Numerical investigation of sugarcane bagasse as potential feedstock for biohydrogen production through gasification in Pakistan

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Spring-2021-MSCSE 00000359906

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Islamabad, Pakistan
(June, 2023)

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A thesis submitted to the National University of Sciences and Technology, Islamabad,

in partial fulfillment of the requirements for the degree of

Master of Science in
Computational Science
and Engineering

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“I would like to dedicate this thesis to my loving parents and husband, whose unwavering support and encouragement have been the driving force behind my academic journey.”

ABSTRACT

Rising energy demand drives increased fossil fuel consumption, exacerbating global warming. Unsustainable fossil fuel use exceeds dangerous CO_2 levels. Since the 1800s, burning fossil fuels released over 1,100 Gt CO_2. Hydrogen fuel has the potential to reduce annual CO2 emissions by 6 gigatons. Biomass-based hydrogen generation is a favorable technique, contributing to decarbonization. In this study, numerical investigations of the integrated biohydrogen production process through gasification using sugarcane bagasse as a biomass source have been presented. Aspen Plus/ Hysys Adsorption software was used for the simulation and analysis of various processes involved in hydrogen production. Literature contains descriptions of different components of biohydrogen production processes for various biomasses. However, there is a lack of comprehensive research that explores the entire biohydrogen production process with the specific goal of obtaining pure hydrogen from a particular biomass. Moreover, there is a lack of scholarly studies that specifically investigate this topic within the context of Pakistan. The purpose of this study is to address this research gap by providing an integrated analysis of biohydrogen production, specifically focusing on utilizing the most suitable biomass found in Pakistan as the raw material. The steam-blown circulating fluidized bed gasifier was fed with biomass residue to obtain the product gas. Sensitivity analysis of the gasification process revealed that increasing the temperature and steam-to-biomass ratio positively affect hydrogen production, while an increase in gasifier pressure has a negative effect on hydrogen production. The product gas was then introduced as an inlet to the hydrogen enrichment process, where it was processed to remove hydrocarbon content and underwent water gas shift reaction to obtain the hydrogen rich synthesis gas containing 61.7% hydrogen by volume. Parametric analyses of the enrichment process showed that the lower inlet temperature of the water gas shift reactor and higher steam flow rate favours the hydrogen enrichment process. Finally, the synthesis gas was passed through the pressure swing adsorber yielding hydrogen with a purity exceeding 99%. Parametric analysis of the purification process disclosed that higher adsorber pressure and lower syngas flow rate result in delayed breakthrough points. Overall, sugarcane bagasse possesses significant potential for hydrogen production in Pakistan.

Keywords: Hydrogen production, Biomass gasification, Sugarcane bagasse, Process simulation, Water gas shift, Hydrogen purification

ACKNOWLEDGEMENTS

In the name of Allah, the most compassionate, the most merciful, I would like to begin by expressing my sincere appreciation to my Supervisor, Dr. Absaar-ul-sJabbar, for his invaluable assistance in finalizing my Master's thesis. I am extremely grateful to Dr. Abdul Qyyum, Dr. Muhammad Tariq Saeed and Dr. Mian Ilyas Ahmad, members of my Guidance and Examinations Committee, for generously sharing their expertise and dedicating their time.

I would like to express my sincere gratitude to Dr. Hammad Cheema, our principal, for his encouragement and leadership, which played a significant role in the successful completion of my academic journey. I am grateful for the support provided by my academic institution, which allowed me to conduct my research and offered any assistance I needed.

Furthermore, I am deeply appreciative of the administrators and mentor teachers in our school division who contributed to this work. Their enthusiasm and willingness to provide insights made completing this study a truly enjoyable experience.

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CHAPTER 1: INTRODUCTION

This chapter explores the obstacles that can be surmounted through the implementation of a hydrogen economy. It also addresses the necessity of biohydrogen production. Additionally, it delves into the research methodology employed and highlights the study's contribution to national requirements and the pursuit of sustainable development goals.

1.1 Hydrogen Economy

The hydrogen economy refers to a vision of using hydrogen as a primary energy carrier and fuel source, replacing or supplementing traditional fossil fuels. The idea behind the hydrogen economy is to harness hydrogen's potential as a clean and abundant energy resource to address environmental concerns and energy security.

Hydrogen (H_2) is a versatile element that can be produced from various sources, including water (through electrolysis), natural gas (through steam methane reforming), biomass, or even renewable energy sources like solar and wind power. Once produced, hydrogen can be used directly as a fuel or converted into electricity through fuel cells.

Advocates of the hydrogen economy propose using hydrogen in various sectors, such as transportation, power generation, and industrial processes. In transportation, hydrogen fuel cells can power electric vehicles, offering long driving ranges and quick refueling times compared to battery-powered electric vehicles. Hydrogen can also be used in combustion engines or blended with natural gas for heating applications.

The potential advantages of a hydrogen economy include reduced greenhouse gas emissions, as hydrogen combustion or fuel cell reactions produce water as a byproduct, and increased energy security by diversifying energy sources. Hydrogen can be produced from a wide range of resources, including renewable sources, reducing dependence on fossil fuels. Additionally, hydrogen can be stored and transported easily, enabling efficient distribution and utilization.

However, there are challenges associated with the hydrogen economy. One major obstacle is the cost and energy-intensive nature of hydrogen production, especially when using electrolysis. Additionally, there is a need to establish a robust infrastructure for hydrogen storage, transportation, and distribution. Safety concerns related to hydrogen handling and storage also need to be addressed.

Overall, the hydrogen economy represents a potential pathway toward a sustainable and low-carbon energy future, but significant technological advancements, supportive policies, and infrastructure development are required to realize its full potential.

Pakistan has shown interest in developing a hydrogen economy and has taken initial steps toward its implementation. The country recognizes the potential of hydrogen as a clean energy resource and aims to leverage it to address energy challenges, reduce greenhouse gas emissions, and enhance energy security.

The government of Pakistan has expressed its commitment to the development of a hydrogen economy through various policy initiatives. In 2021, Pakistan's Ministry of Energy issued the National Energy Efficiency and Conservation Policy, which includes a roadmap for the deployment of hydrogen technologies. The policy aims to promote the production, storage, and utilization of hydrogen to diversify the energy mix and reduce reliance on imported fossil fuels. Figure 1.1 depicts the process for the development of biohydrogen economy in Pakistan.

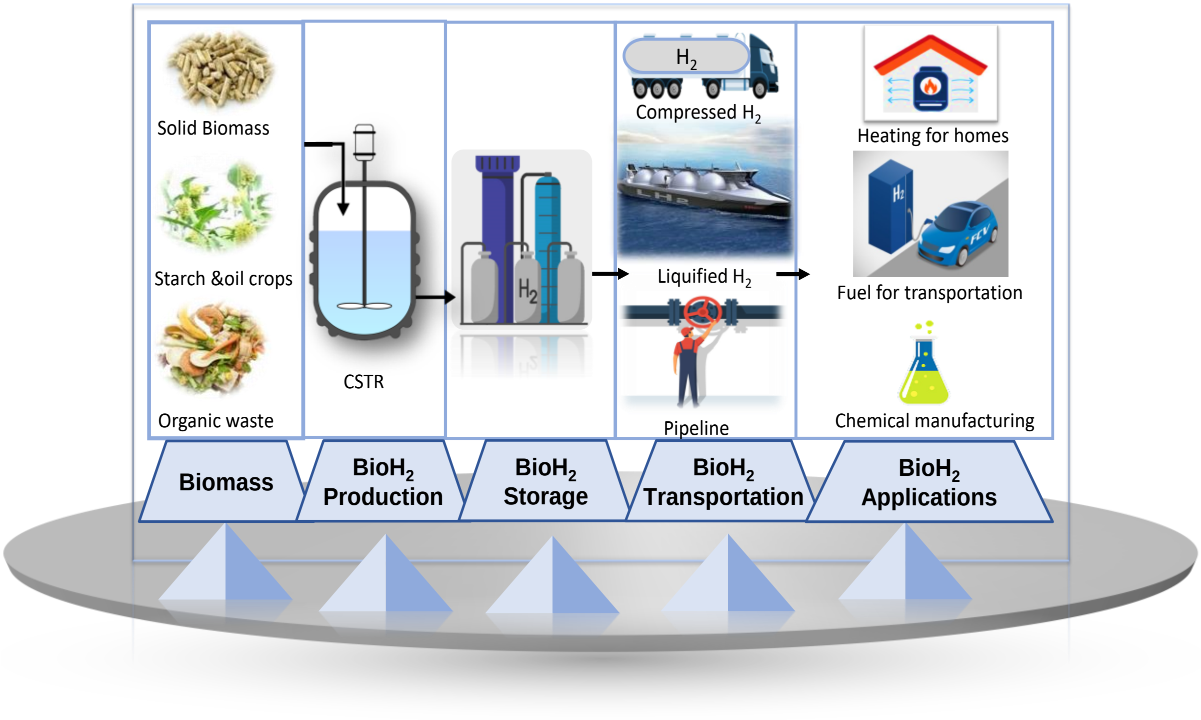


Figure 1.1: Process for development of biohydrogen economy for Pakistan

1.2 Benefits of hydrogen economy

This study will lay the foundation in the micro-level research in Pakistan on waste management and finding suitable routes that are both economical and environment-friendly for converting waste into renewable energy and valuable products. The future vision of Pakistan is to strive for better utilization of renewable resources to develop a sustainable energy economy. A pollution-free and clean environment is one of the objectives included in Pakistan's 2030 Agenda, which is also directly related to SDG 7. Developing the hydrogen economy for Pakistan will be one of the initiatives towards the UNFCC Paris agreement, limiting global warming to well below 2 degrees Celsius.

In Pakistan, the benefits of developing biomass to biohydrogen producing plants are numerous such as opening new channels in the cleaner and sustainable power production, solving the country's solid waste issues, new small and medium-sized businesses (SMBs), and job creation, minimizing environmental pollution, and improving public health. The development process for a biohydrogen-based economy will initiate an industrial and technological revolution to attain a globally competitive hydrogen economy. Figure 1.2 shows the benefits of developing a hydrogen-based economy for Pakistan.

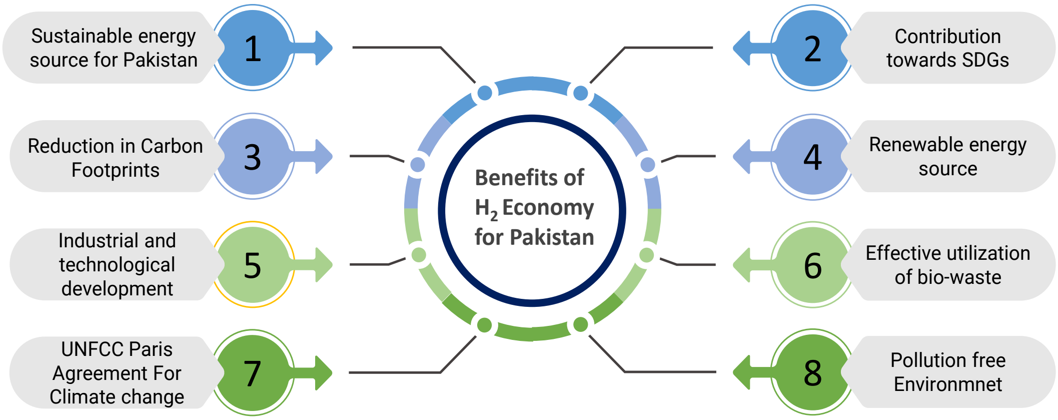


Figure 1.2: Benefits of hydrogen economy for Pakistan

1.3 Biohydrogen

Over the last few years, due to the increase in energy demand, the consumption of fossils fuels increased drastically, contributing a lot to global warming. To address this problem, the world is now looking forward to renewable energy sources like solar energy, tidal energy, wind energy, biowaste etc[1]. Due to the unsustainable fossil fuel consumption, the level of GHGs accumulation in the atmosphere has already passed the threshold of 450 ppm CO_2, which is considered dangerously high. Since the mid-nineteenth century, over 1,100 Gt CO_2 has been released into the air due to the burning of fossil fuels. Combustion of fossil fuels for heat supply, electricity generation, and transport make up to 70% of the total emissions, including methane, CO_2, and nitrous oxide[2].

Using hydrogen as fuel will reduce the annual carbon dioxide emissions by 6 gigatons[2]. Apart from that, it can also be used for domestic purposes. The use of hydrogen for domestic purposes is still in the early stages of development, it has the potential to be a sustainable and low-emission alternative to traditional fossil fuel-based systems.

Hydrogen generation from biomass will be a favorable technique keeping in view the emission of GHGs and carbon dioxide from burning fossil fuels. Using hydrogen as fuel will play a significant part in decarbonization, and biohydrogen production is a promising solution compared to fossil fuel-based hydrogen[1]. The burning of hydrogen as fuel produces water as the final combustion product. Also, hydrogen has the highest energy (143 GJ Ton^{-1}) among all the investigated gaseous fuels[3].

Biohydrogen can be produced from a variety of biomass feedstocks, such as agricultural residues, forestry waste, and municipal solid waste. The production of biohydrogen from biomass has the potential to be a sustainable and renewable source of energy, as it utilizes waste materials and has a low carbon footprint.

The technology for producing biohydrogen is sustainable as compared to hydrogen produced from fossil fuels. The substrate utilized for biohydrogen-producing technology is primarily free or available at a very low cost. These substrates include biomass, organic waste, industrial organic by-products, etc[4]. The produced biohydrogen can be used as a source of heat, electricity, combined heat and power (CHP), transport fuel, and renewable energy.

1.4 Aspen Plus Software

Aspen Plus Software is utilized for simulations involved in this research study. Aspen Plus is a widely used process simulation software developed by Aspen Technology. It is specifically designed for the modeling and simulation of chemical processes and is commonly used in industries such as oil and gas, chemical engineering, pharmaceuticals, and more.

Aspen Plus allows engineers and researchers to create detailed process models by representing various unit operations, such as reactors, separators, heat exchangers, distillation columns, and other equipment. The software offers a wide range of thermodynamic models and property databases to accurately simulate the behavior of different components and mixtures under various process conditions.

Some key features of Aspen Plus include:

- Process Modeling: Aspen Plus provides a graphical interface where users can build process models by connecting predefined unit operation blocks and specifying their operating parameters.
- Thermodynamics and Property Databases: The software offers a comprehensive set of thermodynamic models and property databases, including the popular Aspen Properties database, to accurately calculate phase equilibria, thermodynamic properties, and physical properties of components.
- Reaction Modeling: Aspen Plus allows users to define and simulate chemical reactions, including elementary, complex, and user-defined reactions. It also provides tools for reaction optimization and kinetic parameter estimation.
- Heat and Mass Balances: Aspen Plus performs rigorous heat and mass balances to calculate stream properties, energy consumption, and material flow rates throughout

the process.

- Process Optimization: The software includes optimization capabilities that enable users to find the optimal operating conditions, design parameters, or product specifications by defining objective functions and constraints.
- Simulation and Analysis: Aspen Plus provides tools for steady-state and dynamic simulation, sensitivity analysis, parameter estimation, and model validation. It also offers various reporting and visualization options to analyze and interpret simulation results.

Aspen Plus is a powerful tool for process design, analysis, and optimization, helping engineers and researchers in the chemical process industries to improve efficiency, reduce costs, and develop new processes.

1.5 Contribution towards SDGs

This research study aligns with the United Nations (UN) sustainable development goals (SDGs). This study would contribute to achieving the following SGDs in Pakistan.

