponding authors at: Department of Mechanical and Automation Engineering, ADGITM, New Delhi 110053, India (R. Kumar), Department of Mechanical Engineering, Delhi Technological University, Delhi 110042, India (A. Kumar).

E-mail addresses: ravindra87kumar@gmail.com (R. Kumar), anilkumar76@dtu.ac.in (A. Kumar).

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REVIEW ARTICLE

Advancement in steam reforming of methanol to produce hydrogen: A review

Ravindra Kumar[1], **Anil Kumar**[1,2,*]

[1] *Department of Mechanical Engineering, Delhi Technological University, Delhi 110042, India*
[2] *Centre for Energy and Environment, Delhi Technological University, Delhi 110042, India*
*** Corresponding author:** Anil Kumar, anilkumar76@dtu.ac.in

ABSTRACT

The main deliberation of this review paper is on metallic catalysts, including Cu-based catalysts, with distinct formulations and compositions, utilized for steam reforming of methanol (SRM). The review critically examines the performance of these catalysts, considering the active components, supports, promoters, and their interactions. Additionally, the review identifies and elucidates the various kinds of reaction mechanisms and routes involved in SRM. This comprehensive analysis provides valuable insights into the progress of well-organized and effective catalysts for SRM. To achieve high yields of H_2, it is crucial to conduct a fundamental study of the role of copper as a component in both mono and multimetallic systems, as well as the nature of support. These factors are essential to understand the catalytic mechanisms involved in the steam reforming of methanol and to develop effective strategies for optimizing hydrogen production. Therefore, a thorough investigation of copper-based catalysts and their interaction with the support material is essential for the development of highly efficient steam reforming processes.

Keywords: methanol reforming; hydrogen production; catalyst reaction scheme

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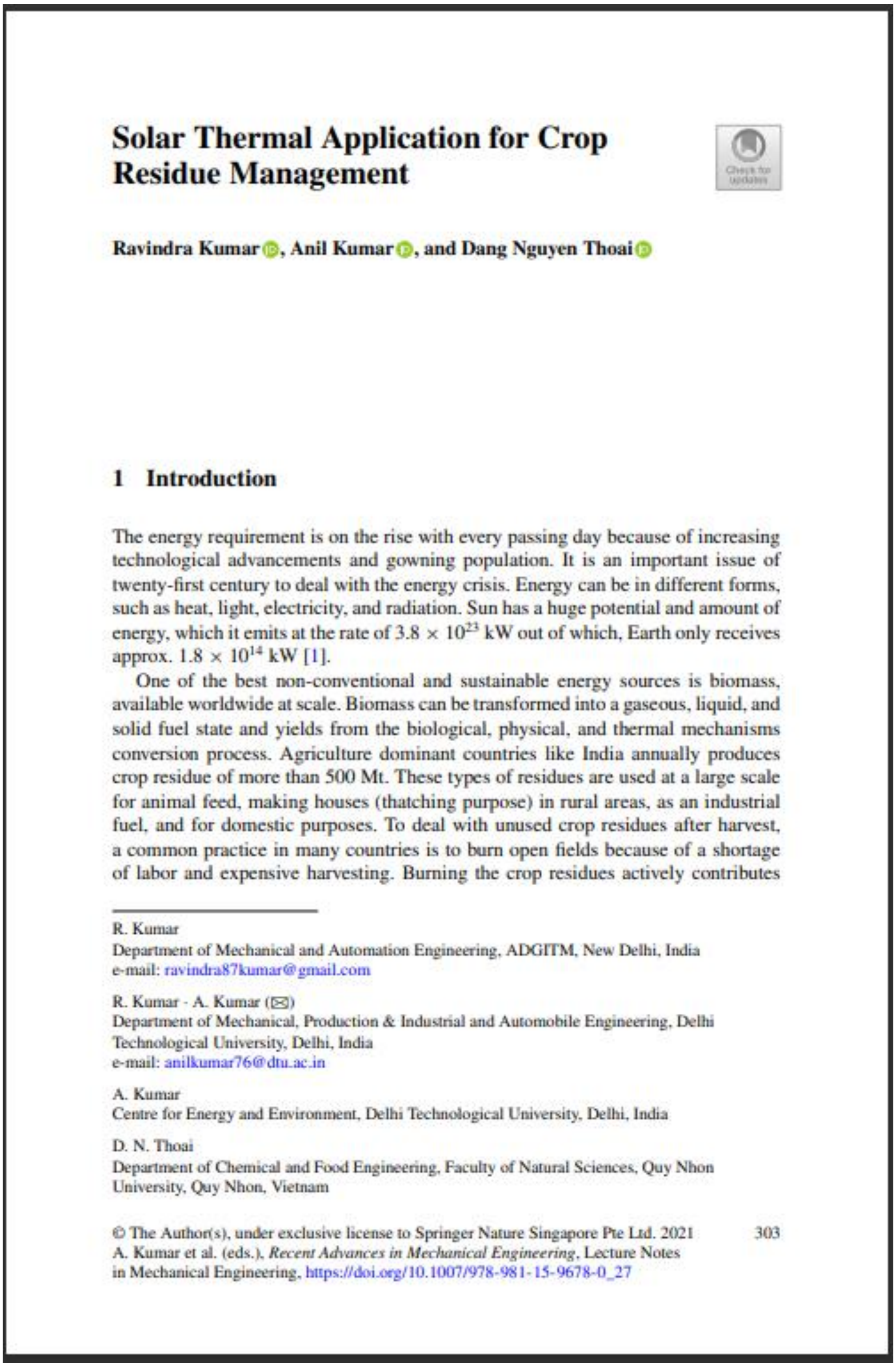
1. Introduction

In the present day, achieving stability between economic evolution, growth, and sustainability while safeguarding the environment poses a monumental challenge to the world. Energy and the environment are intricately linked, and the path toward achieving this balance grows more complex each day. According to a report in 2019 by the International Energy Agency (IEA), a 1% increase in global economic output results in a 0.5% rise in CO_2 emissions annually[1]. In recent decades, there has been a significant focus on using non-carbon renewable sources, such as solar, wind, hydrothermal, and tidal energy, as well as hydrogen energy. However, all of these sources, except hydrogen, experience availability issues throughout the year[2]. Hydrogen is becoming an increasingly popular alternative to traditional energy sources in fuel cells, thanks to its higher energy density and lack of greenhouse gas emissions[3]. Specifically, when it comes to energy sources for transportation, polymer electrolyte membrane fuel cells (PEMFC) are extensively utilized[4]. However, unlike fossil fuels that can be directly extracted from the environment, hydrogen needs to be obtained through different reforming reactions, including steam reforming, auto-thermal reforming, and partial oxidation[5]. Methane is often used as a feedstock for hydrogen generation, but this process has significant



Solar Thermal Application for Crop Residue Management

Ravindra Kumar, Anil Kumar, and Dang Nguyen Thoai

1 Introduction

The energy requirement is on the rise with every passing day because of increasing technological advancements and gowning population. It is an important issue of twenty-first century to deal with the energy crisis. Energy can be in different forms, such as heat, light, electricity, and radiation. Sun has a huge potential and amount of energy, which it emits at the rate of 3.8×10^{23} kW out of which, Earth only receives approx. 1.8×10^{14} kW [1].