- SDG-7: Generating renewable, affordable, and clean power and valuable products from waste
- SDG-6: Improving the efficiency of the waste management and sanitation system
- SDG-3: Improving the good health and well-being of the public
- SDG-8: Increasing waste recycling practices
- SDG-4: Increasing research and development activities
- SDG-1: Creating new business and job opportunities for local people to reduce hunger and poverty

1.6 Relevance to national needs

Biohydrogen production can have several relevant applications for the national needs of Pakistan. Here are a few areas where biohydrogen production can be beneficial:

- Energy Security: Pakistan faces significant challenges in meeting its energy demands, with frequent power shortages and reliance on imported fossil fuels. Biohydrogen production can contribute to energy security by providing a renewable and sustainable energy source. It can help reduce dependence on fossil fuels, diversify the energy mix, and enhance energy self-sufficiency.
- Environmental Sustainability: Pakistan, like many other countries, is grappling with environmental issues such as air pollution and greenhouse gas emissions. Biohydrogen production offers a clean and environmentally friendly alternative to conventional energy sources. It generates hydrogen through the fermentation of organic waste, agricultural residues, or dedicated energy crops, thereby reducing carbon emissions and promoting sustainable waste management practices.
- Rural Development and Agriculture: Pakistan has a significant agricultural sector, and biohydrogen production can create opportunities for rural development. Utilizing agricultural waste, crop residues, or dedicated energy crops as feedstock for biohydrogen production can provide additional income streams for farmers. It can also contribute to sustainable waste management practices and reduce agricultural waste burning, which causes air pollution.
- Economic Growth and Job Creation: Investing in biohydrogen production can stimulate economic growth and job creation in Pakistan. It can foster the development of a bioenergy industry, attracting investments, and creating employment opportunities in various sectors, such as biomass collection and processing, bioreactor manufacturing,

and hydrogen infrastructure development.

- Technological Advancement: Biohydrogen production requires research, development, and innovation, which can drive technological advancement in Pakistan. This can lead to the development of efficient and cost-effective biohydrogen production processes, improved bioreactor designs, and advancements in microbial engineering. Such technological progress can contribute to the country's knowledge economy and pave the way for other renewable energy innovations.
- Climate Change Mitigation: Pakistan is highly vulnerable to the impacts of climate change. Biohydrogen, as a clean energy source, can help mitigate climate change by reducing greenhouse gas emissions. By transitioning to hydrogen-based systems in sectors such as transportation, industry, and power generation, Pakistan can reduce its carbon footprint and contribute to global efforts to combat climate change.

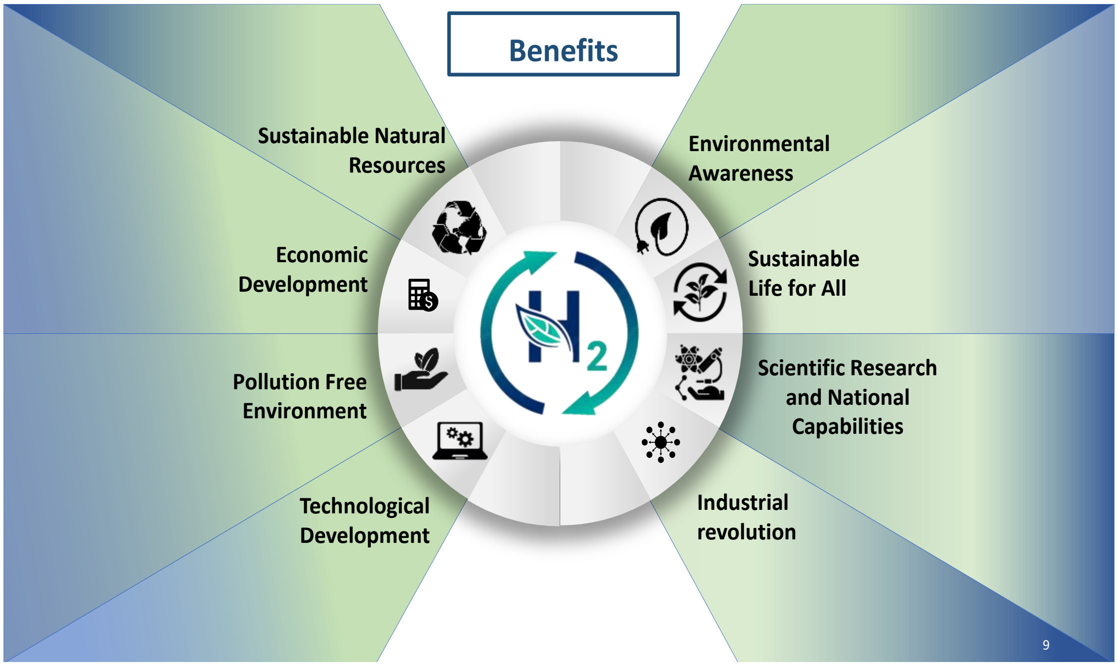


Figure 1.3: Relevance of biohydrogen production to national needs

The rest of the thesis is formulated as follows:

Chapter 2 delves into an extensive exploration of various biohydrogen production technologies, the concept of different colors of hydrogen, and the diverse applications of hydrogen. Additionally, it encompasses a comprehensive overview of hydrogen storage and transportation methods.

In chapter 3 of the paper, a comprehensive description is provided regarding the methodology employed for simulating various processes. Initially, the gasification process is simulated, followed by the simulation of the hydrogen enrichment process aimed at obtaining syngas that is rich in hydrogen. Additionally, the utilization of Pressure Swing Adsorption (PSA) technology for the purification of hydrogen is also elucidated.

Moving on to chapter 4, a detailed account is given of the sensitivity analysis carried out for the gasification process. Furthermore, parametric studies are conducted for both the hydrogen enrichment process and the hydrogen purification process using PSA technology. These analyses explore the influence of various parameters on the respective processes, enabling a deeper understanding of their behavior and performance.

Lastly, in chapter 5, the study concludes by presenting the final outcomes and results derived from the simulated gasification, hydrogen enrichment, and hydrogen purification processes. This Chapter serves as a synthesis of all the discussed processes, summarizing the key findings and implications arising from the study. This chapter also includes future recommendations.

CHAPTER 2: LITERATURE REVIEW

This chapter delves into an extensive exploration of various biohydrogen production technologies, the concept of different colors of hydrogen, and the diverse applications of hydrogen. Additionally, it encompasses a comprehensive overview of hydrogen storage and transportation methods.

2.1 Hydrogen production methods

There are two divisions of producing hydrogen, conventional methods and alternative methods. Conventional methods are to produce hydrogen from methane reforming, but a high amount of carbon dioxide is produced along with hydrogen. Some alternative methods are electrolysis of water, bio photolysis, and biological production of hydrogen from biomass. Biological production from biomass has two advantages compared to the conventional process. It produces less GHGs and helps dispose of organic waste with simultaneous hydrogen emission[5].

The waste is no longer treated as refuse in a waste-to-energy plant but a potential source of renewable energy and valuable products. The conversion technologies such as gasification, pyrolysis, anaerobic digestion, fermentation treat different waste sources to produce energy and value-added products.

2.2 Colors of Hydrogen

Different resources can be utilized for producing hydrogen like nuclear energy, fossil fuels, renewable energy resources, and biomass. Several processes can be adopted to produce hydrogen. If renewable resources are used for hydrogen production, then it will be a clean and sustainable source of energy.

The most common method of producing hydrogen is through steam reforming of methane and is called grey hydrogen. This method produces hydrogen with carbon emissions.

When the carbon emissions generated during the reforming process of hydrogen production are captured and securely stored using industrial carbon capture and storage (CCS) technologies, the resulting hydrogen is categorized as "blue hydrogen."[6]. Blue hydrogen represents a significant advancement in mitigating the environmental impact associated with hydrogen production from fossil fuels.

There is another way of producing hydrogen through renewable energy sources like solar power or wind power with the help of electrolysis to split water into hydrogen and oxygen. This is called green hydrogen. Green hydrogen can be used for the decarbonization of industrial and transportation section[6].

Hydrogen can also be produced from biomass. Hydrogen produced this way is called biohydrogen. Biohydrogen production involves the utilization of various biomass feedstocks, including agricultural residues, energy crops, organic wastes, and algae. The process typically relies on biochemical or thermochemical conversion pathways to extract hydrogen from the organic matter present in the biomass. This is the new technology for producing hydrogen, and there are different approaches to produce biohydrogen which include indirect photolysis, bio photolysis, photo fermentation and dark fermentation[7]. Figure 2.1 shows the difference between grey, blue, green, and biohydrogen.

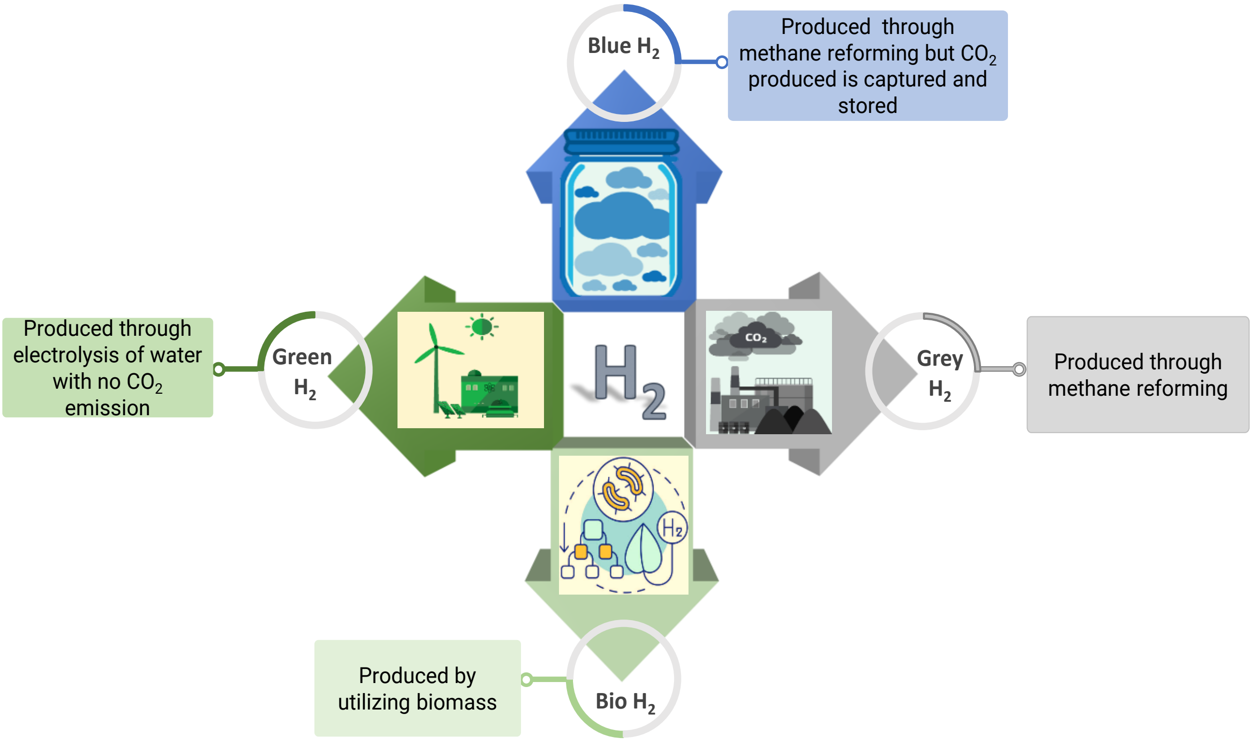


Figure 2.1: Difference between grey, blue, green, and biohydrogen[6]

2.3 Applications of Hydrogen

- Hydrogen plays a vital role in the chemical sector, serving various purposes such as hydrogenation, desulphurization, and hydrocracking. Hydrogenation involves the addition of hydrogen to unsaturated compounds, enabling the synthesis of a wide range of chemicals, including pharmaceuticals, fats, and oils. It is a crucial process in industries such as food processing, petrochemicals, and pharmaceuticals, where precise control of chemical reactions and the modification of molecular structures are required.

- Desulphurization, on the other hand, involves the removal of sulfur compounds from petroleum products and natural gas. Hydrogen is employed in desulphurization processes to convert sulfur-containing compounds into hydrogen sulfide, which can be easily separated. This is particularly important for meeting stringent environmental regulations and improving the quality of fuels, as sulfur compounds contribute to air pollution and the formation of harmful emissions.[8]

- In the refining industry, hydrogen is used for the hydrocracking process, which involves breaking down complex hydrocarbon molecules into smaller, more valuable ones. Hydrocracking improves the quality and yield of petroleum products, such as gasoline and diesel, by breaking heavy hydrocarbons into lighter fractions. Hydrogen is a critical component in this process as it provides the necessary hydrogenation reactions to enhance product quality and meet market demands for cleaner fuels.
- The synthesis of ammonia, a compound crucial to produce fertilizers, relies heavily on hydrogen. Ammonia synthesis accounts for approximately 60% of global hydrogen consumption. The Haber-Bosch process combines hydrogen and nitrogen to produce ammonia, which is then utilized as a key ingredient in nitrogen-based fertilizers. This process plays a vital role in global food production, as fertilizers containing ammonia are essential for maintaining crop yields and supporting agricultural productivity.
- Hydrogen also finds application in the refining of oil, particularly in the hydrogenation and desulphurization of naphtha. Hydrogenation processes help to upgrade naphtha into higher-quality products, such as gasoline or feedstock for petrochemical production. Desulphurization of naphtha is essential to reduce the sulfur content, improving the environmental performance of gasoline and other petroleum products.
- In the transportation sector, hydrogen is gaining attention as a fuel option. Fuel cell

vehicles (FCVs) equipped with hydrogen fuel cells offer zero-emission transportation, with water vapor being the only byproduct of the electrochemical reaction. Hydrogen fuel cells provide an alternative to traditional internal combustion engines, reducing greenhouse gas emissions and contributing to air quality improvement. The adoption of hydrogen as a fuel for transportation purposes has the potential to meet the growing market demand for sustainable and clean energy solutions[8].

Moreover, the integration of hydrogen energy in fuel cell-powered electric vehicles (FCEVs) enables the fulfillment of zero carbon emission requirements. FCEVs utilize fuel cells to convert hydrogen and oxygen into electricity, providing a sustainable and efficient means of powering electric vehicles. This technology combines the benefits of hydrogen as an energy carrier with the advantages of electric vehicles, offering long driving ranges and shorter refueling times compared to battery electric vehicles.

2.4 Biomass available in Pakistan

The scope for producing sustainable biohydrogen from different waste streams in Pakistan is highly promising. Pakistan, being an agrarian country, generates a significant amount of agricultural solid waste, presenting a valuable resource for biohydrogen production.

The agricultural sector in Pakistan produces a substantial volume of waste materials, including crop residues, such as rice straw, wheat straw, and sugarcane bagasse. The production of important crops in Pakistan is shown in Table 2.1.

Table 2.1: Production of important crops (Pakistan Economy Survey 2020-2021)

Production of important crops					**(Tonnes)**
Year	**Cotton (bales)**	**Sugarcane**	**Rice**	**Maize**	**Wheat**
2014-15	13,960	62,826	7,003	4,937	25,086
2015-16	9,917	65,482	6,801	5,271	25,633
2016-17	10,671	75,482	6,849	6,134	26,674
2017-18	11,946	83,333	7,450	5,902	25,076
2018-19	9,861	67,174	7,202	6,826	24,349
2019-20	9,148	66,380	7,414	7,883	25,248
2020-21	7,064	81,009	8,419	8,465	27,293

The results of this survey indicate that sugarcane is the crop with the highest production volume compared to rice, maize, and wheat.

The survey provides valuable insights into the agricultural landscape, specifically regarding the production levels of different crops. Among the crops studied, sugarcane emerges as the leading contender in terms of overall yield and cultivation. This finding highlights the significance of sugarcane cultivation within the agricultural sector.

Approximately 27% by weight of sugarcane bagasse is produced during the milling of sugar cane, indicating that a substantial amount is available for biohydrogen production[9]. The global production of sugarcane bagasse, which is the second most produced commodity crop, amounted to 1.89 billion tonnes in 2016[10]. Using sugarcane bagasse for process of gasification brings advantages related to logistics and final cost as sugar cane bagasse is already available onsite[11]. Table 2 shows the increasing inclination of bagasse Table 2 shows the increasing trend of bagasse usage until 2030. until 2030. Table 3 displays the proximate and ultimate analyses of sugarcane bagasse collected from identified sugar cane fields located near the city of Faisalabad[12].

Table 2.2: Gradual increasing inclination of bagasse in Pakistan[13]

Category	Type of biomass	2009	2012	2030
Crops in trillion tonnes	Bagasse	49.4	53.1	82.6

Table 2.3: Proximate and ultimate analysis of sugarcane bagasse on dry basis[12]

Proximate Analysis	
Volatile matter (%)	81.5
Fixed carbon (%)	13.3
Ash (%)	5.2
Ultimate Analysis	
C (%)	43.79
H (%)	5.96
O (%)	43.36
N (%)	1.69
S (%)	-
Cl (%)	-

Ultimate analysis of sugar cane bagasse shows that it contains 5.96% hydrogen. Ultimate analysis of rice husk and wheat husk show that these two contain 5.3% and 5.8% hydrogen[14]. Ultimate analysis of maize show that it contains 5.8% hydrogen[15].

2.5 Different technologies for biohydrogen production

Since ancient times, biomass has been used to produce energy and valuable products. For example, wood biomass was utilized for cooking and heating food and other important stuff. Similarly, biomass-based ethanol was employed as a transport fuel in vehicles. Plant-based oils were used to operate diesel engines. Significant exploitation of coal, oil, and natural gas has occurred afterward for economic development, resulting in GHG emissions, natural resource depletion, and environmental pollution. Thermochemical, physicochemical, and biochemical technologies convert various biomass streams to different biofuels and value-added products. Some of the biohydrogen producing technologies are discussed below.

2.5.1 Anaerobic digestion and dry reformation

One of the methods of producing H_2 is through anaerobic digestion of biomass and dry reformation of biogas. Dry reformation of CH_4 is a process that produces hydrogen by consuming carbon dioxide. This process is modelled and simulated by Balaji et al., 2020 primarily using Aspen HYSYS®. Cow manure (biomass) was selected for simulation study. The first process to take place is anaerobic digestion for production of biogas, in which processes like hydrolysis, acidogenesis, acetogenesis and methanogenesis take place. It is assumed that biomass is hydrolysed (pre-treated) and is processed directly in a continuous stirred tank reactor. The operational conditions for CSTR are pressure=atmospheric pressure and temperature=40°C. Biogas is produced because of anaerobic digestion along with undigested slurry. This slurry is considered as beneficial product for agricultural purposes. Dry reformation of biogas takes place in an isothermal fixed bed catalytic reactor for the conversion of methane into hydrogen[16].

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \text{(Eq. 2.1)}$$

Hydrogen is separated from the mixture of gases through membrane separation. Two streams are produced because of this separation process. One stream has high concentration of hydrogen and other stream contains unreacted reactants and by-products. Process flow diagram of this process is shown in Figure 2.2[16].

As a result of simulation study, conclusion was drawn that optimal values of 99.99% CO_2 conversion, 89.9% CH_4 conversion, and H_2 selectivity 1.21 can be obtained if biogas containing 38 mol% CO_2, 52 mol% CH_4, and 10 mol% H_2O is utilized for producing hydrogen by dry reformation at temperature and pressure conditions of

837.5°C and 101.3 kPa.

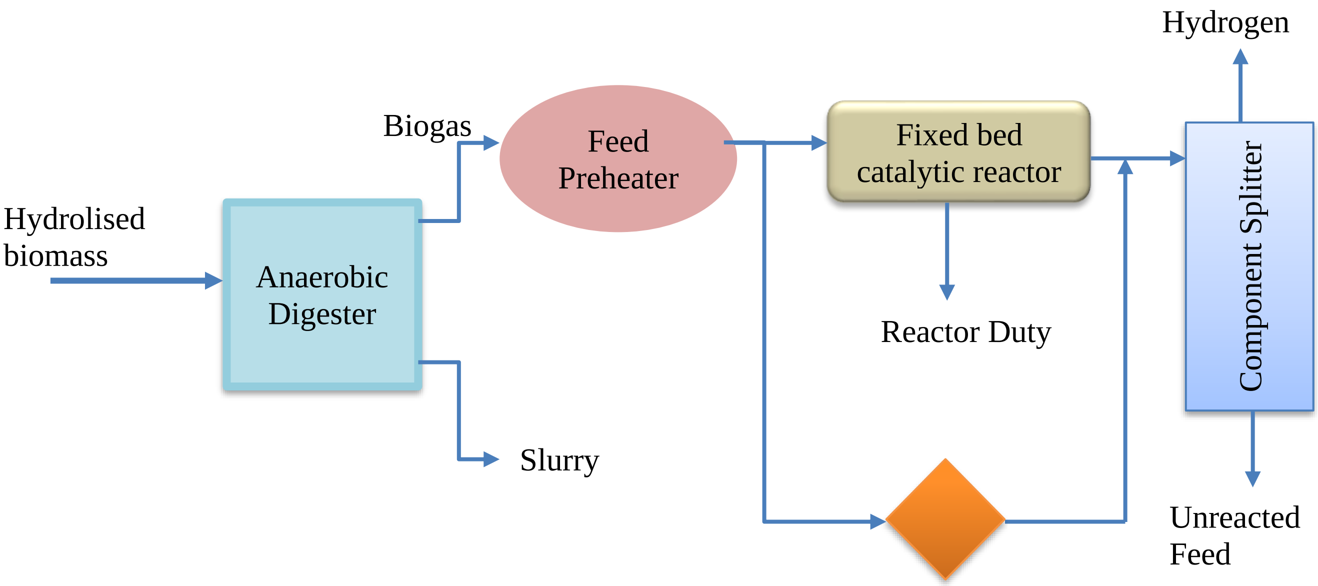


Figure 2.2: Process flow diagram of anaerobic digestion and dry reformation in HYSYS[16]

2.5.2 Dark Fermentation

Biological methods of producing hydrogen are less energy intensive and more environmentally friendly as compared to conventional methods of producing hydrogen from natural gas through steam reforming. Dark fermentation of biomass is a promising method to produce biohydrogen but this biohydrogen production method needs further research and growth to enhance the biohydrogen yield.

Dark fermentation is a process in which biomass rich in carbohydrate is broken down by hydrogen producing microorganism and this process is carried out anaerobically[17]. The common reactions carried out by facultative bacteria during Dark fermentation are

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \qquad \text{(Eq. 2.2)}$$

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 \qquad \text{(Eq. 2.3)}$$

Two main obstructions for commercial biohydrogen production through dark fermentation are low biohydrogen yield and incomplete conversion of biomass. Major residues of DF process are volatile fatty acids. These residues if utilized properly, complete conversion of biomass can be achieved.

For this purpose, dual system strategy can be opted in which dark fermentation of biomass is carried out in the first stage and by-products are converted to H_2 (photo fermentation, bio electrochemical cells) or CH_4 (Anaerobic Digestion). Various methods of combining Dark fermentation process with post treatment methods are shown in Figure 2.3[17].

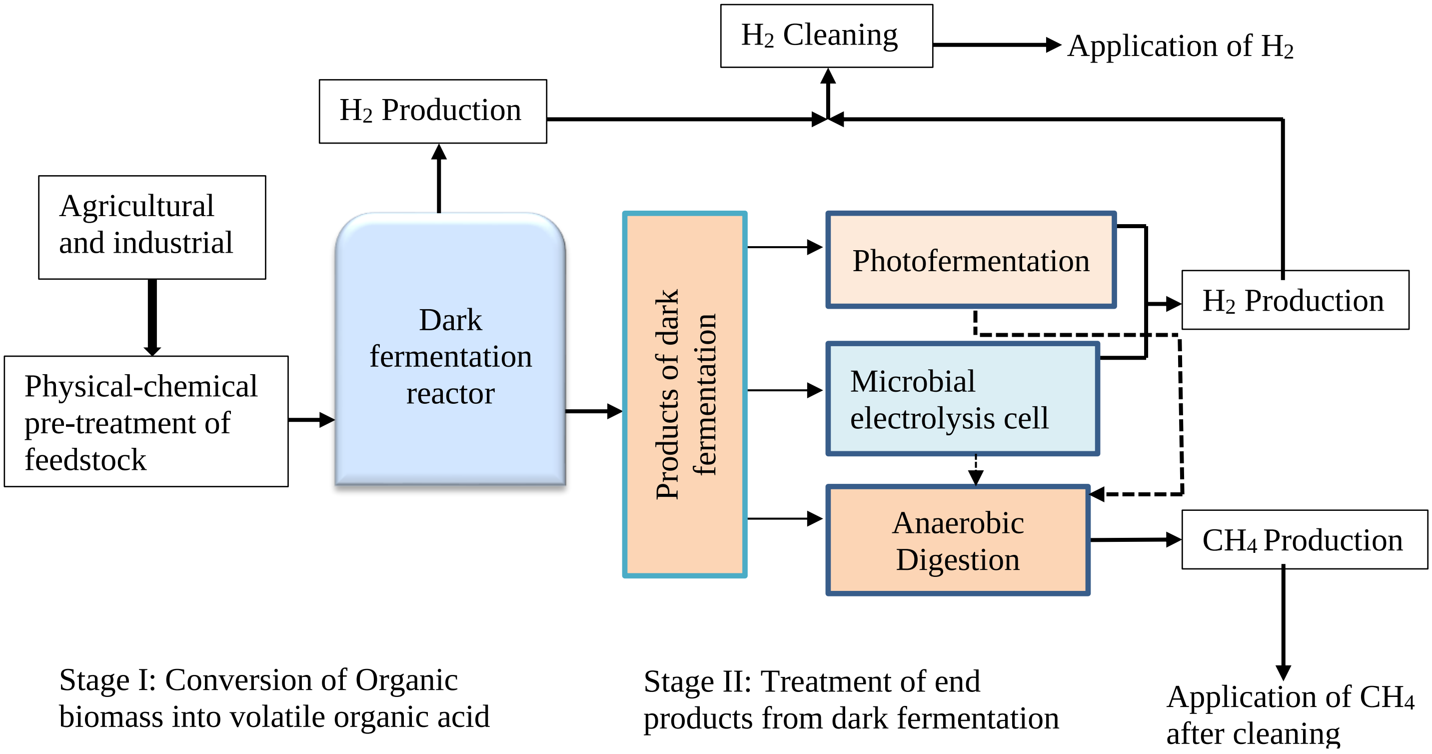


Figure 2.3: Different methods for integrating DF with post treatment processes[17]

2.5.3 Gasification

Gasification is a thermochemical process that converts carbonaceous materials, such as coal, biomass, or waste, into a mixture of gases known as syngas (synthesis gas). It is a versatile technology used for various purposes, including energy production, chemical synthesis, and waste management. Gasification is considered the most productive and cost-effective method for the beneficial disposal of forest and agricultural residues [18].

Currently, the production of hydrogen through biomass gasification is more costly compared to the traditional method of steam reforming. However, it is still possible to produce hydrogen through the gasification of biomass[19].

The gasification process involves the partial oxidation of the carbonaceous feedstock at high temperatures (typically above 700°C) in the presence of a controlled amount of oxygen or steam. The oxygen-starved or oxygen-free environment prevents complete combustion and allows to produce syngas instead of solely carbon dioxide. Thermochemical gasification of solid biomass is a method to obtain gaseous fuels. This process involves a series of steps, including drying, pyrolysis, and gasification, which trigger various chain reactions[20].

The main reactions that occur during gasification are:

- Pyrolysis: By subjecting the feedstock to heat without the presence of oxygen, volatile elements such as tar, methane, and various hydrocarbons are emitted.
- Partial Oxidation: The volatile components are reacted with a limited amount of oxygen or steam to produce hydrogen and carbon monoxide, which are the main components of syngas.

When steam alone is employed as the gasifying agent, the gasifier functions as an indirectly heated or allothermal system. This implies that an external heat source is necessary to sustain the temperature of the reactor[21].

Primary gasification reactions are given in Table 1.

Table 2.4: Gasification reactions[22]

Reaction number	Reactions
R1	$C + 0.5O_2 \rightarrow CO$
R2	$C + 2H_2 \rightarrow CH_4$
R3	$CO + 0.5O_2 \rightarrow CO_2$
R4	$H_2 + 0.5O_2 \rightarrow H_2O$
R5	$C + CO_2 \leftrightarrow 2CO$
R6	$C + H_2O \leftrightarrow CO + H_2$
R7	$CO + H_2O \leftrightarrow CO_2 + H_2$
R8	$CH_4 + H_2O \leftrightarrow CO + 3H_2$
R9	$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$
R10	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

The gasification process produces three primary products: product gas in the gas phase, tar in the liquid phase, and char in the solid phase[23]. The resulting gas product consists of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and nitrogen (N_2)[20]. Lignocellulosic biomasses are essential in biorefineries due to their low cost and widespread availability[24]. The most commonly utilized lignocellulosic source is wood[25].

Apart from wood, alternative sources of lignocellulose can be employed for bioenergy generation, including sugarcane bagasse, which is a predominant byproduct of the sugar cane industry. Several experimental conditions can affect the gasification performance.

The emphasis of this study has been on the selected gasification parameters, namely pressure (P), temperature (T), biomass moisture content (MC) and steam to biomass ratio (S/B). Choosing the appropriate gasification temperature is of utmost importance due to the potential negative effects of temperatures exceeding 1000°C. Such high temperatures can lead to undesirable outcomes like ash melting and sintering, which are unsuitable for ensuring the stable operation of the gasifier[26].

Gasifiers that operate under high pressure generate pressurized synthesis gas. This gas can be directly fed to turbines and synthesis reactors, following a cleaning process, resulting in an enhancement of the overall cold gas efficiency (CGE) of the system. However, pressurized biomass feeding is a challenge in high-pressure gasifiers[27]. The introduction of steam into the gasifier can accelerate the endothermic steam gasification reactions, leading to the formation of crucial compounds such as H_2 and CO, which play significant roles in various synthesis processes. Therefore, steam injection is a widely employed technique to control the hydrogen to carbon monoxide ratio (H_2/CO) of the resulting gas product[28].

Moisture content, which represents water, is typically undesirable as it can lower the temperature of the gasifier when it vaporizes. Consequently, higher amounts of heat or oxidant sources are required to sustain the gasifier temperature, resulting in increased costs.[26]. In this study, fluidized bed reactors have been chosen as gasifiers due to their reported benefits, including feeding flexibility and scalability, high rates of heat and mass transfer, and rapid reaction rates[29].

In this study, circulating fluidized bed reactors have been utilized as fluidized bed gasifiers, with steam serving as the gasifying agent. This gasifying agent produces product gas mixtures with moderate to high heating values (10-15 MJ/Nm^3), which are desirable attributes for synthesis processes[26].

2.6 Benefits of Gasification Process

Following are some benefits of Gasification Process

2.6.1 Efficiency Benefits

The gasification process's effectiveness is crucial in evaluating the technical and economic feasibility of utilizing gasification technology for energy production. It is measured by comparing the energy content of the produced gas to the energy content of the input material. Enhanced process efficiencies lead to more economically efficient electricity generation[30].

The primary utilization involves employing purified product gases to power a gas turbine for the purpose of generating electricity. The second application involves harnessing the heat produced during gasification and the high-temperature exhaust from the gas turbine to generate steam, which can be utilized in steam turbines or generators. This combined cycle approach enables a more efficient conversion of biomass energy into usable energy, resulting in a dual method of electricity generation.

By implementing a combined cycle, gasification power plants can achieve higher overall efficiency and maximize the utilization of the energy potential of the biomass feedstock. This approach enhances the economic viability and sustainability of biomass gasification for energy production[31].

2.6.2 Environmental benefits

Compared to direct biomass combustion, biomass gasification presents notable environmental advantages by achieving low levels of sulfur oxide (SOx) and nitrogen oxide (NOX) emissions, as well as reduced emissions of particulate matter. Biomass feedstocks, including SCB (sugarcane bagasse), typically have low sulfur concentrations, and any sulfur present can be captured using existing chemical industry processes.

By minimizing SOx, NOx, and particulate emissions, as well as providing opportunities for CO_2 capture and utilization, biomass gasification demonstrates its potential to mitigate air pollution, reduce greenhouse gas emissions, and contribute to a more sustainable energy system[31].

2.6.3 Feedstock Flexibility

Gasification systems have been engineered to accommodate a wide range of feedstock types. To optimize the control of syngas properties, a deeper understanding of gasifier operation is needed, particularly regarding the variability of feedstock.

This approach enables the sugarcane industry to diversify its feedstock sources and maintain a consistent energy supply throughout the year. By optimizing the co-gasification process and managing the feedstock variability, the industry can maximize the utilization of available resources and reduce its carbon footprint[32].

Overall, understanding gasifier operation and adapting it to varying feedstock characteristics allows for greater feedstock flexibility in gasification systems, leading to improved energy efficiency, reduced emissions, and enhanced sustainability in industries such as the sugarcane sector.