One of the best non-conventional and sustainable energy sources is biomass, available worldwide at scale. Biomass can be transformed into a gaseous, liquid, and solid fuel state and yields from the biological, physical, and thermal mechanisms conversion process. Agriculture dominant countries like India annually produces crop residue of more than 500 Mt. These types of residues are used at a large scale for animal feed, making houses (thatching purpose) in rural areas, as an industrial fuel, and for domestic purposes. To deal with unused crop residues after harvest, a common practice in many countries is to burn open fields because of a shortage of labor and expensive harvesting. Burning the crop residues actively contributes

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R. Kumar
Department of Mechanical and Automation Engineering, ADGITM, New Delhi, India
e-mail: ravindra87kumar@gmail.com

R. Kumar · A. Kumar (✉)
Department of Mechanical, Production & Industrial and Automobile Engineering, Delhi Technological University, Delhi, India
e-mail: anilkumar76@dtu.ac.in

A. Kumar
Centre for Energy and Environment, Delhi Technological University, Delhi, India

D. N. Thoai
Department of Chemical and Food Engineering, Faculty of Natural Sciences, Quy Nhon University, Quy Nhon, Vietnam

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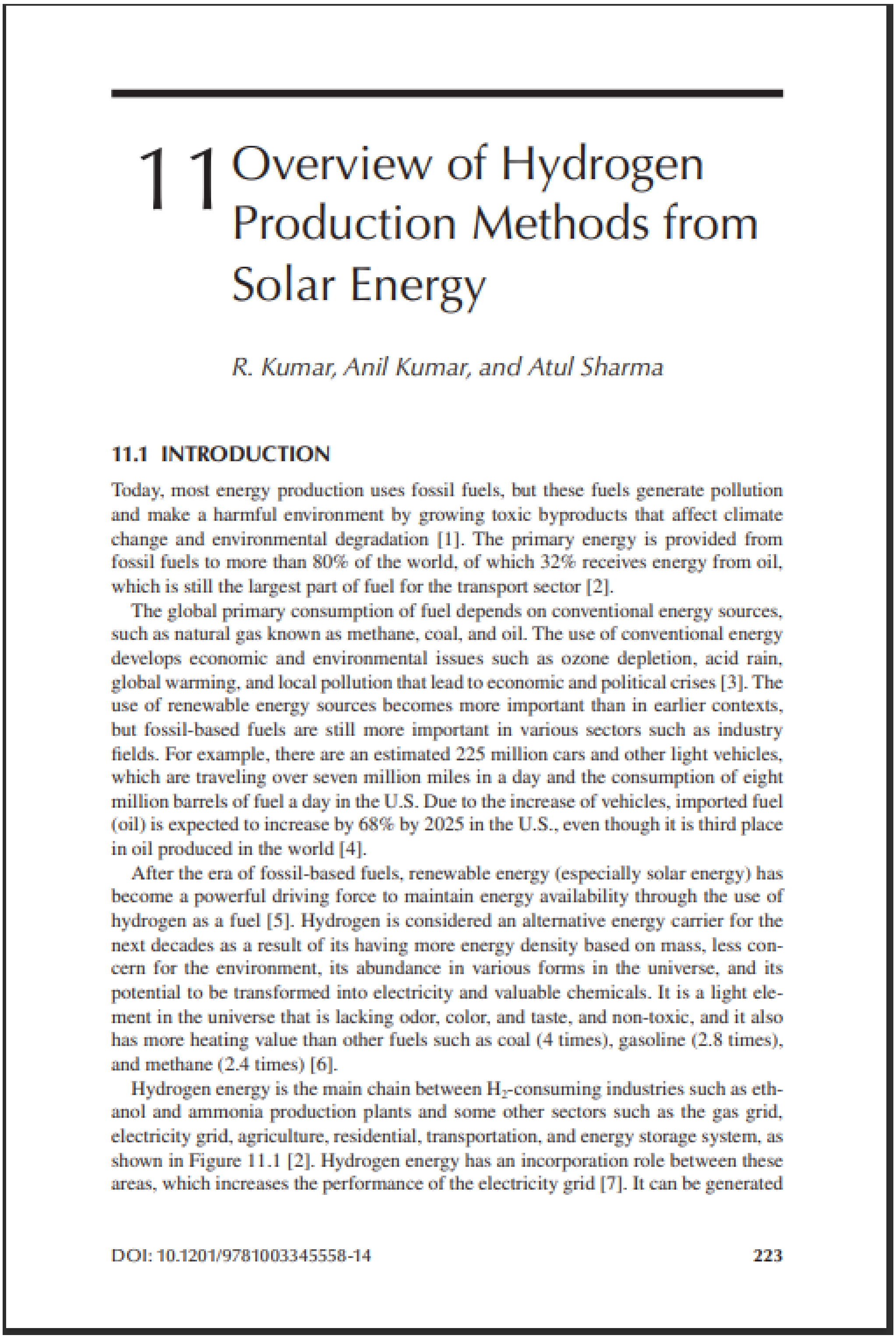

11 Overview of Hydrogen Production Methods from Solar Energy

R. Kumar, Anil Kumar, and Atul Sharma

11.1 INTRODUCTION

Today, most energy production uses fossil fuels, but these fuels generate pollution and make a harmful environment by growing toxic byproducts that affect climate change and environmental degradation [1]. The primary energy is provided from fossil fuels to more than 80% of the world, of which 32% receives energy from oil, which is still the largest part of fuel for the transport sector [2].

The global primary consumption of fuel depends on conventional energy sources, such as natural gas known as methane, coal, and oil. The use of conventional energy develops economic and environmental issues such as ozone depletion, acid rain, global warming, and local pollution that lead to economic and political crises [3]. The use of renewable energy sources becomes more important than in earlier contexts, but fossil-based fuels are still more important in various sectors such as industry fields. For example, there are an estimated 225 million cars and other light vehicles, which are traveling over seven million miles in a day and the consumption of eight million barrels of fuel a day in the U.S. Due to the increase of vehicles, imported fuel (oil) is expected to increase by 68% by 2025 in the U.S., even though it is third place in oil produced in the world [4].

After the era of fossil-based fuels, renewable energy (especially solar energy) has become a powerful driving force to maintain energy availability through the use of hydrogen as a fuel [5]. Hydrogen is considered an alternative energy carrier for the next decades as a result of its having more energy density based on mass, less concern for the environment, its abundance in various forms in the universe, and its potential to be transformed into electricity and valuable chemicals. It is a light element in the universe that is lacking odor, color, and taste, and non-toxic, and it also has more heating value than other fuels such as coal (4 times), gasoline (2.8 times), and methane (2.4 times) [6].

Hydrogen energy is the main chain between H_2-consuming industries such as ethanol and ammonia production plants and some other sectors such as the gas grid, electricity grid, agriculture, residential, transportation, and energy storage system, as shown in Figure 11.1 [2]. Hydrogen energy has an incorporation role between these areas, which increases the performance of the electricity grid [7]. It can be generated

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27th-28th August, 2020

Organized by

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Author(s) : R. Kumar, Anil Kumar, Amit Pal

Presented by : R. Kumar

Rev. Fr. Roy Vadakkan
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Dr. Sunny Joseph Kalayathankal
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Dr. Deepanraj B.
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DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering), Delhi-110042 (India)
Department of Mechanical & Production Engineering,
Centre for Energy and Environment

Certificate of Presentation

Prof./Dr./Mr./Ms. Ravindra Kumar

has participated in the 2nd International Conference on

"RECENT ADVANCES IN MECHANICAL ENGINEERING", (RAME-2020)

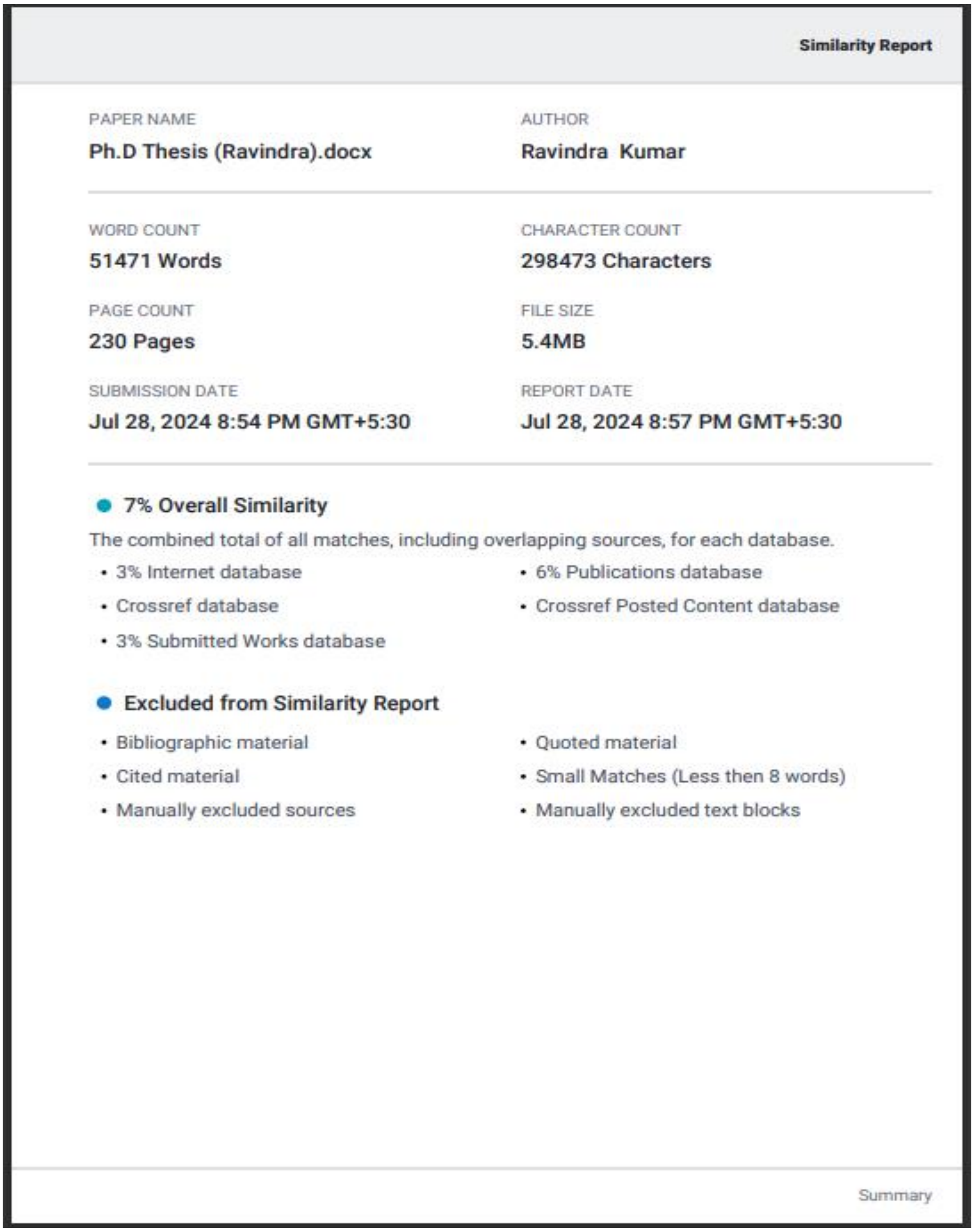
held on **September 18-19, 2020** and also presented the paper titled,

"**Solar Thermal Application For Crop Residue Management**".

We wish him/her a bright success in all his future endeavors.

Dr. Anil Kumar
Organizing Secretary

Prof. Amit Pal
Convener



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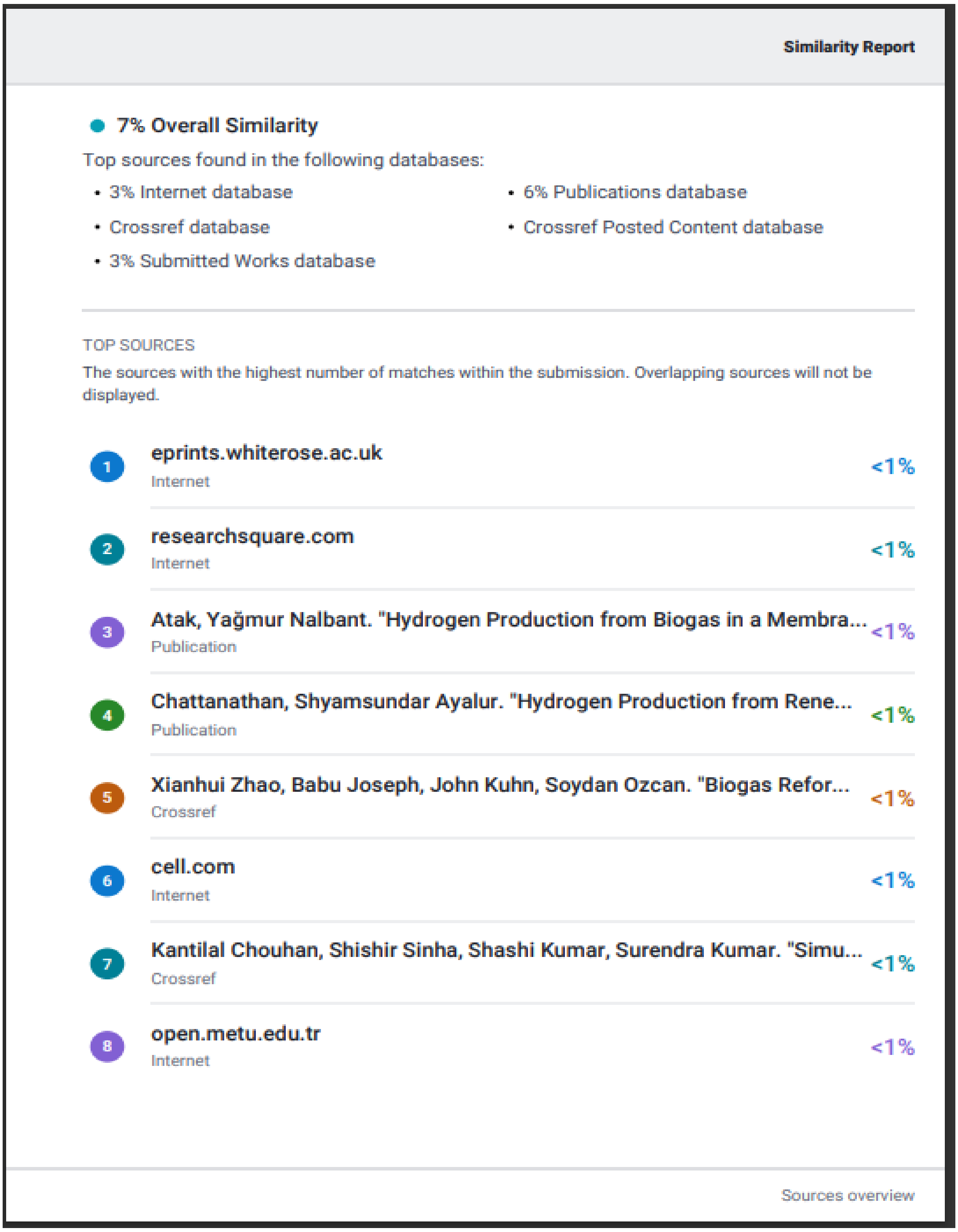