2.6.4 Product Flexibility

Gasification technology possesses a notable advantage in its capacity to generate syngas, which can undergo further processing to yield high-energy dense products. This versatility allows to produce valuable end-products from the syngas generated through biomass gasification.

Liquid fuels, including diesel, gasoline, jet fuel, and synthetic natural gas like hydrogen, are among the valuable products that can be derived from syngas through gasification technology. These fuels have high energy density and can be used as alternatives to traditional fossil fuels[31].

By converting biomass into syngas and further processing it into high-energy dense products, gasification technology contributes to the development of a more sustainable and efficient energy system. It enables the production of cleaner fuels, reduces dependence on fossil fuels, and facilitates the production of valuable chemicals and fertilizers, contributing to a more circular and environmentally friendly economy.

2.6.5 **CO_2 capture and storage**

Carbon capture, storage, and utilization (CCSU) refer to a variety of technological processes that aim to alleviate greenhouse gas (GHG) emissions. These processes involve capturing carbon dioxide (CO_2) and either storing it or utilizing it for other purposes.

The CCSU (Carbon Capture, Storage, and Utilization) process consists of four stages that are applicable to large, centralized sources such as gasification power plants. The initial stage involves the capture of CO_2 from the gasification plant, followed by its transportation to a suitable storage site where it is injected into deep geological formations and securely trapped beneath impermeable rocks. Monitoring of the injected CO_2 is of utmost importance to ensure long-term storage, as well as to guarantee its safety for both human health and the environment[33].

CCSU technologies play a vital role in mitigating GHG emissions by capturing and effectively managing CO_2 produced during gasification and other industrial processes. By implementing CCSU, we can reduce the release of CO_2 into the atmosphere, mitigate climate change, and enhance the sustainability of energy production from biomass and other sources.

2.7 Hydrogen enrichment process

This study involves subjecting the product gas acquired from gasification to a hydrogen enrichment process. The simulation of this process is conducted utilizing the Aspen HYSYS chemical process simulation software. The product gas undergoes a sequence of cleaning, reforming, and shift processes to generate "synthesis gas" (syn gas) consisting of CO and H_2. Pure hydrogen gas is then produced through a separation stage. It should be noted that the "product gas" cannot be directly used and needs to be processed to obtain "synthesis gas" consisting of CO, CO_2, and H_2 [20].

The water gas shift (WGS) reactor is typically the largest and heaviest component in most hydrocarbon processing systems due to the relatively slow rate of the reaction compared to other reactions, and its inhibition at higher temperatures by thermodynamics[34]. The water gas shift reaction is an intermediate step employed for hydrogen enrichment and CO reduction in the Product gas. The reaction is reversible and exhibits a moderate exothermic nature. As the temperature increases, the equilibrium constant of the reaction decreases.

The reaction exhibits thermodynamic favorability at low temperatures and kinetic favorability at high temperatures. Since there is no change in volume between reactants and products, the pressure has no effect on the reaction. The proposed process model utilizes circulating fluidized bed (CFB) technology with secondary agents to achieve staged gasification of biomass, resulting in the production of raw syngas. The Gibbs free energy minimization method is applied to all reactor units, including the gasifier, tar reformer, and water gas shift reactor, within the proposed process model[20]

2.8 Hydrogen purification process

The raw syngas is then subjected to several purification steps, including hydrocarbon reforming, water gas shift conversion of CO content, and hydrogen separation through pressure swing adsorption (PSA) technique[20].

2.9 Hydrogen storage methods

Hydrogen produced needs to be stored to be used by vehicles. There are two main approaches to store hydrogen, physical and chemical techniques. Different physical methods include cryogenic hydrogen, compressed hydrogen, metal hydrides etc. hydrogen can be compressed at constant temperature by increasing pressure. Still, research is needed for compressed hydrogen storage systems due to their low capacity. The method to obtain cryogenic hydrogen is by decreasing temperature at constant pressure, but a high amount of cooling energy is required.

Recent studies have shown that carbon nanotubes have high hydrogen uptake capacity; thus, they can be used as a promising solution for hydrogen storage. Another favourable candidate for hydrogen storage is liquid organic hydrides; hydrogenation and dehydrogenation processes are carried out during storage through liquid organic hydrides. Storage through liquid organic hydrides has some advantages, as they have high volumetric hydrogen storage density.

This storage process can be carried out at near ambient conditions; thus, the current infrastructure for transportation of fossil fuels can be utilized for its transport. Also, during this process, no CO, CO_2, and other by-product gases are released[35]. A comparison of different hydrogen storage technologies has been made in Table 2.5.

Table 2.5: Comparative analysis of different methods for storing hydrogen [35]

Hydrogen storage methods	**Example**	**Storage capacity (weight%)**	**Weakness**	**Strengths**
Pressurized hydrogen	-	1-3	low hydrogen storage capacity, high-pressure vessel needed, large amount of energy is consumed, costly transportation, poor safety	high speed of filling gas and exhausting gas, low cost, good maneuverability under normal temperature
Liquid hydrogen	-	>10	liquefied energy consumed is high, requirements for maintenance and storage are strict	volumetric energy density is high, volume of container needed for storage is small
Carbonaceous materials	nanofibers, Carbon nanotubes,	3-10	relevant technology is immature, costly	specific surface area is high, high hydrogen storage capacity, convenient transportation
Metal hydrides	Mg_2Ni, Mg,	1-8	hydrogen storage performance is poor, easy pulverization, transportation is inconvenient	high operability, stability, and safety

Complexation hydride	$NaAlH_4$, $NaBH_4$	5.5-18.5	complexation reaction speed is slow, pressure and temperature required for hydrogenation is high	high hydrogen storage capacity, low costs
Glass microspheres	-	>15	technology for high strength hollow microsphere is immature, costly	high hydrogen storage capacity, good maneuverability
Organic liquid	N-ethyl carbazole, Benzene	5-10	there must be Catalysts for dehydrogenation/ hydrogenation	high capacity for hydrogen storage, convenient and safe transportation

2.10 Hydrogen transportation

Suitable infrastructure is needed for hydrogen transport and delivery for a practicable hydrogen economy. There are different methods to transport hydrogen, including compressed tube trailers, compressed gas pipelines, and cryogenic liquid trucks. Tube trailers can be used when the demand is low for the introductory period.

Cryogenic liquid trucks can manage larger quantities compared to tube trailers and can be utilized to meet the needs of the growing market. For those areas with high demand, pipelines can be used to transport hydrogen. Different aspects of various hydrogen delivery methods are discussed in Table 2.6[36].

Table 2.6: Different methods of hydrogen delivery [36]

	Pipeline	**Liquid (road)**	**Liquid (ship)**	**Tube trailer**
Advantages	– efficiency is high –high volumes – variable cost is low – also provides storage and buffering	– efficiency is high – volumes are higher as compared to compressed gas	– volumes are very high –International transport is convenient	– easy installation at small scales
Disadvantages	– high volumes of hydrogen are needed to justify pipeline costs – capital intensive – volume required increases with distance	– losses due to boil-off – expense and inefficient liquefaction process –iIncreases road traffic	– not feasible without large supply and demand existence – inexperience with LH_2 shipment – losses due to Boil-off are more notable than road	– energy inefficient –large capacities cannot be handled – increases traffic
Suitable for	– where pipeline storage is used – large and very large gas quantities	– where liquid storage is used – Large gas quantities	– international transport – Very large gas quantities	– small distances – Small gas quantities
Capacity	– up to 100,000 kg/h (3.9 GW)	– up to 4000 kg per truck	– up to 10 million kg per shipment	– up to 400 kg per truck
Capital costs	– \$0.1–2.0/kg hydrogen or more depends on distance and capacity – \$200,000–1,000,000 per kilometer	– \$0.3/kg hydrogen (excluding liquefaction plant) –\$300,000–400,000 per truck	– LNG barge could be 3–4 times higher for LH_2 barge – \$155 million	– \$0.10–0.40/kg –w\$300,000 per truck

2.11 Research Gap

The research on the feasibility of biohydrogen production utilizing the biomass resources available in Pakistan appears to be absent from existing literature. There is a lack of scholarly studies or publications that specifically investigate this topic within the context of Pakistan. The absence of such research highlights a significant knowledge gap in the field and emphasizes the need for further exploration and investigation to assess the viability and potential of biohydrogen production from the available biomass sources in Pakistan. Literature contains descriptions of different components of biohydrogen production processes for various biomasses. However, there is a lack of comprehensive research that explores the entire biohydrogen production process with the specific goal of obtaining pure hydrogen from a particular biomass. The purpose of this study is to address this research gap by providing an integrated analysis of biohydrogen production, specifically focusing on utilizing the most suitable biomass found in Pakistan as the raw material. Conducting this study would contribute valuable insights and generate new knowledge in biohydrogen production, specifically tailored to the unique circumstances and resources found within Pakistan.

2.12 Problem Statement

The objective of this study is to thoroughly examine the feasibility of biohydrogen production through the process of gasification, utilizing the most promising biomass resources available in Pakistan. Gasification is a well-known and established technology that converts biomass feedstock into a gaseous fuel known as syngas, which can be further processed to obtain hydrogen.

By focusing on the most promising biomass sources within Pakistan, such as agricultural residues, crop wastes, or dedicated energy crops, this study aims to assess their potential for biohydrogen production. Factors such as availability, abundance, sustainability, and compatibility with gasification processes will be carefully evaluated.

2.13 Objectives

Following objectives will be achieved through this study:

- We will measure the abundance of different crop wastes and analyze their ultimate and proximate analysis. Based on abundance and ultimate and proximate analysis we will select biomass for hydrogen production.
- Simulation of gasification process of selected biomass will be carried out to calculate the yield of synthesis gas obtained from biomass.
- Simulation of hydrogen enrichment process of synthesis gas will be carried out to calculate how much % of hydrogen has increased through enrichment process.
- Simulation of purification of enriched synthesis gas is carried out to obtain pure hydrogen and yield of purified hydrogen will be calculated.

CHAPTER 3: PROCESS DESCRIPTION

This chapter details the methodology used to simulate the gasification process, followed by the hydrogen enrichment process to obtain hydrogen-rich syngas, and the use of Pressure Swing Adsorption (PSA) technology for hydrogen purification.

3.1 Research methodology

Phase 1: Detailed literature review will be carried out for gap analysis in the available information on waste to biohydrogen production systems. Potential waste sources for generating biohydrogen in Pakistan will be identified through literature review and most feasible biowaste sources will be selected for biohydrogen production process modelling.

We will measure the abundance of different crop wastes and analyze their ultimate and proximate analysis. Based on abundance and ultimate and proximate analysis we will select biomass for hydrogen production.

Phase 2: The project will utilize specific bio-waste as biomass to produce biohydrogen. Through the analysis of bio-waste data, simulation studies will be conducted to assess the gasification technology. The simulation will involve the gasification process of the chosen biomass to determine the quantity of product gas obtained from it. Additionally, a sensitivity analysis of the gasification process will be performed.

Phase 3: The project will involve conducting simulations to explore the process of enriching the product gas with hydrogen, resulting in a synthesis gas that is rich in hydrogen. Parametric analysis of the hydrogen enrichment process will also be conducted.

Phase 4: The project will entail simulating the pressure swing adsorption process to obtain pure hydrogen. Additionally, a parametric analysis of the pressure swing adsorption process will be conducted.

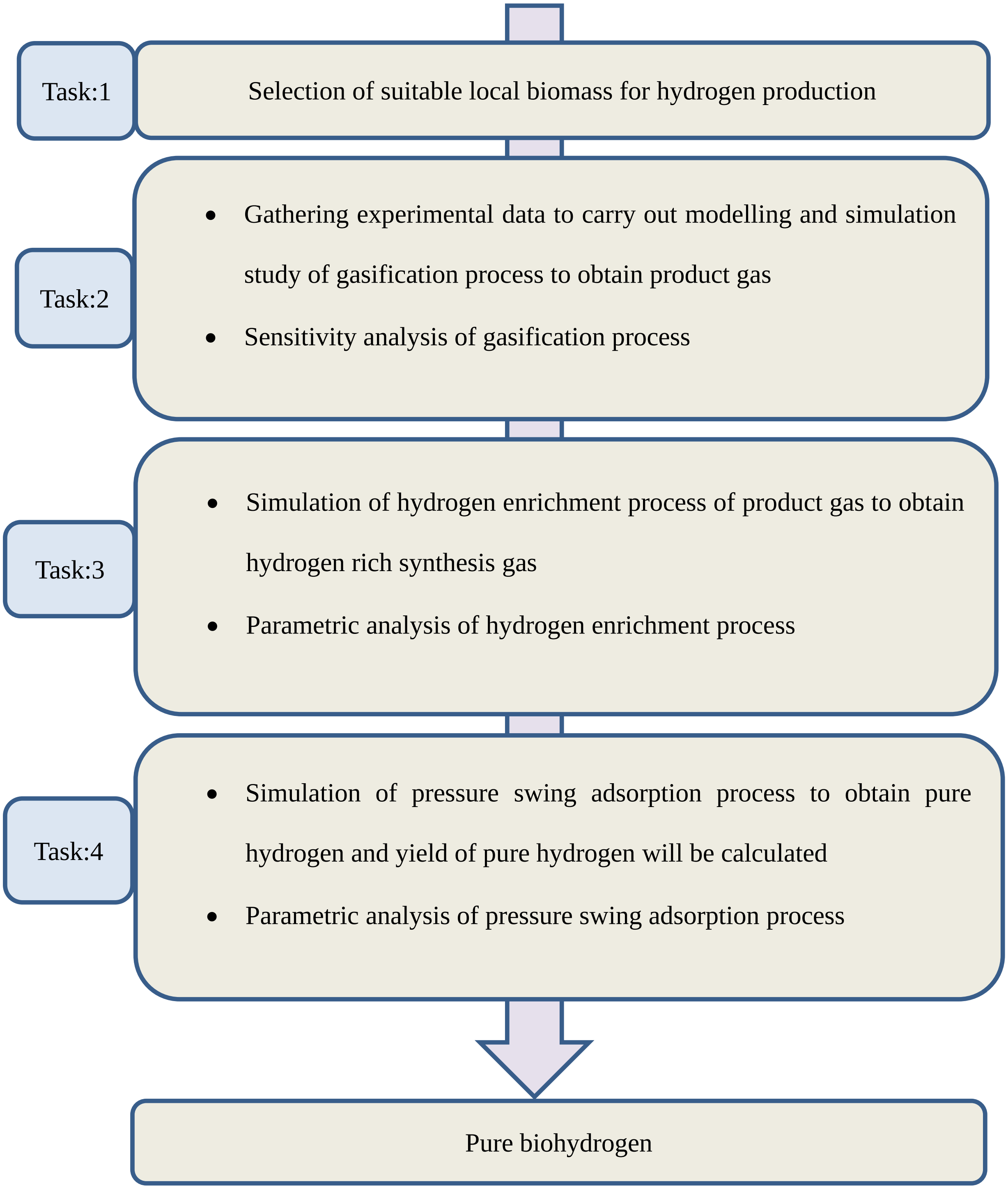


Figure 3.1: Research Methodology

3.2 Gasification process

The gasification process simulations were conducted using Aspen Plus, as depicted in Figure 3.1. The simulations incorporated the below mentioned assumptions and considerations: a zero-dimensional simulation was employed, encompassing biomass drying and gasification stages; the gasifier operated under steady-state conditions; the gasifier was assumed to maintain an isothermal state; the ash was regarded as inert; the char was assumed to consist entirely of carbon; all fuel-bound nitrogen (N_2), sulfur (S), and chlorine (Cl_2) were converted to ammonia (NH_3), hydrogen sulfide (H_2S), and hydrogen chloride (HCl) respectively; instantaneous occurrences of drying and pyrolysis were assumed; tar formation was disregarded; heat loss from the gasifier was not taken into account; and the thermodynamic model employed was the Peng-Robinson model with Boston-Mathias modifications (PR-BM)[11]. The gasification section contains the reactions that are presented in Table 2.4.

3.2.1 Circulating fluidized bed

Based on the restricted equilibrium with temperature approach [38], the simulation of the circulating fluidized bed reactor, as shown in Figure 3.1, was performed using a gasifier with similar characteristics that utilizes air as the fluidizing agent[37].

Incorporating the biomass properties into the simulation involved the utilization of two approaches. Firstly, the HCOALGEN and DCOALIGT property methods were employed to determine the enthalpy of formation, specific heat capacity, and density of the biomass. This was achieved by incorporating the heating value of the feedstock. Secondly, the ultimate and proximate analyses of the sugar cane bagasse, shown in Table 2.4, were incorporated in the non-conventional stream called WET-BIOM (wet biomass).

The biomass drying process consists of two blocks, namely DRIER and FLASH. In Figure 3.1, the DRIER block, known as RStoic, replicates the conversion process of a fraction of biomass into water. This conversion occurs when the biomass is exposed to either a flue gas or a nitrogen stream, symbolized by the DRY-GAS stream. The FLASH block, referred to as Flash2, is responsible for the separation of the dry biomass (DRY-BIOM) from a mixture comprising the removed moisture content and the drying media (WET-GAS).

A design specification is used to adjust the flow rate of WET-BIOM such that the flow rate of DRY-BIOM is 20 kg/h. Detailed information on setting up the drying stage can be found elsewhere[39]. In Figure 3.1, the simulation of the gasification stage encompasses four blocks: DECOMP, CSEP, GASIF, and GASIF2.

The DECOMP block uses biomass's ultimate analysis data to convert the non-conventional stream DRY-BIOM into conventional components. The CSEP block separates the char, assuming it is composed of only carbon.

Within the gasification process, the GASIF block employs RGibbs to facilitate the gasification reaction between the stream ELEM2 and the gasifying agents. In the case of a steam-blown gasifier, these gasifying agents include the material streams ELEM2 and STEAM, along with the heat streams QDECOMP and QEXT.

To reconcile the gas composition with experimental data, the GASIF2 block, also utilizing the RGibbs method, modifies the equilibrium of reactions R7 and R8 by employing temperature approaches. This approach has been suggested in earlier studies[38].

The gasification reactions listed in Table 2.4 are incorporated into the GASIF block utilizing a zero temperature approach[38][37][40]. To raise the temperature of the char separated in the CARBON stream to match the gasifier temperature prior to recirculation, the HEATER block is employed. The HEATER block effectively increases the temperature of the char to match the desired gasifier temperature.

Subsequently, the char is combined with the outlet stream GASI2OUT through the use of a Mixer block (MIX). The resulting stream, TOCYCLO, is directed into the CSEP block, specifically the CYCLONE component. This CYCLONE model simulates a cyclone mechanism responsible for separating the gas phase (stream SYNGAS) from the ash and char (stream SOLIDS).

The block split fraction is used to input the cyclone efficiency, which is set at 85%, an acceptable value for cyclone efficiency[37]. The ASHSEP block marks the point where the stream SOLIDS reaches and gets separated into ash and char.

Within the ASHSEP block, two streams are generated: RECYCLE and ASH. Most of the char intended for recirculation back into the gasifier GASIF is found in the RECYCLE stream. On the other hand, the ASH stream comprises primarily ash along with a small proportion of char, approximately 2% by weight.

The presence of char in the ASH stream is governed by a design specification that sets the acceptable char level. To model the removal of water from the syngas, the WATERSEP block is employed.

3.2.2 Simulation validation and sensitivity analysis

To verify the accuracy of the circulating fluidized bed simulation, its results were compared with the outcomes of a separate simulation involving a steam circulating fluidized bed with miscanthus as the feedstock[11]. During the process of validating the simulation, properties specific to miscanthus, such as ultimate and proximate analysis (as shown in Table 4), were employed, along with a biomass flow rate of 20 kg/h. Once the validation process was completed, the composition of bagasse, as outlined in Table 3.1, was substituted in place of the miscanthus composition.

Table 3.1: Proximate and ultimate analysis of Miscanthus[11].

Proximate Analysis	
Volatile matter (%)	80.2
Fixed carbon (%)	17.5
Ash (%)	2.3
Ultimate Analysis	
Moisture content (%)	9.4
C (%)	47.1
H (%)	5.38
O (%)	46.946
N (%)	0.44
S (%)	0.06
Cl (%)	0.074

In the sensitivity analysis, the influence of temperature (T), pressure (P), steam-to-biomass ratio (S/B), and moisture content (MC) on the composition of syngas (measured in terms of volume percentages of H_2, CO, CO_2, and CH_4 on a dry basis) was assessed. To isolate the impact of each parameter, the sensitivity analyses involved varying one factor at a time within the range specified in Table 3.2 while keeping the other factors constant, following the base case conditions.

Table 3.2: The simulation runs for the sensitivity analyses of the gasification process were conducted under the following conditions.

Parameter	Base case	Range	Mass flow rate of DRY-BIOM		
			Dry biomass (kg/h)	Moisture content (kg/h)	Total (kg/h)
T (°C)	850	750–950	18	2	20
P (bar)	1	1–15	18	2	20
S/B	1	0.5–1.5	18	2	20
MC (%)	10	10–30	18	Variable	Variable

3.3 Hydrogen enrichment process

Aspen Hysys was used to conduct simulations of the hydrogen enrichment process, as shown in Figure 3.2. The product gas from the gasifier was utilized as the fundamental feed stream for the hydrogen enrichment process. The product gas included several components, including H_2, CO, CO_2, CH_4, H_2O and N_2.

3.3.1 Enrichment process description

The gasifier's main product, referred to as Stream-100, is directed into a reformer unit, where the tar components present in the raw syngas undergo conversion. Gas cleaning units are employed to remove undesired components and other impurities from the syngas. To ensure the desired temperature is maintained for the water gas shift reactor, the temperature of the stream exiting the tar reformer is reduced using a heat exchanger, thereby preserving the inlet temperature.

Within the water gas shift (WGS) reactor, the carbon monoxide (CO) present in the gas mixture is converted to hydrogen (H_2) and carbon dioxide (CO_2) through the utilization of water. A separator is employed to separate water from the resulting gaseous mixture. The gas that is obtained after separation undergoes compression and is subsequently directed towards a pressure swing adsorption (PSA) unit.

To increase the hydrogen content in the syngas stream, a water gas shift reactor is utilized as the subsequent stage. However, if there is an insufficient amount of water to effectively convert the CO content in the inlet stream of the WGS reactor, additional superheated steam is introduced to the raw syngas from the tar reformer. This additional steam facilitates the water gas shift reaction.

The tar reformer and water gas shift reactor function at temperatures of approximately 700°C and 400°C, respectively. Both reactors operate at pressures close to atmospheric levels[20]. This study incorporates various assumptions for the process simulations, which have been detailed elsewhere[20]. The simulations utilize the Peng-Robinson equation of state as the chosen property fluid package method.

3.3.2 Simulation validation

The accuracy of the hydrogen enrichment process simulation was confirmed by comparing its results with those obtained from simulation for product gas obtained from gasification of wood[20].

3.4 Hydrogen purification process

Aspen Adsorption was utilized to simulate the hydrogen purification process. Currently, pressure swing adsorption technology is employed in more than 85% global hydrogen production units use for hydrogen purification[41]. To achieve a purity level of above 99%, either the PSA method or catalytic purification can be employed[42]. The breakthrough curve (bt curve), which is a plot of gas molar fraction at the outlet of the adsorption bed over time, is crucial in evaluating the performance of the adsorption process[43]. In Fig. 11(b), the evolution of molar fractions of each component in a quaternary gas mixture (H_2, CO_2, CO, N_2), simulated using Aspen Adsorption, is presented. The components H2O and CH4 are not considered in the purification process as they have very low concentrations at the outlet of the enrichment process. The IAST (Ideal Absorbed Solution Theory) is used to model the breakthrough curve, and the adsorbent properties parameters and adsorption bed characteristics are listed in Table 3.3. Details of the operational conditions used are shown in Table 3.4.

Table 3.3: Adsorption bed characteristics and adsorbent properties parameters

Parameter	Value	Parameter	Value
Internal bed diameter (cm)	2.1	Adsorbent particle radius (cm)	0.07
Bed length (cm)	100	Adsorbent specific heat capacity (MJ/kg/K)	0.00147
Wall thickness used of bed (cm)	0.22	Wall specific heat capacity (J/kg/k)	502.8
Inter-particle voidage (m^3void/m^3bed)	0.323	Heat transfer coefficient between wall and ambient (MW/m2/K)	1.00E-09
Intra-particle voidage (m^3void/m^3bed)	0.451	Constant for heat transfer coefficient (MW/m2/K)	1
Bulk solid density of adsorbent (kg/m^3)	650	Constant heat transfer coefficient between gas and wall (MW/kg/K)	1.00E-06
Wall thermal conductivity (W/m/k)	16	Wall density (kg/m3)	7830

Table 3.4: Operational conditions used for modelling of breakthrough curves of pressure swing adsorption process.

Feed Molar fraction	H_2:CO_2:CO:N_2=0.3822:0.2418:0.0431:0.3233
Feeding rate (kmol/hr)	0.00792582
Adsorption pressure (bar)	35
Feeding temperature (k)	298.16

CHAPTER 4: RESULTS AND DISCUSSION

In this chapter, a comprehensive sensitivity analysis of the gasification process is presented, aiming to assess the impact of various key parameters on the overall performance. The gasification process, which involves the conversion of biomass into hydrogen-rich gas through thermochemical reactions, is a complex and intricate process influenced by multiple factors.

Furthermore, parametric studies are conducted to investigate the enrichment and purification processes, which play a crucial role in obtaining high-purity hydrogen. Enrichment involves the removal of impurities and undesired gases from the gasification product, while purification focuses on further refining the gas to meet stringent quality standards.

4.1 Gasification process of sugarcane bagasse

Product gas of composition H_2 (52.6%), CH_4 (6.2%), CO (21.1%), N_2(0.084%) and CO_2 (20%) is obtained after gasification process at following conditions, T= 850°C, P=1 bar, S/B=1 and MC=10%.

Table 4.1: Streams operating conditions (Gasification process)

Stream name	**wet-biom**	**dry-gas**	**dry-out**	**dry-biom**	**elem**
Temperature (°C)	25	132.22	132.17	132.17	25
Pressure (kPa)	100	101.35	101.35	101.353	101.353
Molar Flow (kgmol/hr)	28.77 (kg/hr)	22679.6	22680.2	18 (kg/hr)	0.7627
Heat Flow (Btu/hr)	-5.4e+5	6.7e+7	6.7e+7	-3.7e+5	-275.9
Stream name	**elem2**	**gasif2 out**	**Tocyclo**	**syngas**	**dry syngas**
Temperature (°C)	25	850	825.7	825.676	825.67

Pressure (kPa)	101.353	100	100	99.99	99.99
Molar Flow (kgmol/hr)	0.76267	2.1744	2.1744	2.174	1.53
Heat Flow (Btu/hr)	-275.9	-2.4e+5	-2.4e+5	-2.4e+5	-1.1e+5
Stream name	**Solids**	**Recycle**	**Ash**	**H2O**	**Carbon 2**
Temperature (°C)	825.67	825.67	825.67	825.67	204.44
Pressure (kPa)	99.99	99.99	99.99	99.99	101.353
Molar Flow (kgmol/hr)	0.00044	1.49 (kg/hr)	0.00044	0.6424	1.8 (kg/hr)
Heat Flow (Btu/hr)	2091	2039	52.09	-1.3e+5	292
Stream name	**carbon**	**wet-gas**			
Temperature (°C)	25	132.172			
Pressure (kPa)	101.353	101.353			
Molar Flow (kgmol/hr)	1.8 (kg/hr)	22680.2			
Heat Flow (Btu/hr)	-1.6e+13	-6.7e+7			

Table 4.2: Stream compositions (Gasification process)

Stream name		**gasi2out**	**syngas**	**dry syngas**
Comp Mole Fraction	H_2	0.37031	0.37039	0.5258
	CH_4	0.044	0.044	0.062
	CO	0.1488	0.1488	0.211
	CO_2	0.1996	0.1411	0.200
	H_2O	0.2954	0.2955	0.00
	N_2	0.00059	0.00059	0.00083
	O_2	3.4e-18	3.4e-18	0.00

4.1.1 Sensitivity analyses of gasification process

The following sections discuss the sensitivity analyses conducted to evaluate the influence of parameter variations (temperature, pressure, steam-to-biomass ratio, and moisture content) on the concentrations of product gas constituents in the four proposed scenarios.

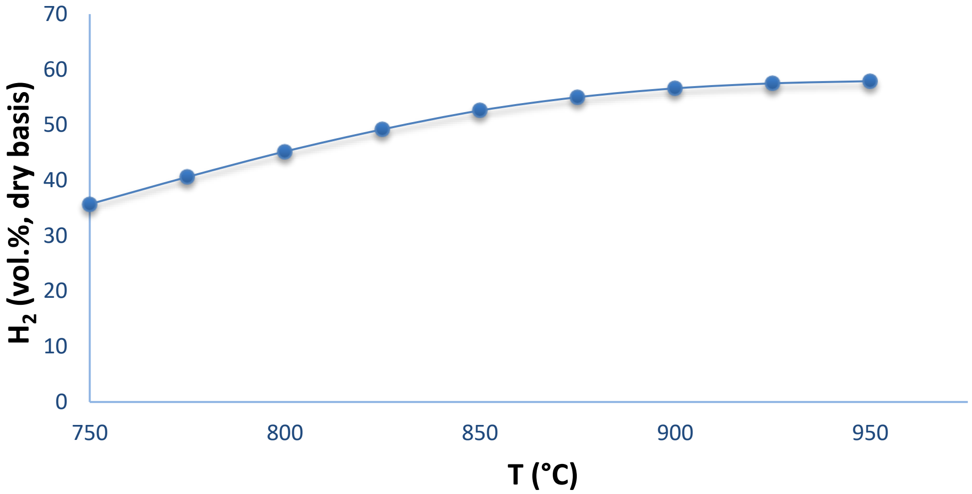
4.1.2 Effect of Temperature

As shown in Figure 4.1(a), an increase in temperature has a positive impact on the production of H_2. Le Chatelier's principle can elucidate this phenomenon by stating that in gas-phase systems, elevated temperatures promote the formation of reactants in exothermic reactions and the production of products in endothermic reactions.

When considering homogeneous reactions involving H_2, higher temperatures are advantageous for exothermic reactions such as R4 (H_2 partial combustion) and R7 (water-gas shift reaction). However, endothermic reactions like R8 and R9 (steam-methane reforming reactions) are not favored by increased temperatures.

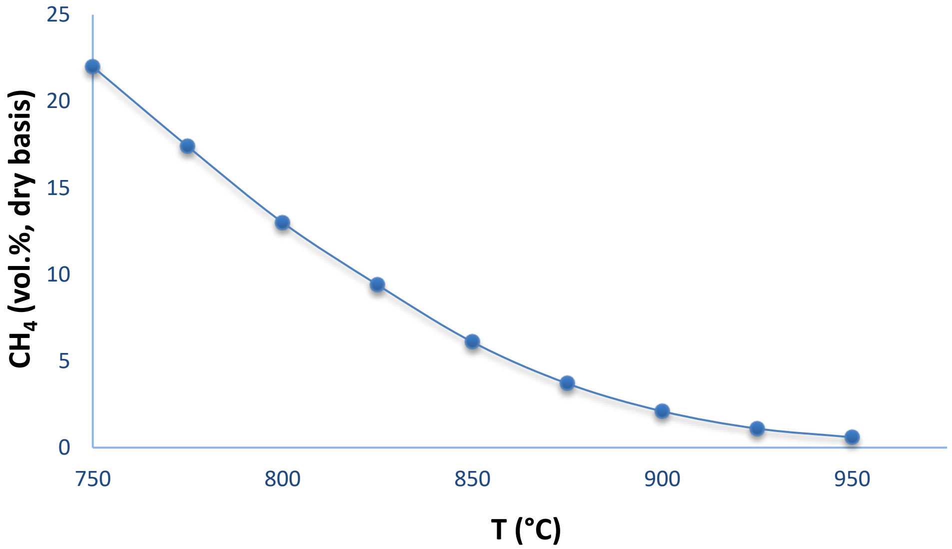
Despite reaction R7 consuming H_2 at higher temperatures, reactions R4, R8, and R9 produce a greater amount of H_2. This results in an overall increase in the H_2 content, as depicted in Figure 4.1(a). Multiple studies, both simulated [44],[38] and experimental [45],[46],[47],[48],[49] have reported consistent findings regarding the behavior of various biomass feedstocks, gasifying agents, and gasifiers.