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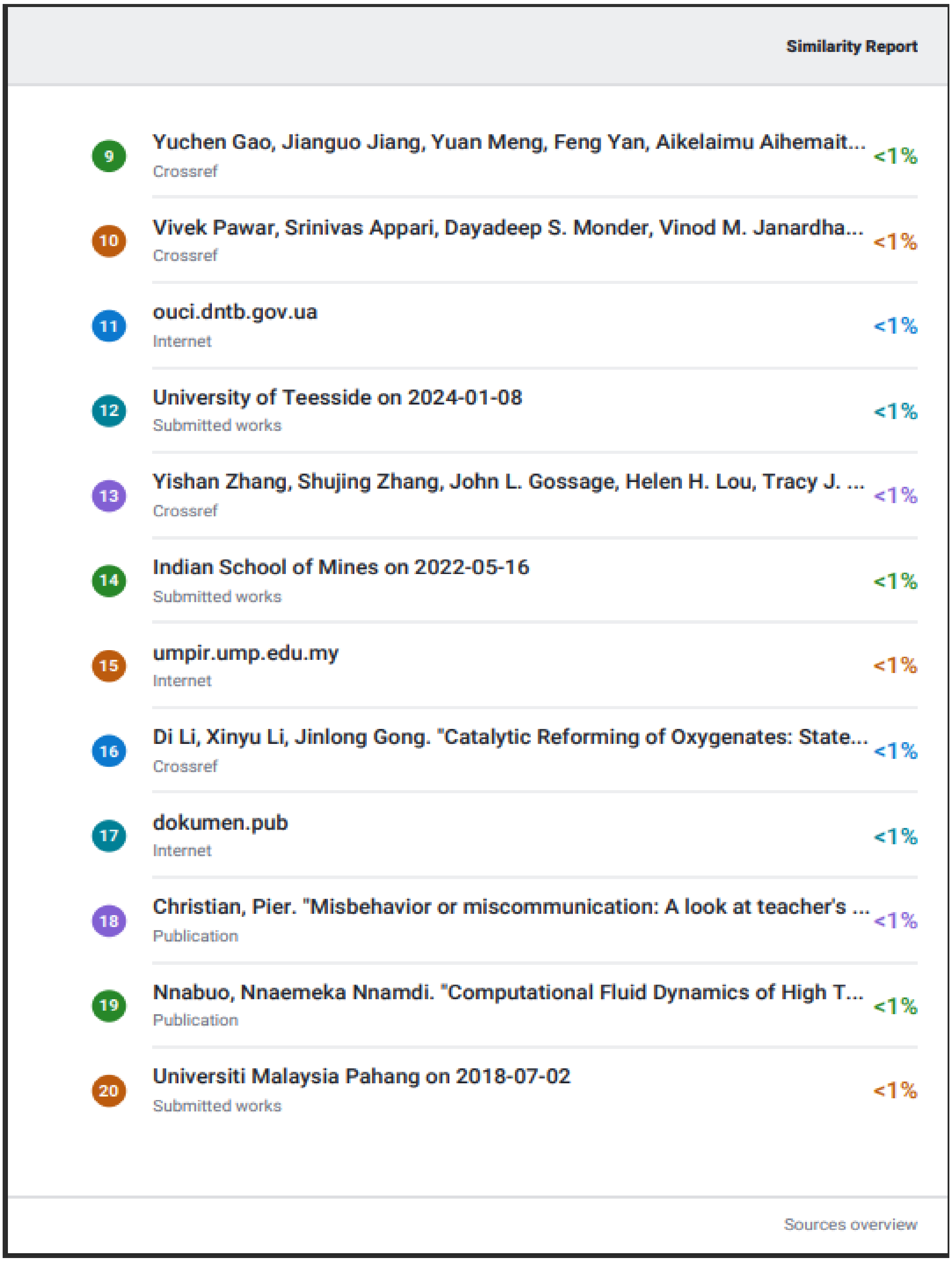

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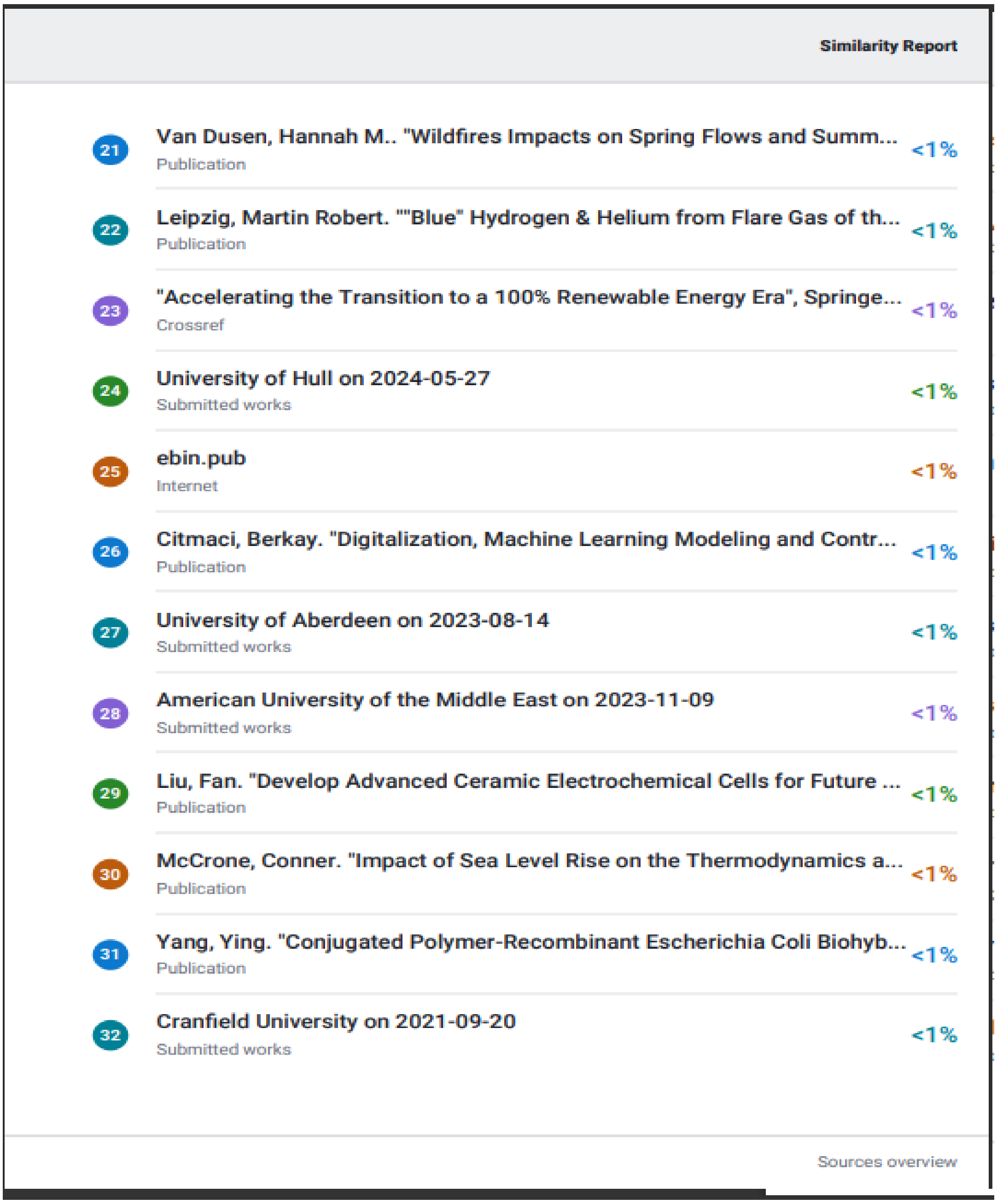

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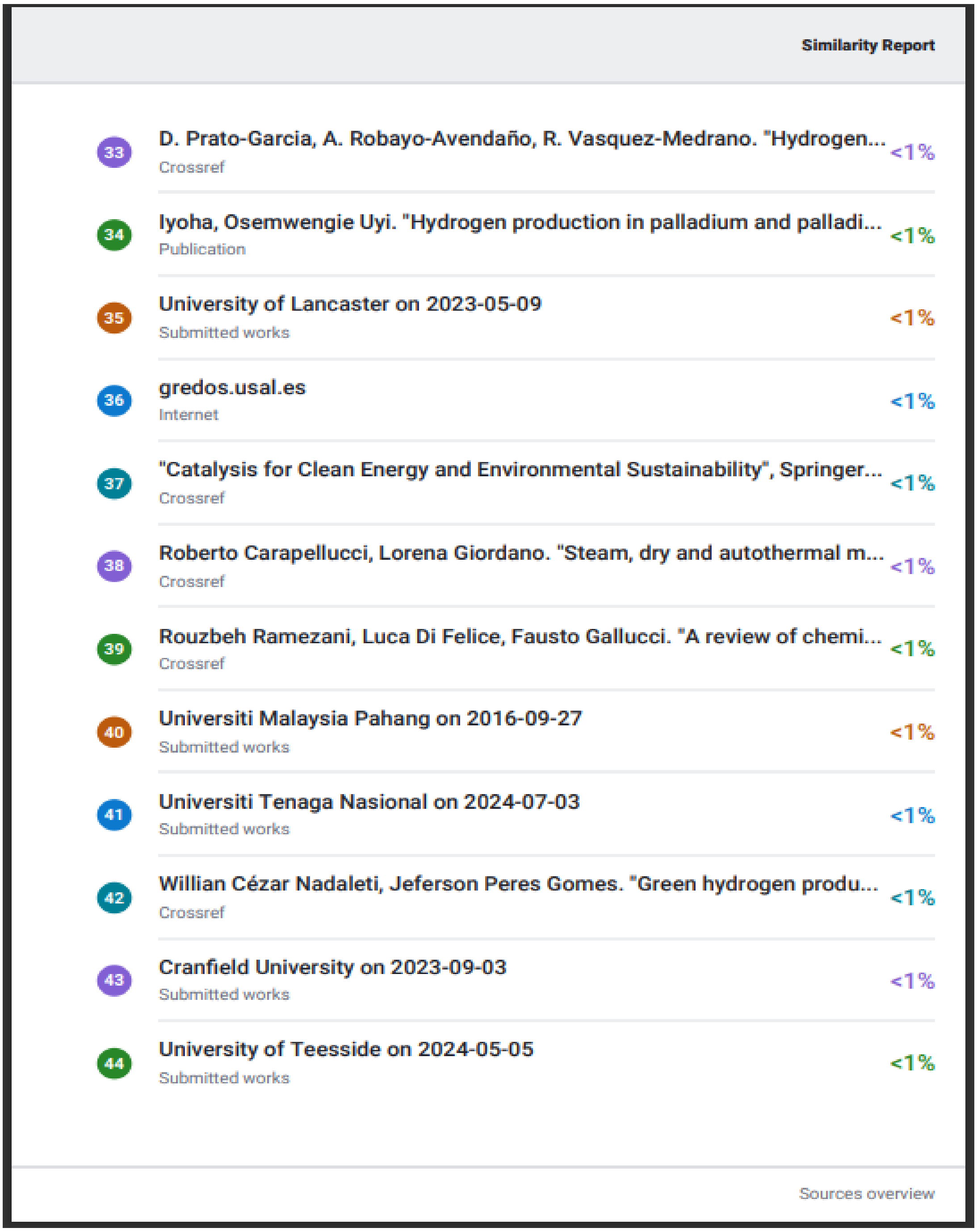

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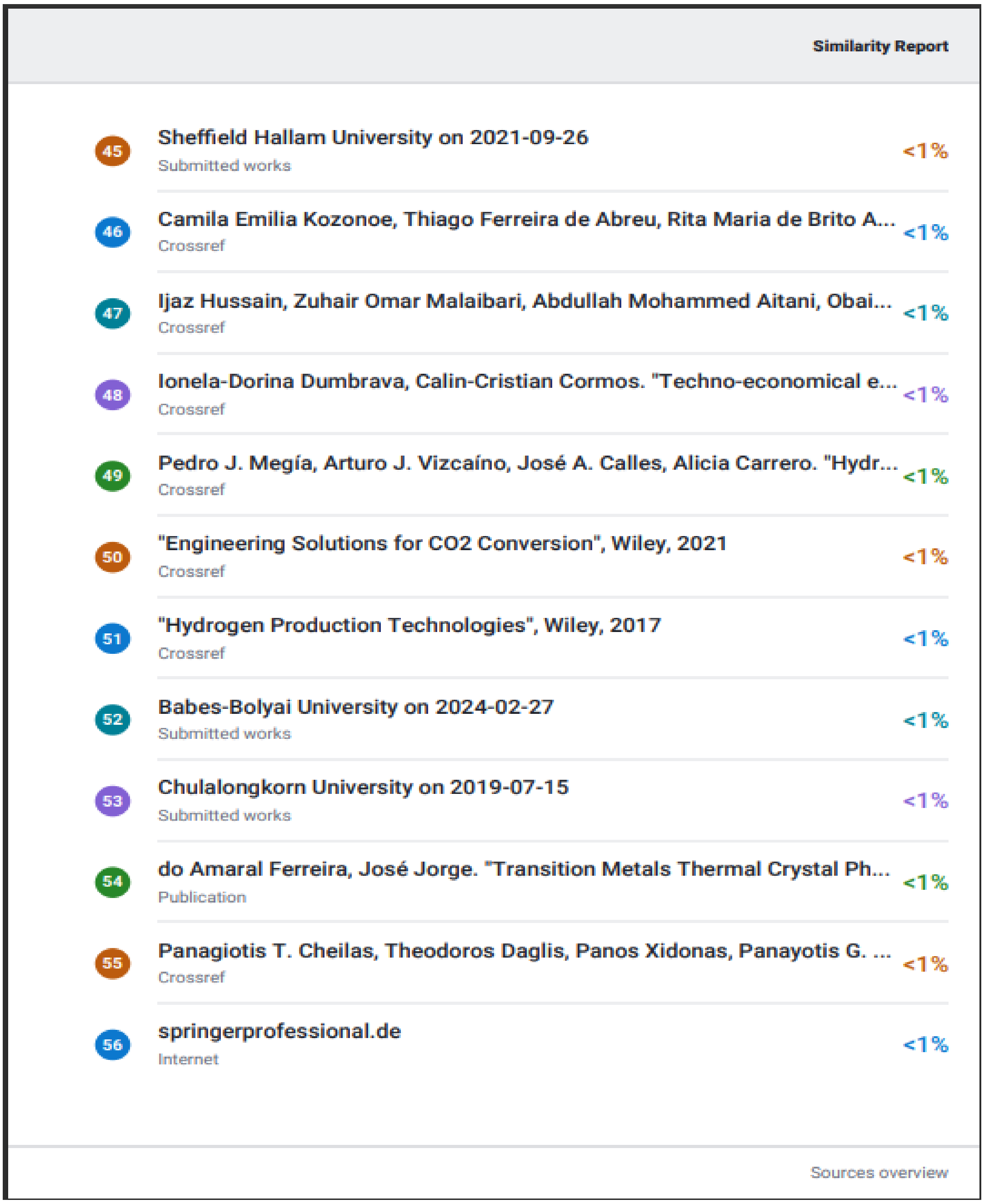