(a)



70
60
50
40
30
20
10
0
H_2 (vol.%, dry basis)
750
800
850
900
950
T (°C)

(b)



25
20
15
10
5
0
CH_4 (vol.%, dry basis)
750
800
850
900
950
T (°C)

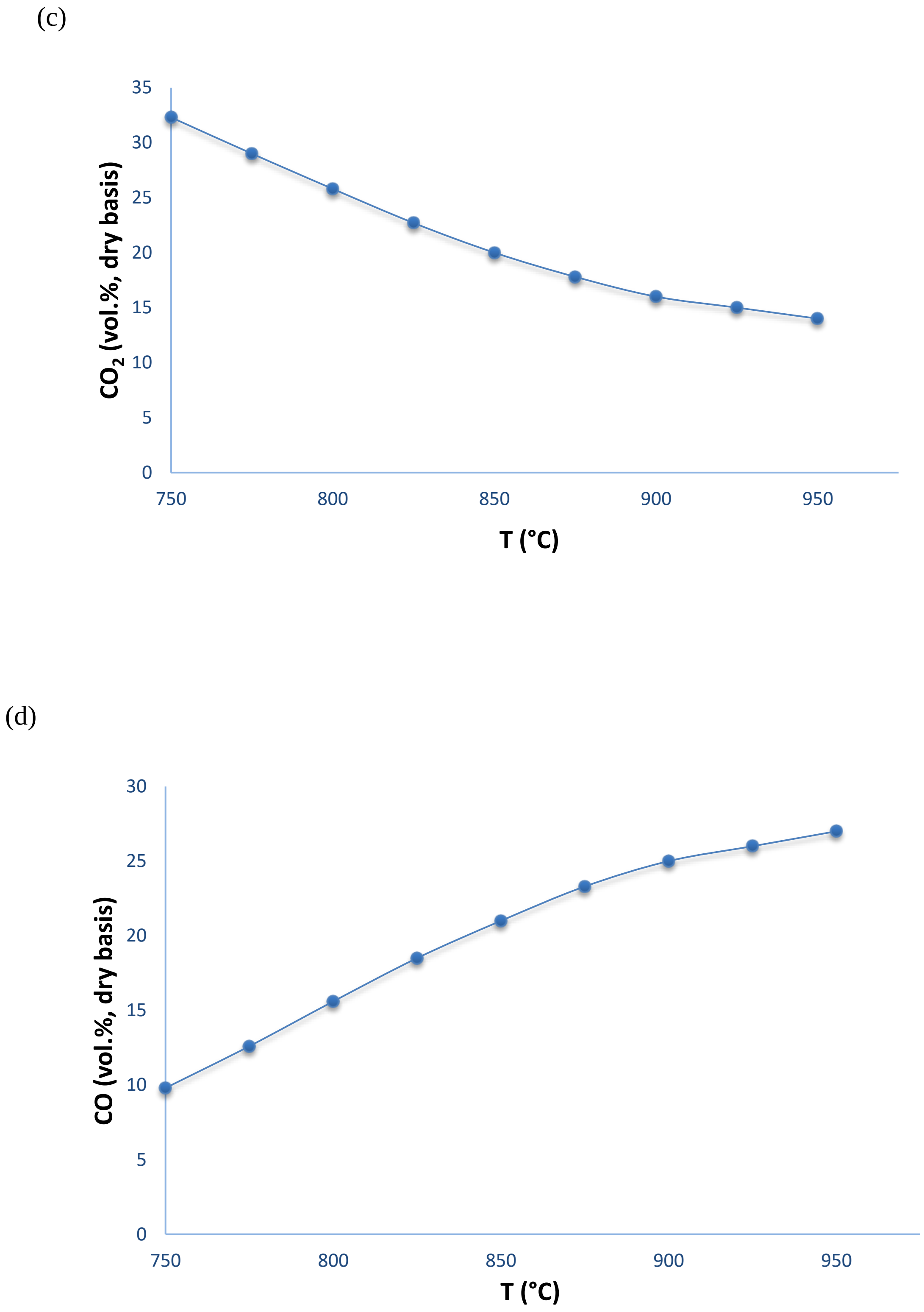


Figure 4.1: Effect of temperature on product gas (a) H_2 (b) CH_4 (c) CO_2 and (d) CO concentrations

As depicted in Figure 4.1(b), an increase in temperature has a negative effect on the concentration of CH_4. The reason for this is that higher temperatures facilitate the consumption of CH_4 due to its involvement in the endothermic steam-methane reforming reactions (R8 and R9), despite CH_4 being generated in the exothermic CH_4 combustion reaction (R10)[50].

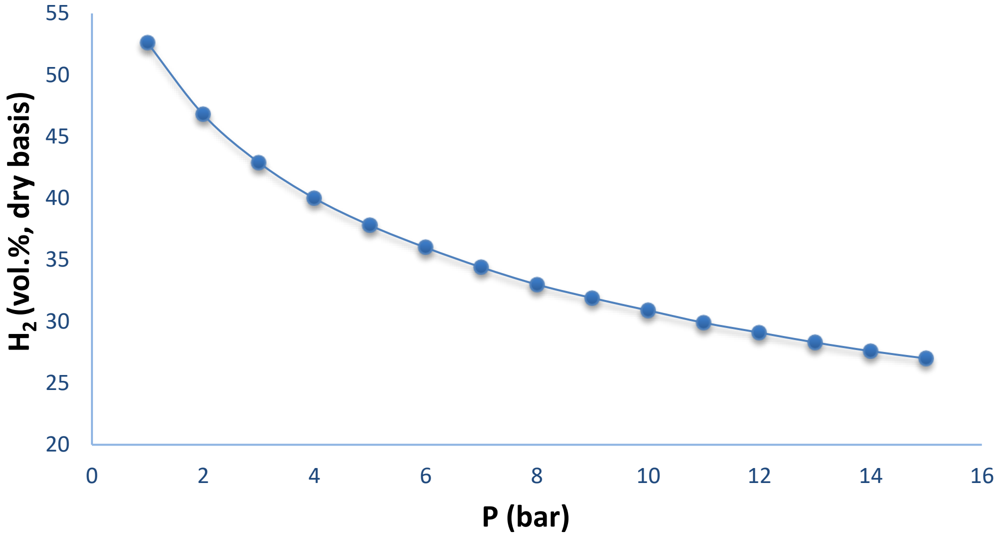
Figure 4.1(c) illustrates that an elevation in temperature adversely affects the concentration of CO_2. The reason for this is that higher temperatures promote the consumption of CO_2 in exothermic reactions such as CO combustion (R3), water-gas shift (R7), and CH_4 combustion (R10), even though temperature also results in CO_2 generation in the endothermic steam-methane reforming reaction (R9). This decrease in CO_2 content aligns with findings observed in other gasification studies[49].

Figure 4.1(d) shows that an increase in temperature has a positive effect on the concentration of CO. Higher temperatures promote CO production, which is consistent with the findings of previous studies[44], The shift towards CO formation at higher temperatures is attributed to the influence of temperature on the chemical equilibrium in both exothermic reactions (R3 and R7) and endothermic reactions (R6 and R8).

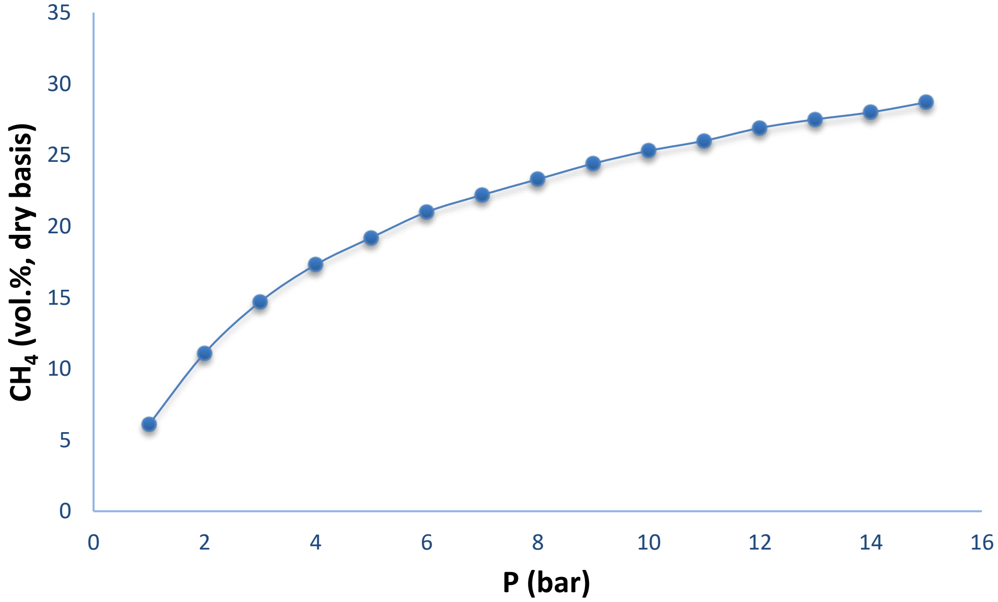
4.1.3 Effect of pressure

In line with Le Chatelier's principle, in gas-phase systems, an elevation in pressure promotes the formation of products with lower volumes in non-equimolar reactions, such as reactions R4, R8, and R9. Consequently, higher pressures cause a shift in the equilibrium towards H_2 consumption, as depicted in Figure 4.2(a). Other works[51], also observed an H_2 content reduction as pressure increases.

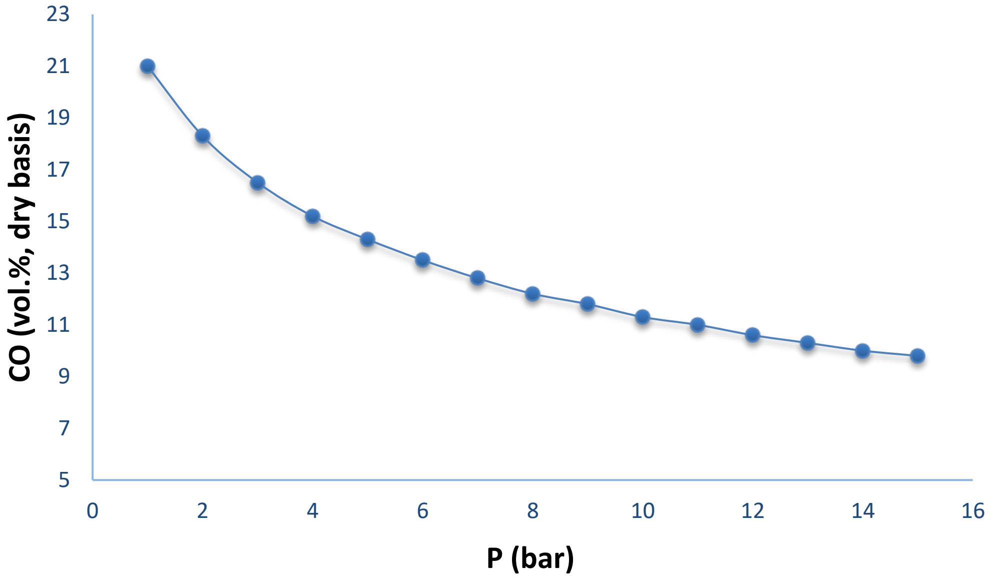
(a)


55
50
45
40
35
30
25
20
H_2 (vol.%, dry basis)
0
2
4
6
8
10
12
14
16
P (bar)

(b)


35
30
25
20
15
10
5
0
CH_4 (vol.%, dry basis)
0
2
4
6
8
10
12
14
16
P (bar)

(c)



(d)

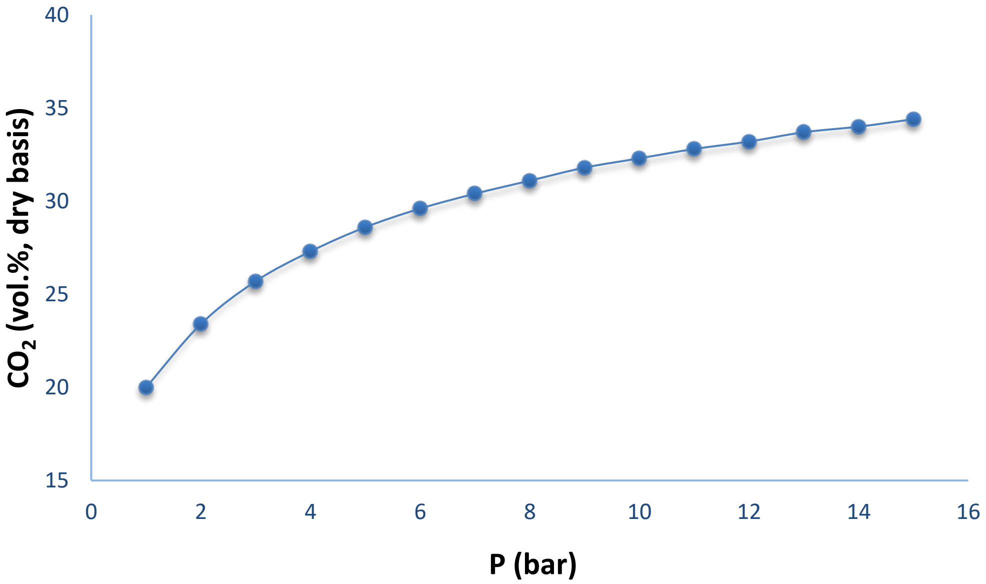


Figure 4.2: Effect of Pressure on product gas (a) H_2 (b) CH_4 (c) CO_2 and (d) CO concentrations

Figure 4.2(b) illustrates that an increase in pressure has a positive impact on the concentration of CH_4. In reactions involving non-equimolar gases, higher pressures promote the steam-methane reforming reactions (R8 and R9), which occur at lower volumes. As a result, there is an increase in the concentration of CH_4[52].

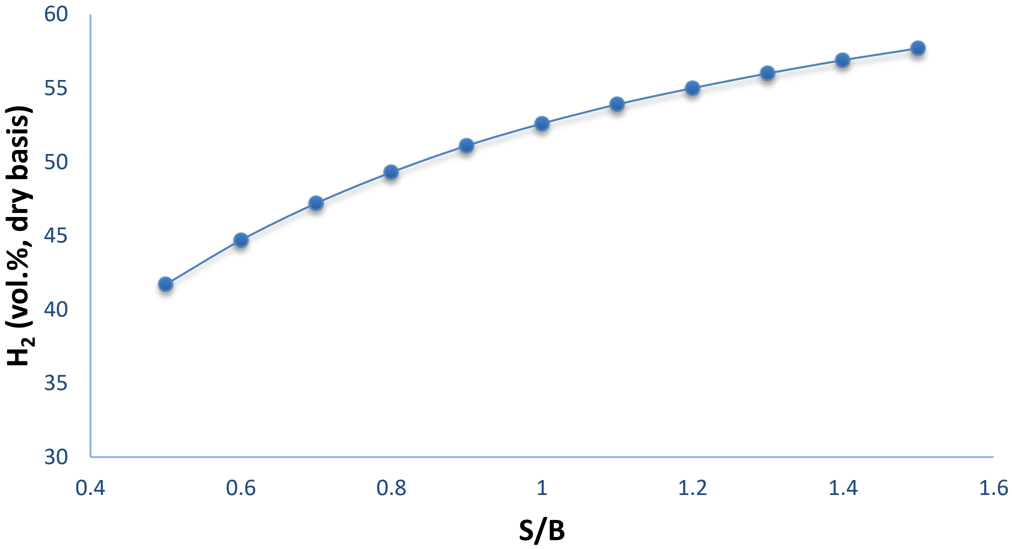
As depicted in Figure 4.2(c), an increase in pressure has a negative effect on the concentration of CO. Higher pressures promote CO consumption[49]. The reason for this is that CO is present on the side with higher volumes in non-equimolar gas-phase reactions involving CO as a participant, such as reactions R3 and R8. Consequently, higher pressures cause a shift in the equilibrium towards CO consumption.

As shown in Figure 4.2(d), an increase in pressure has a positive effect on the concentration of CO_2. Higher pressures promote CO_2 generation, which is consistent with the findings of previous studies[52].