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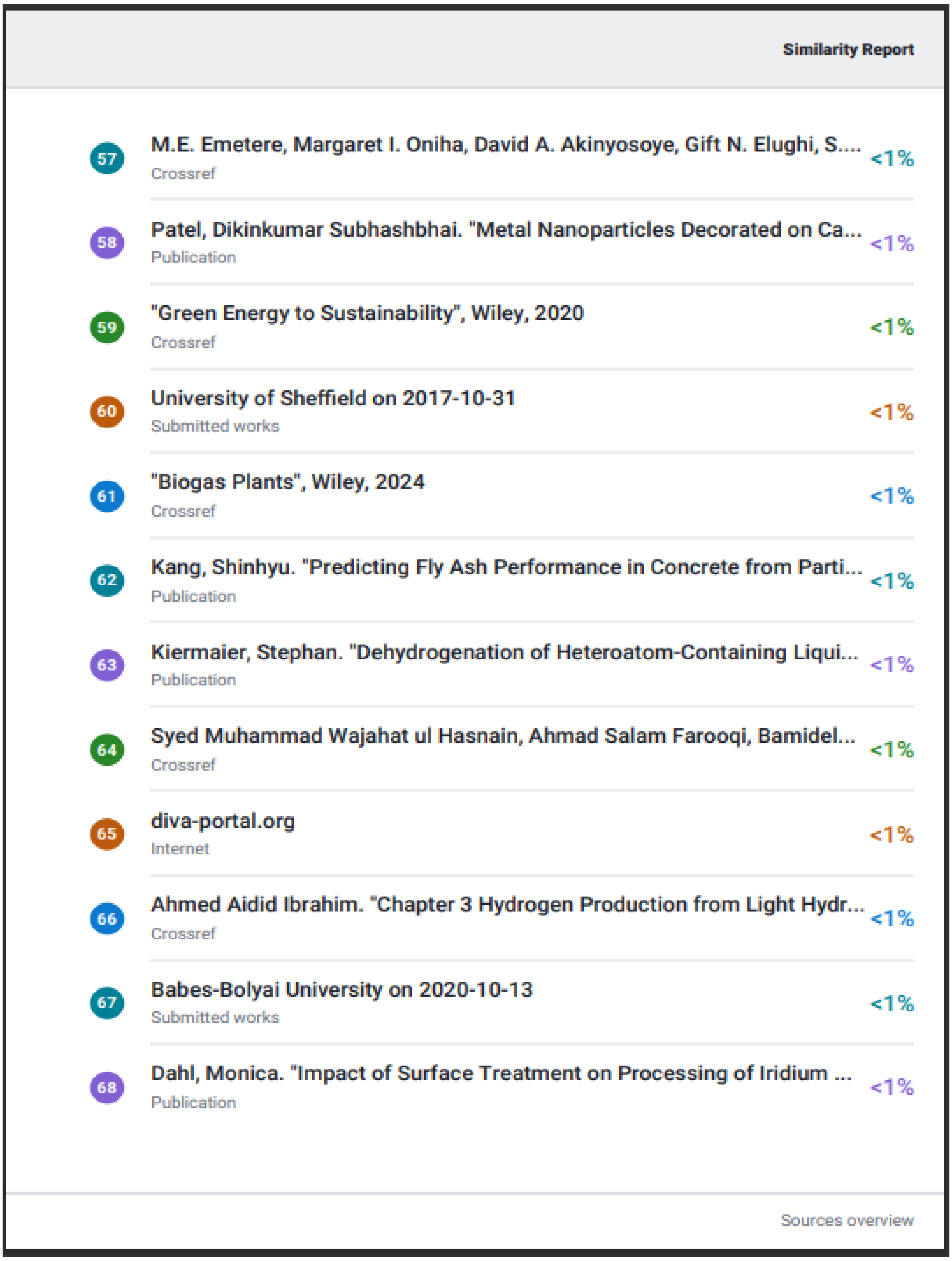

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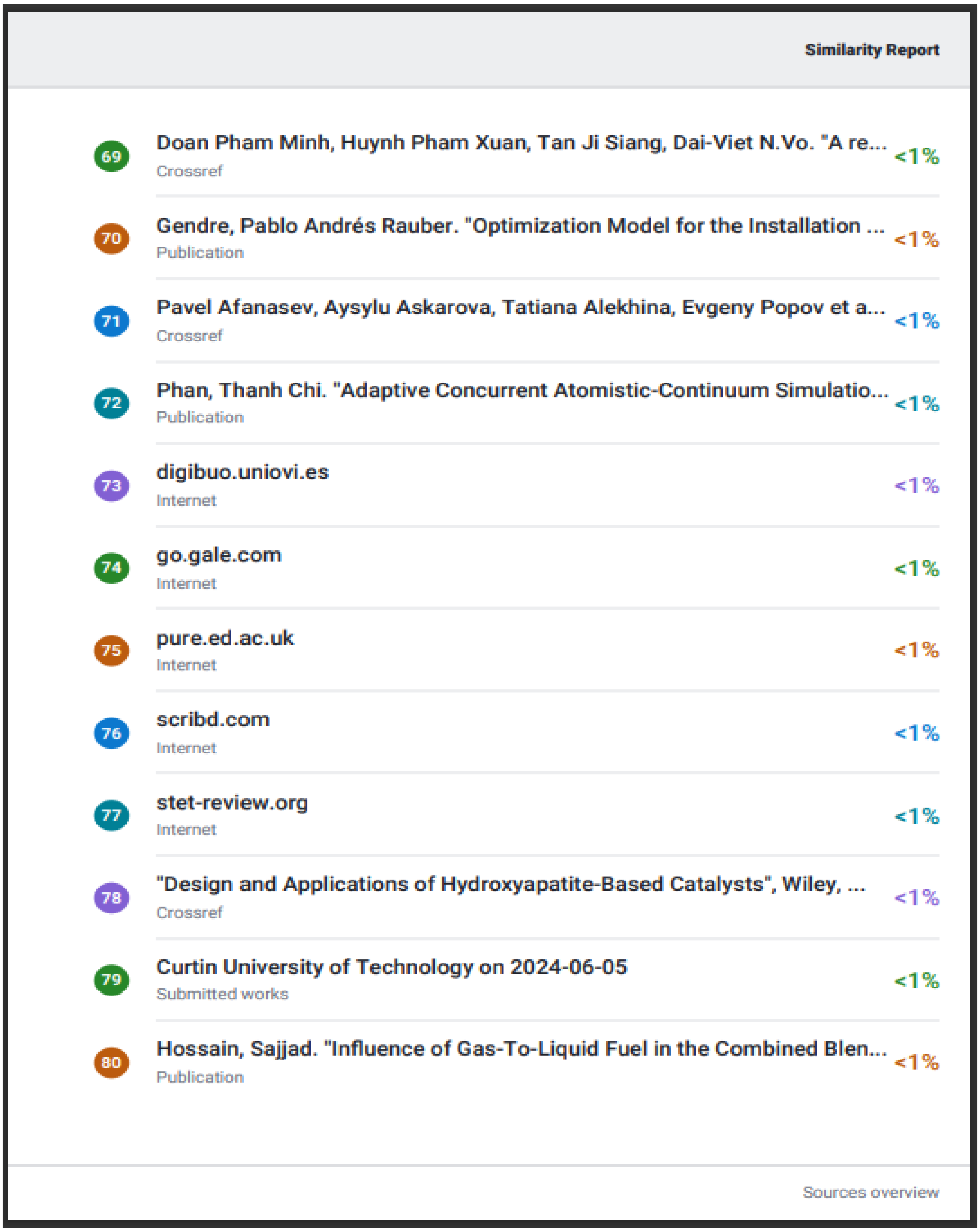

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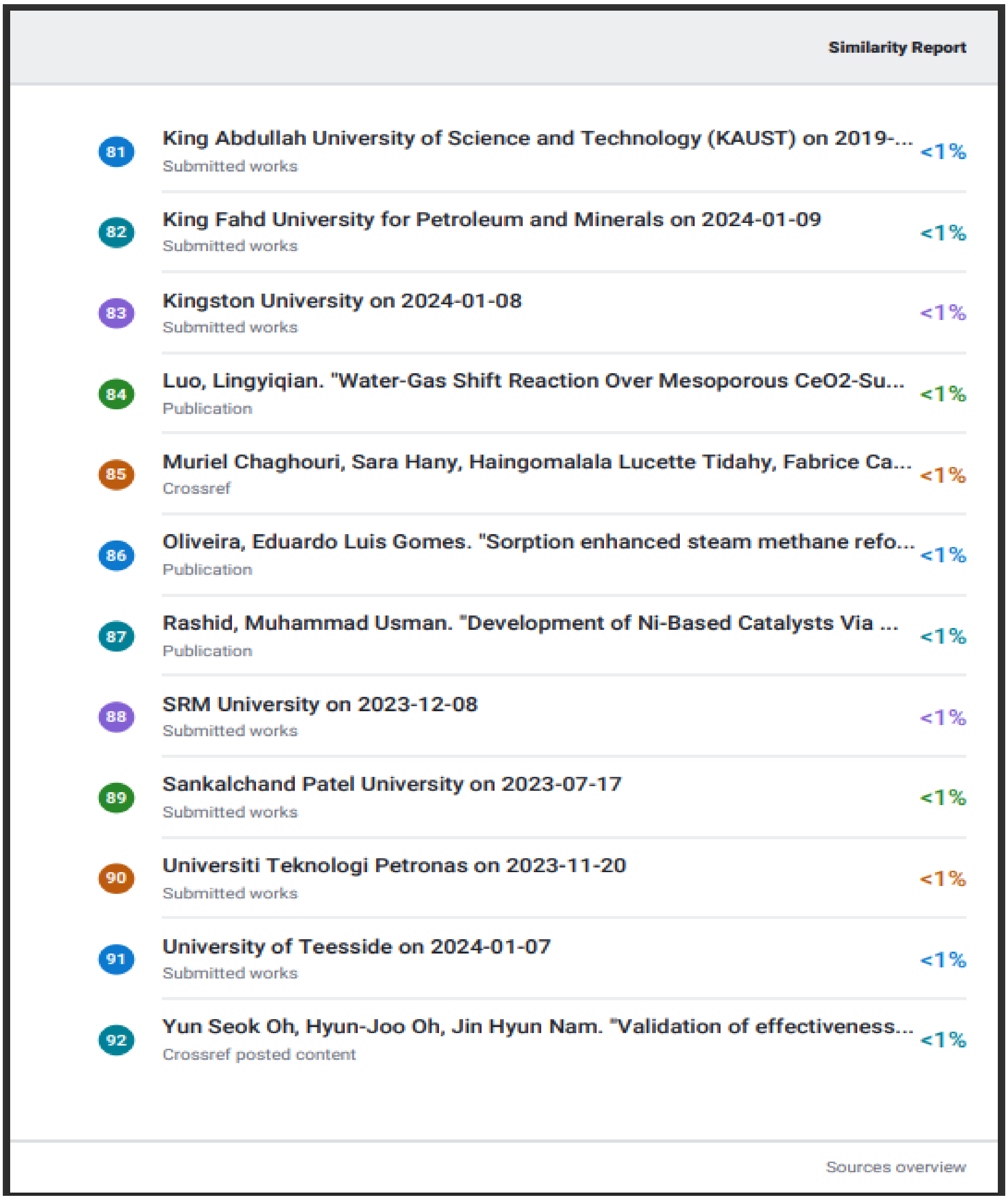

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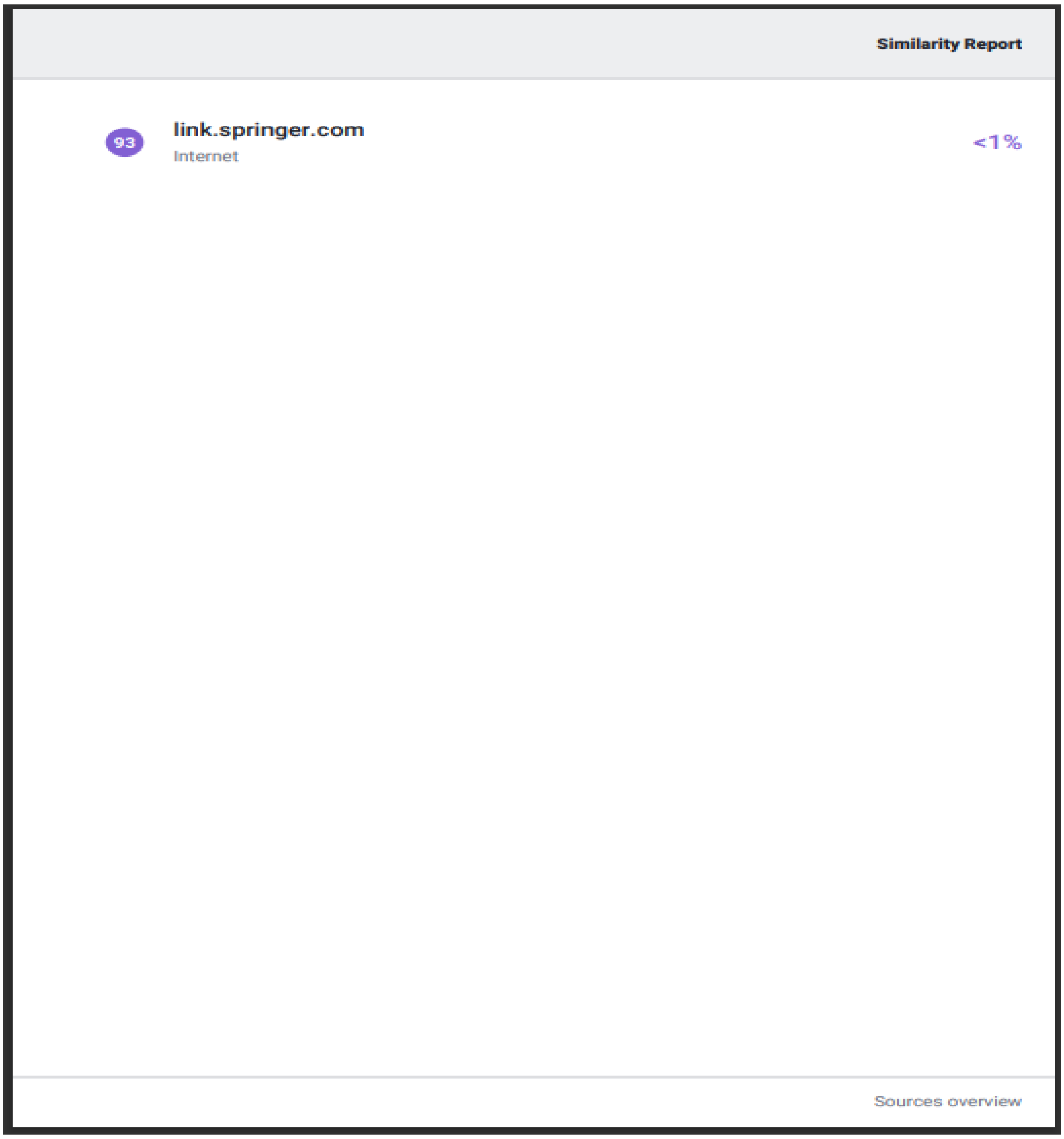

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CONTACT INFORMATION

Ravindra Kumar

E-mail ID: ravindra87kumar@gmail.com,

ravindra.kumar@adgitmdelhi.ac.in

Google scholar link : https://scholar.google.com/citations?user=Mr_xY2MAAAAJ&hl=en

ORCID :https://orcid.org/0000-0003-2681-0418

Career objective

Seeking a challenging career where the acquired skills can be exemplified to the best of my abilities. To associate with an organization where there is ample scope for personal development, with an environment that encourages learning and gives exposure to new ideas in the field of design and development.

Brief Introduction

I would like to introduce myself as **Ravindra Kumar** a research scholar and pursuing his Ph.D. in Mechanical Engineering Department with specialization in Thermal Engineering from Delhi Technological University, Delhi. Delighted to have authored numerous research articles published in **high-impact SCI** Journals, my noteworthy contributions include **three** significant publications as the First Author. Over the past two years, I have published three SCI-indexed journals and scopus index journal moreover one paper is currently under review in **International journal of hydrogen energy**. My dedication to research was recognized with the **Commendable Research Excellence Award** at **Delhi Technological University** in April 2023.

My dedication and hard work are evident in my sincere approach to my responsibilities. I have made significant contributions to the department through my exemplary teaching, research endeavors, and diligent fulfillment of various departmental duties (**including NBA, NAAC accreditation work**).