4.1.4 Effect of steam to biomass ratio

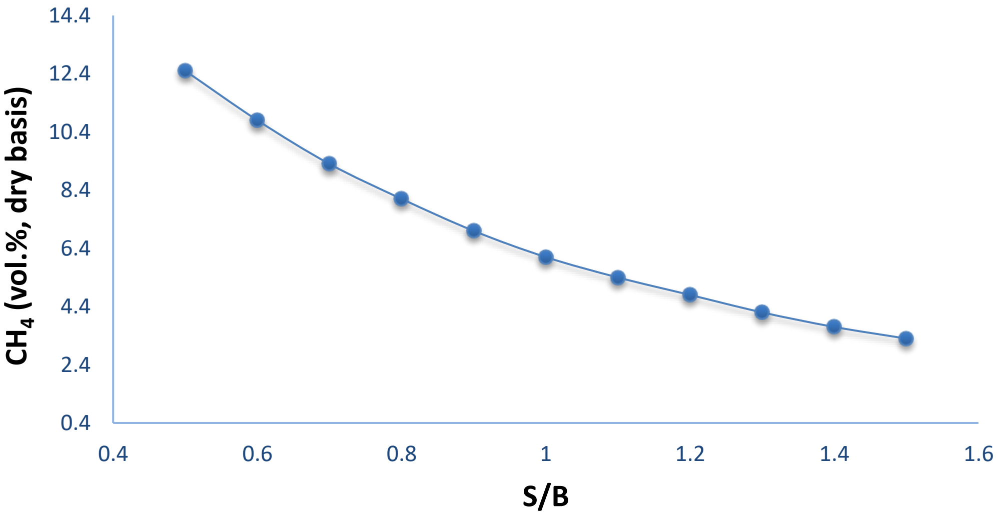
In relation to the steam-to-biomass (S/B) ratio (as depicted in Figure 4.3(a)), an increase in steam injection promotes H_2 production. This is due to the shifting of the water-gas shift reaction (R7) and steam-methane reforming reactions (R8 and R9) towards H_2 production. Similar trends have been observed in previous experimental [49] and simulation [50] studies conducted on different gasifier reactors.

(a)



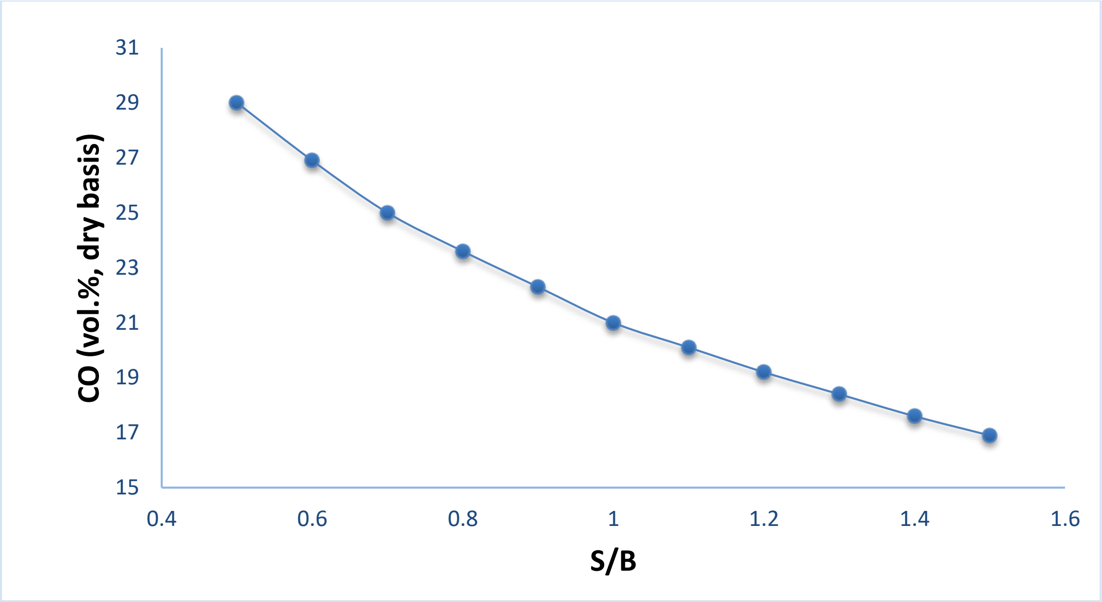
60
55
50
45
40
35
30
0.4
0.6
0.8
1
1.2
1.4
1.6
S/B
H_2 (vol.%, dry basis)

(b)



14.4
12.4
10.4
8.4
6.4
4.4
2.4
0.4
0.4
0.6
0.8
1
1.2
1.4
1.6
S/B
CH_4 (vol.%, dry basis)

(c)



(d)

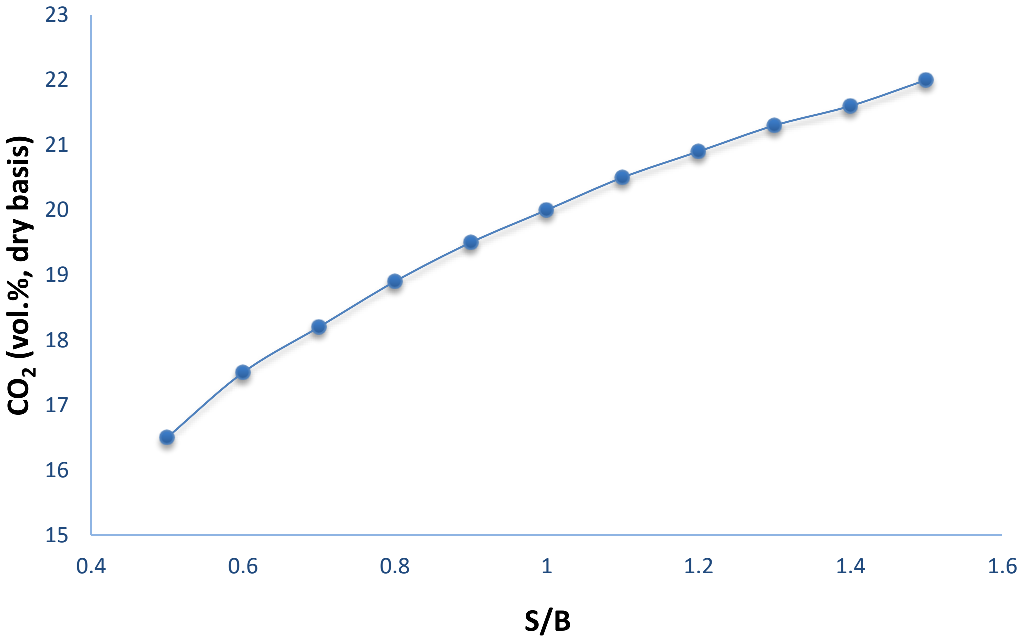


Figure 4.3: Effect of S/B on product gas (a) H_2 (b) CH_4 (c) CO_2 and (d) CO concentrations

The consumption of methane with the addition of steam is justified by steam-methane reforming reactions (R8 and R9), as shown in Figure 4.3(b).

The concentration of CO is adversely affected by the steam-to-biomass (S/B) ratio, as demonstrated in Figure 4.3(c). This is attributed to the water-gas shift reaction (R7), where CO is converted into CO_2 and H_2 in the presence of water molecules[53].

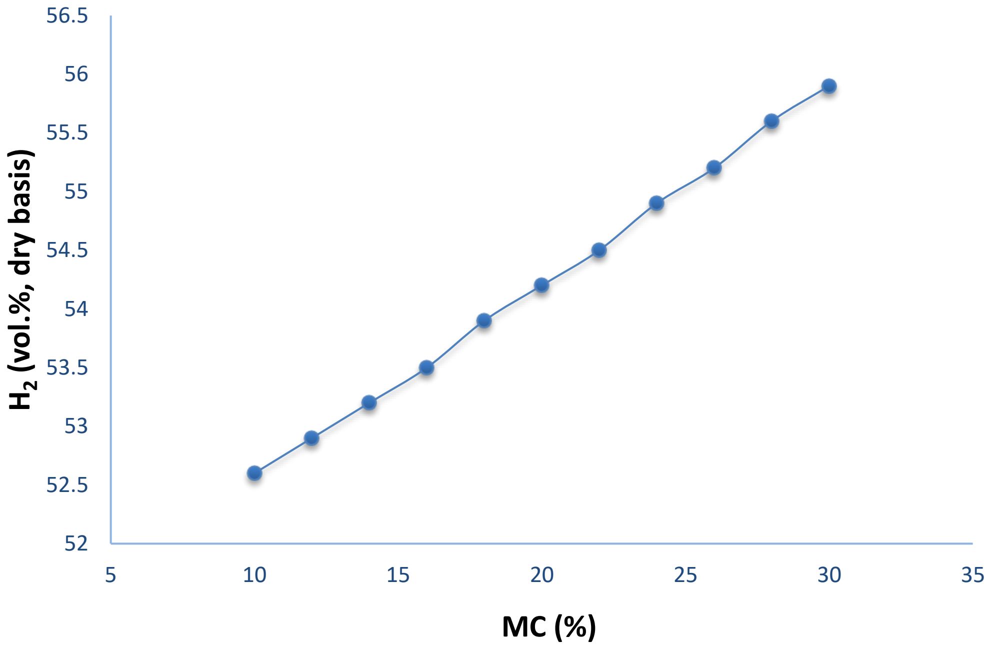
The concentration of CO_2 is positively influenced by the presence of steam and moisture, as depicted in Figure 4.3(d). This is because H_2O promotes the water-gas shift reaction (R7) and steam-methane reforming reactions (R9), leading to an increase in the formation of CO_2[50].

4.1.5 Effect of moisture content

It is worth mentioning that, despite moisture content being a form of water, it has a lesser influence on H_2 production compared to steam, as observed in Figure 4.4(a). This can be attributed to the lower temperature at which moisture content is introduced and its chemical binding to the biomass particles.

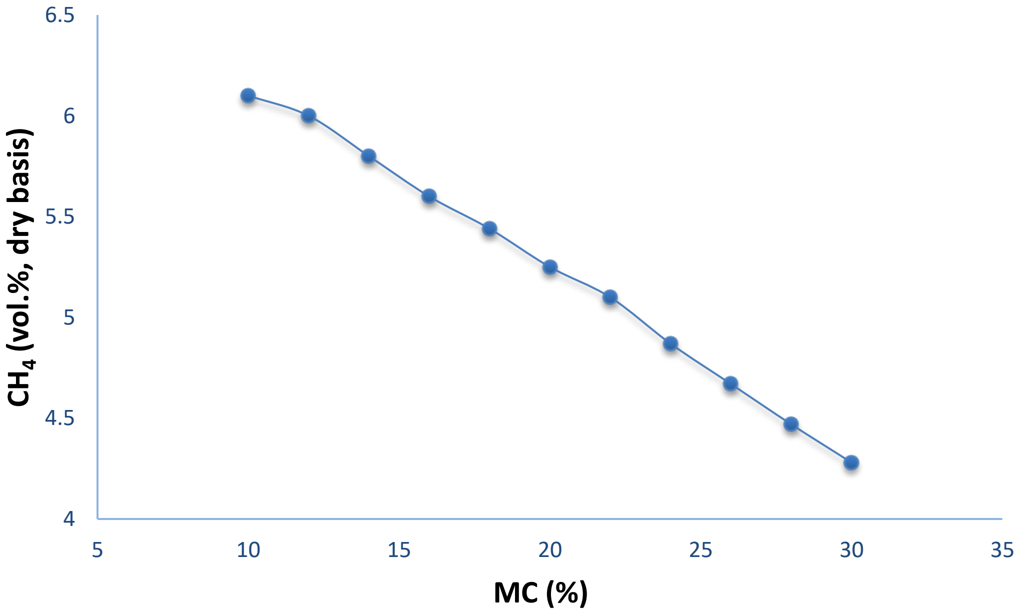
It is only available after evaporation and diffusion, while steam is readily available for reaction. This observation is supported by a separate study [37] that examined the effects of steam injection and biomass moisture content. The study concluded that steam exhibits higher reactivity compared to moisture.

(a)



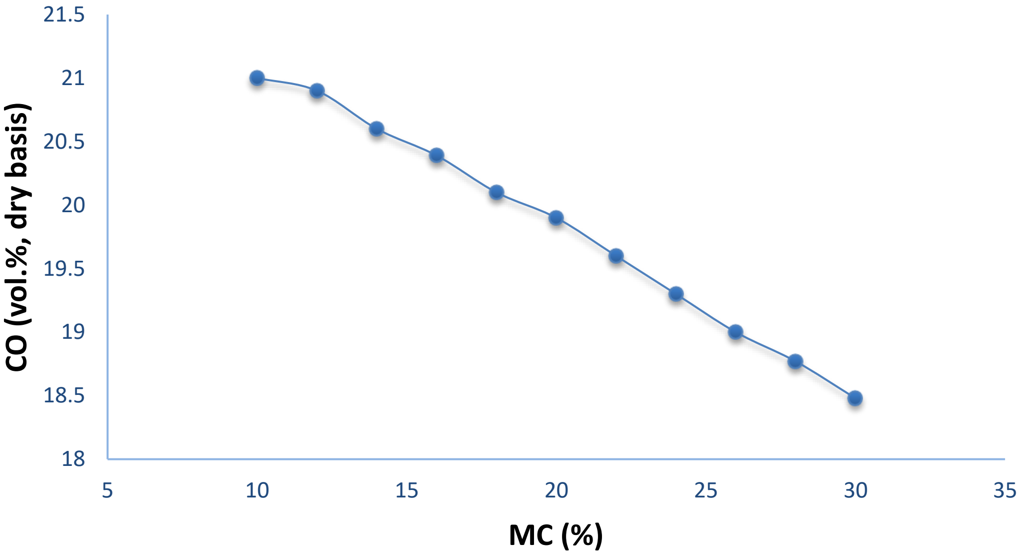
56.5
56
55.5
55
54.5
54
53.5
53
52.5
52
5
10
15
20
25
30
35
H_2 (vol.%, dry basis)
MC (%)

(b)



6.5
6
5.5
5
4.5
4
5
10
15
20
25
30
35
CH_4 (vol.%, dry basis)
MC (%)

(c)



(d)

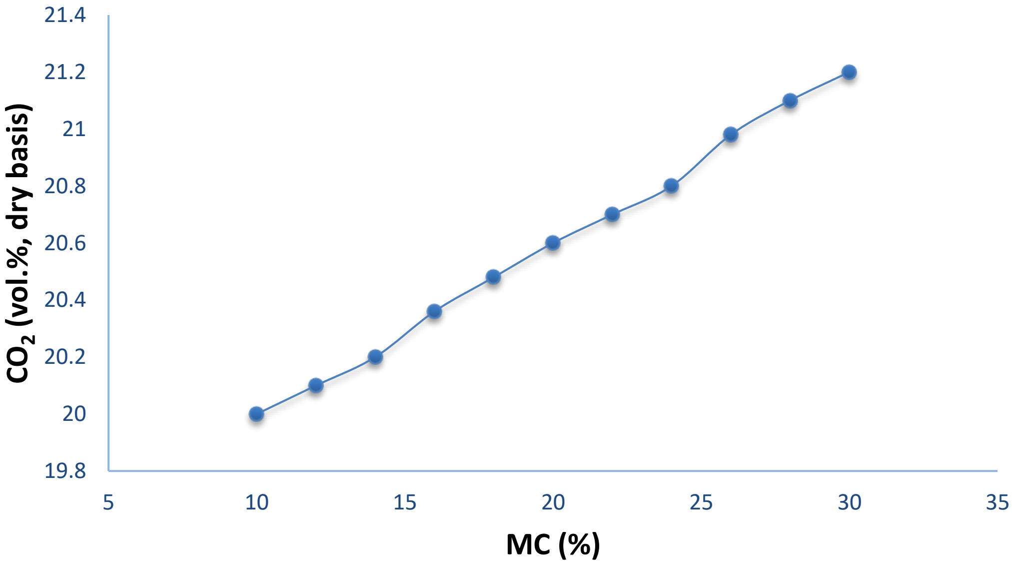


Figure 4.4: Effect of MC on product gas (a) H_2 (b) CH_4 (c) CO_2 and (d) CO concentrations

The consumption of methane in the presence of moisture can be attributed to the steam-methane reforming reactions (R8 and R9), as depicted in Figure 4.2(b).