ACADEMIC QUALIFICATION

QUALIFICATION	UNIVERSITY	PASSING YEAR	Marks (%)
B.Tech. (Mechanical Engg.)	UPTU (Lucknow)	2003-07	68.32%
M.Tech (Thermal Engineering)	NIT Silchar (Assam)	2008-10	8.91 CPI
Ph.D. (Thermal Engineering)	DTU (Delhi)	Pursuing from Aug.2019	73% (Course work)

PROJECT

- "PERFORMANCE OF S.I. ENGINE USING GASOLINE-METHANOL BLENDS" in B. Tech".
- "STUDIES ON COAL COMBUSTION IN CIRCULATING FLUIDIZED BED USING CFD ANALYSIS" using Fluent Software in M.Tech.
- "HYDROGEN PRODUCTION FROM BIOGAS" in Ph.D. (Pursuing) work.

ACHIEVEMENT

- Received **Research Excellence Award 2022** on 6th April 2023 at Delhi Technological University (DTU).
- Organizing member of "Recent Advances In Mechanical Engineering", (RAME-2020) held on September 18-19, 2020. at DELHI TECHNOLOGICAL UNIVERSITY.
- **Reviewer** of 2nd international conference (Future learning aspects of Mechanical Engineering), Flame 2020.
- MHRD Scholarship during M.Tech.
- GATE Qualified in 2007
- Two years served as a teaching assistantship towards the conduct of the tutorial and practical classes of B.Tech students of Mechanical Engineering from July 2008 to May 2010 under the Department of Mechanical Engineering in NIT Silchar (Assam).

KEY SKILLS

Knowledge of **AUTOCAD, CATIA, COMSOL MULTIPHYSICS,** and **ANSYS FLUENT.**

RESEARCH AREAS

Renewable energy, Hydrogen energy, Reforming Processes, Heat Transfer, CFD, and IC Engines.

TEACHING EXPERIENCE

College/University Name	Designation	Duration	Mode of Teaching
ADGITM Delhi (Formerly NIEC)	Assistant Professor	14 Jan 2013 to date	Regular
Savera group of institutions, Gurgaon	Assistant Professor	8 August 2012 to 12th Jan 2013	Regular
GITM, Gurgaon	Lecturer	9 July 2010 to 6 August 2012	Regular
AFSET, Faridabad	Lecturer	30 June 2007 to10 July 2008	Regular

SUBJECT TAUGHT:

Manufacturing process, Heat transfer, Internal combustion engine, Hydraulic Machines, Engineering Mechanics, refrigeration & Air conditioning, Heat Transfer, Workshop Technology, Engineering graphics I & II and Power plant Engineering.

PAPER PRESENTED IN CONFERENCES

- Presented a paper at the *International* Conference on (ICEE-2021): Ravindra Kumar, "**Hydrogen Production from Biogas: Methods and Economic analysis**", *International* Conference on Energy and Environment (ICEE2021), April 09-10 2021 Organized by Mechanical and Civil Department, Jyoti Engineering College, Kerala.
- Presented a paper in the 2nd International Conference on (RAME-2020): Ravindra Kumar, "**Solar Thermal Application for Crop Residue Management**", "RECENT ADVANCES IN MECHANICAL ENGINEERING" (RAME-2020) September 18-19, 2020 *Organized by* Centre for Energy and Environment, DTU Delhi.
- Presented a paper in the *1st International* Conference on (ICET-2020): Ravindra Kumar, "**An Overview of Conventional and Non-Conventional Hydrogen Production Methods**", Innovations in Clean Energy Technologies

(ICET-2020) 27th-28th August 2020 *Organized by* Energy Centre, Maulana Azad National Institute of Technology, Bhopal.

PUBLICATIONS:

Published a technical paper in SCI indexed journal:

- Kumar, R., Kumar, A., & Pal, A. (2024). Simulation modelling of hydrogen production from steam reforming of methane and biogas. Fuel, 362, 130742. https://doi.org/10.1016/j.fuel.2023.130742.
- Kumar, R., & Kumar, A. (2024). Recent advances of biogas reforming for hydrogen production: Methods, purification, utility and techno-economics analysis. International Journal of Hydrogen Energy. https://doi.org/10.1016/j.ijhydene.2024.02.143.
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Published a technical paper in Scopus indexed journal:

- Kumar R, Kumar A, Sharma A. **Overview of Hydrogen Production Methods from Solar Energy**. In Thermal Energy 2024 (pp. 223-245). CRC Press.
- Kumar, R. and Kumar, A., 2023. **Advancement in steam reforming of methanol to produce hydrogen: A review**. *Applied Chemical Engineering*, *6*(2), p.2123.
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- Md. Kumail Naqvi, Mrinal Anthwal, Ravindra Kumar (2020), ***Generation and analysis of biogas from kitchen waste at a small scale***, WEENTECH Proceedings in Energy, vol. 6(1), pp. 140-148, DOI: *10.32438/WPE.0602134*.
- K.M. Pandey and Ravindra Kumar (2011): ***Numerical Analysis of Coal Combustion in Circulating Fluidized Bed***: International Journal of Chemical Engineering and Applications, Vol. 2, No. 6, December 2011.
- R. Kumar and K.M.Pandey (2012): ***CFD analysis of circulating fluidized bed combustion***: IRACST – Engineering Science and Technology: An International Journal (ESTIJ), ISSN: 2250-3498, Vol.2, No.1, 2012.
- Ravindra Kumar (2012)**: *Analysis of Pressure and Velocity in Coal Combustion System using DPM Method in Fluent Software*:** International Journal of Engineering Research and Applications (IJERA) ISSN: 2248-9622. Vol. 2, Issue 3, May-Jun 2012, pp.2885-2889.

Attended FDP/Participation/Short Term Course/Seminar

- One Week (Online) Professional Development Programme on "**Recent Developments in Renewable Energy**" from 20th to 24th June 2022 at the Department of Mechanical Engineering, Amity School of Engineering and Technology, Noida (India).
- One week **FDP** on **Recent Trends in Renewable Energy** held from 2nd -6th August 2021 organized by the Department of Mechanical and Electrical Engineering, K.R. Mangalam University, Gurugram, Haryana.
- One week **FDP** on **Recent Developments in Renewable Energy Systems** organized by Mechanical, Automobile and Production & Industrial Engineering Delhi Technical University, Delhi from 25-29th November 2019 sponsored by TEQIP-III.
- Attended a seminar on the **Scope of Biofuel as a Green Fuel** organized by the Society of Automotive Engineers, Delhi Technical University, Delhi on 10th August 2021.
- Attended an **FDP** on the **Application of AutoCAD in Engineering**, An ICT-based module program organized by the Department of Civil Engineering, ADGITM New Delhi, 26-30th November 2018, NITTTR Chandigarh.
- Participated in AICTE recognized **short-term course** on **Modeling & Simulation using MATLAB through ICT** conducted by Mechanical

Engineering Department from 21st - 25th May 2018 at ADGITM(Formerly NIEC), New Delhi.

- Participated as faculty in the fourth biennial **seminar-cum workshop** on **Automotive Noise, Vibration & Harshness** held at International Center for Automotive Technology (ICAT) -2017, Manesar.
- Attended a seminar on **India Corporate Governance & Sustainability Vision Summit, Edition 6** organized by the Indian Chamber of Commerce on 19th February 2016, New Delhi.

EXTRA –CURRICULUM ACTIVITIES

- Worked as coordinator in criteria 5 of NBA at the Department level.
- Organizing committee member in an international conference in ADGITM New Delhi-2020.
- Participated as a volunteer at National Conference on Recent Advances in Mechanical Engineering (NCRAME-2008) on Dec 20-21, 2008.
- Project Coordinator (UG Level)
- Set up a project lab (UG Level)
- Subject Coordinator: Engineering Mechanics and Heat Transfer

PERSONAL PROFILE:

Father’s Name	LT. Shiv Shanker
Mother’s Name	Smt. Ram Kumari
Nationality	Indian
Religion	Hindu
Sex	Male
Date of Birth	10th June 1987
Language	English, Hindi
Marital Status	Married

DECLARATION

I do hereby declare that all the statements made herein are true to the best of my knowledge.

Place: New Delhi

Date: 01-11-2024 **RAVINDRA KUMAR**