When it comes to moisture content[51], both parameters have a detrimental effect on the CO composition, as shown in Figure 4.4(c), due to the water-gas shift reaction (R7) converting CO to CO_2 and H_2 in the presence of water molecules. However, steam exhibits a more pronounced effect compared to moisture content, indicating lower reactivity and availability of moisture content[37].

The presence of moisture has a beneficial impact on the CO_2 content, as depicted in Figure 4.4(d), as water molecules (H_2O) facilitate the water-gas shift (R7) and steam-methane reforming (R9) reactions[50].

4.2 Hydrogen enrichment of syngas

According to the preliminary results of process simulation data, the following composition values of hydrogen rich gas are obtained: H_2O (0.8%), H_2(61.7%), CO (12.3%), CO_2 (24%), CH_4(1.1%), N_2(0.06%).

The hydrogen enrichment process involves taking in a gas mixture from the gasifier, which includes H_2 (52.6%), CH_4 (6.2%), CO (21.1%), and CO_2 (20%), and subjecting it to a tar reformer (steam reformer), water gas shift (WGS) reactor, and separator. The water-gas shift (WGS) step entails an exothermic reaction wherein superheated steam reacts with carbon monoxide in the raw syngas, resulting in the production of hydrogen and carbon dioxide.

Parametric case studies were undertaken to examine the operation of the water-gas shift (WGS) process as a method of enriching hydrogen content[20].

Table 4.3: Streams operating conditions (Hydrogen enrichment process)

Stream name	**100**	**102**	**112**	**113**	**103**
Temperature (°C)	700	77.7	20	789	77.7
Pressure (kPa)	200	180	110	100	180
Molar Flow (kgmol/hr)	1.589	1.77	0.57	0.57	1.77
Heat Flow (kJ/hr)	-1.32e+5	-1.4e+5	-1.6e+5	-1.2e+5	-1.4e+5
Stream name	**B2**	**105**	**108**	**106**	**107**
Temperature (°C)	77.7	470	357	4	4
Pressure (kPa)	180	100	1200	90	90
Molar Flow (kgmol/hr)	0	2.34	2.04	2.4	2.04
Heat Flow (kJ/hr)	0	-2.6e+5	-2e+5	-3.1e+5	-2.2e+5
Stream name	**101**	**B4**	**109**	**104**	**111**
Temperature (°C)	813	4	25	286	20
Pressure (kPa)	200	90	1199	100	100
Molar Flow (kgmol/hr)	1.77	0.3	2.04	2.4	0.7
Heat Flow (kJ/hr)	-9.7e+4	-8.6e+4	-2.2e+5	-2.6e+5	-1.6e+5
Stream name	CW1in	CW1out	CW2in	CW2out	
Temperature (°C)	20	80	20	80	
Pressure (kPa)	110	109	110	109	
Molar Flow (kgmol/hr)	10.7	10.66	4.84	4.84	
Heat Flow (kJ/hr)	-3.1e+6	-3e+7	-1.39e+6	-1.4e+6	

Table 4.4: Stream compositions (Hydrogen enrichment process)

Stream name		**100**	**112**	**103**	**104**
Comp Mole Fraction	H_2	0.525	0.000	0.4929	0.3726
	CH_3	0.0619	0.000	0.0126	0.0095
	CO	0.21	0.000	0.3681	0.2783
	CO_2	0.1996	0.000	0.0548	0.0414
	H_2O	0.000	1	0.0709	0.2976
	N_2	0.0008	0.000	0.0008	0.0006
Stream name		**105**	**107**		
Comp Mole Fraction	H_2	0.5338	0.6127		
	CH_3	0.0095	0.0109		
	CO	0.1171	0.1344		
	CO_2	0.2026	0.2325		
	H2O	0.1364	0.0088		
	N_2	0.0006	0.0007		

Table 4.5: Energy Flows (Hydrogen enrichment process)

Unit Name	Q-102	Q-101	Q-103	Q-100	Q-104
Heat Flow (KJ/hr)	2.328e+4	4.987e+4	2.263e+4	3.422e+4	0.1354

4.3 Parametric case studies of enrichment process

In the parametric study, the inlet temperature of the water-gas shift (WGS) process was chosen as the independent variable, ranging from 200°C to 320°C. The effect of this variable has been observed on the dependent variables such as mole fractions of the WGS outlet stream (H_2, H_2O, CO, CO_2, CH_4 and N_2), WGS outlet H_2/CO and WGS conversion[20].

Figure 4.5 demonstrates the influence of WGS temperatures on CO conversion. As illustrated, the thermodynamic equilibrium conversion of carbon monoxide (CO) diminishes with an increase in the water-gas shift (WGS) inlet temperature.

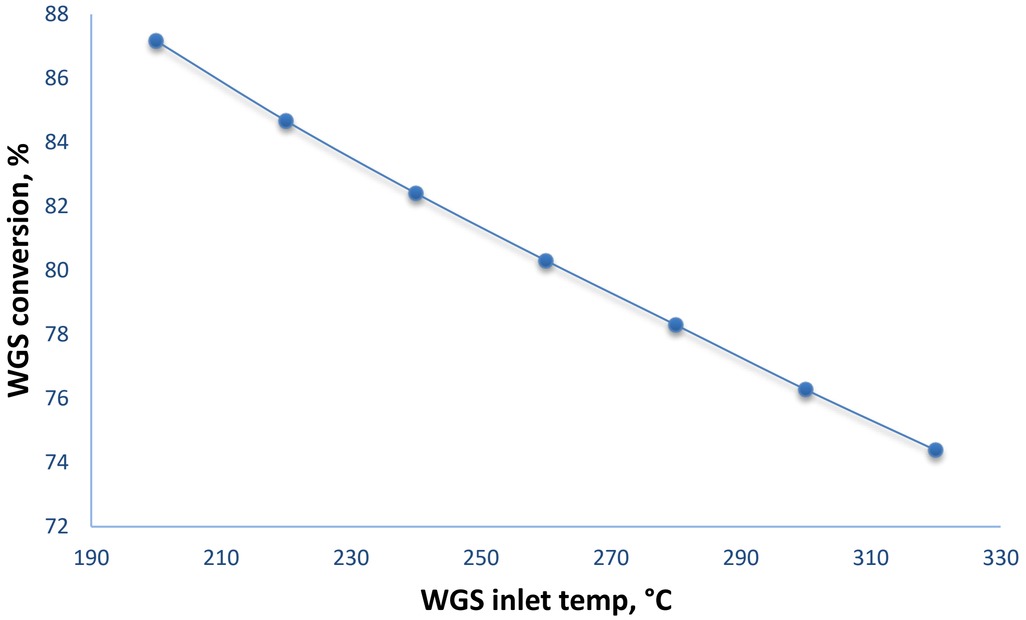


Figure 4.5: Effect of WGS inlet temp. on CO conversion

Figure 4.6 show that with increase in WGS inlet temperature, H_2/CO ratio decreases.

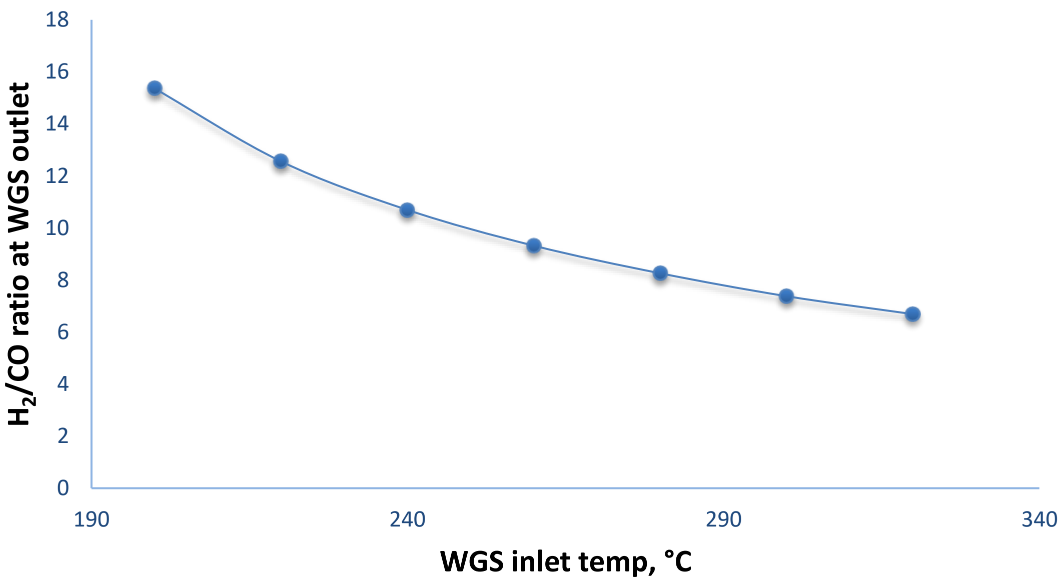


Figure 4.6: Effect of WGS inlet temp. on H_2/CO ratio

Figure 4.7 illustrates the influence of the water-gas shift (WGS) inlet temperature on the compositions of the outlet gases. It is evident from the figure that as the inlet temperature rises, the concentration of carbon monoxide (CO) increases, while the concentrations of hydrogen (H_2) and carbon dioxide (CO_2) decrease.

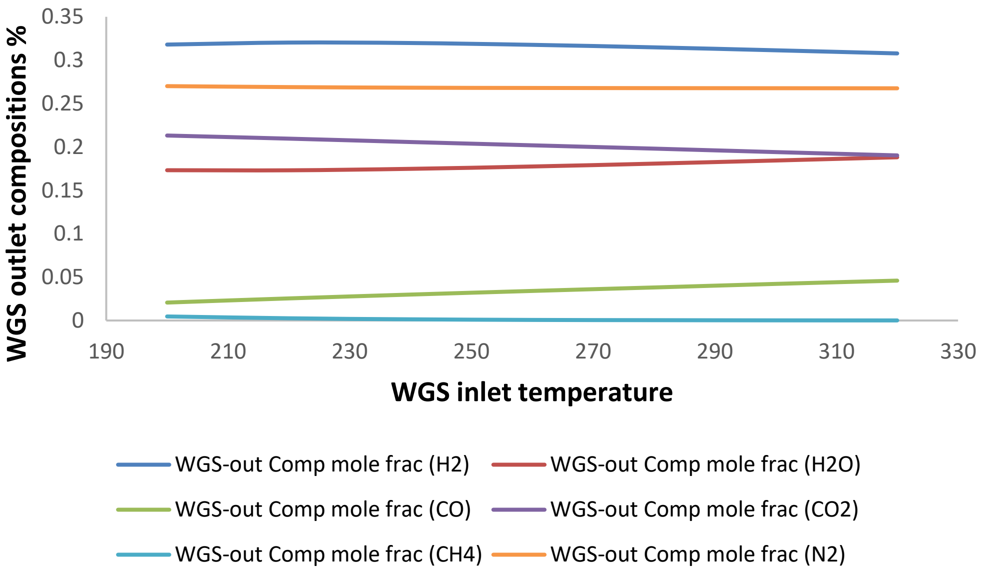


Figure 4.7: Effect of the WGS inlet temp. on the outlet composition

In another study, the molar flow of steam (Stream 112 - WGS inlet) was investigated as the independent variable. It was varied in 11 steps, with an increment of 0.05 kgmole/h, ranging from 0.6 to 1.1 kgmole/h. The dependent variable, WGS reactor conversion, was examined to observe its response to the changes in the independent variable[20].

The reaction set simulated for the water gas shift reactor (Eq. (4.1)) shows that to shift the equilibrium towards the production of more hydrogen, high-temperature steam injection is required.

$$CO + H_2O \rightarrow CO_2 + H_2O \qquad \text{(Eq. 4.1)}$$

CO conversion increases with increase in flowrate of steam as shown in Figure 4.8.

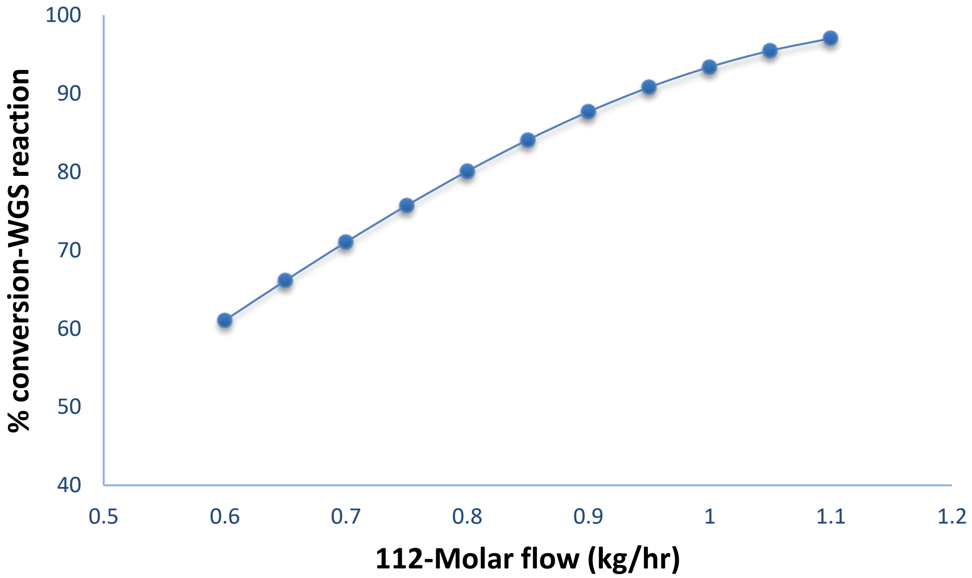


Figure 4.8: Effect of flowrate of steam on CO conversion

4.4 Hydrogen Purification process

In our study, we investigated the influence of the feeding flow rate and adsorption pressure on the breakthrough curves of gas adsorption.

4.5 Parametric study on breakthrough curves

A parametric study was conducted on the breakthrough curves, as depicted in Figure 4.10 (a, b, c), to assess the impact of feeding flow rate on the performance of hydrogen purification for H_2, CO_2, CO, and N_2. The breakthrough curves were analyzed under three different feeding flow rates (0.00592582 kmol/hr, 0.00792582 kmol/hr, 0.00992582 kmol/hr). It was observed that a faster feeding rate resulted in an earlier breakthrough due to a higher number of adsorbates in a certain time, which leads to faster equilibration of the adsorbent.

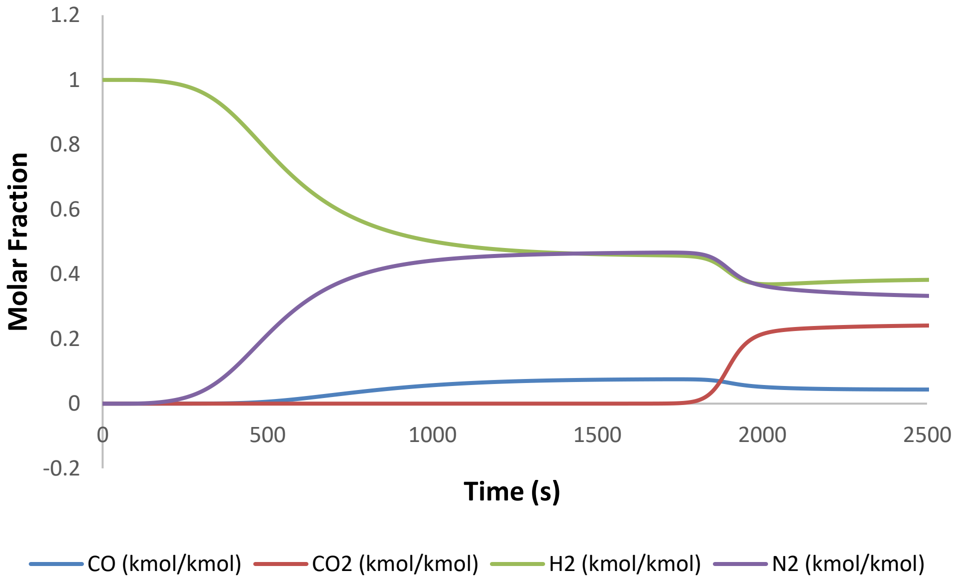


Figure 4.10(a): Breakthrough curve at feeding flowrate 0.00592582 kmol/hr and pressure 35bar

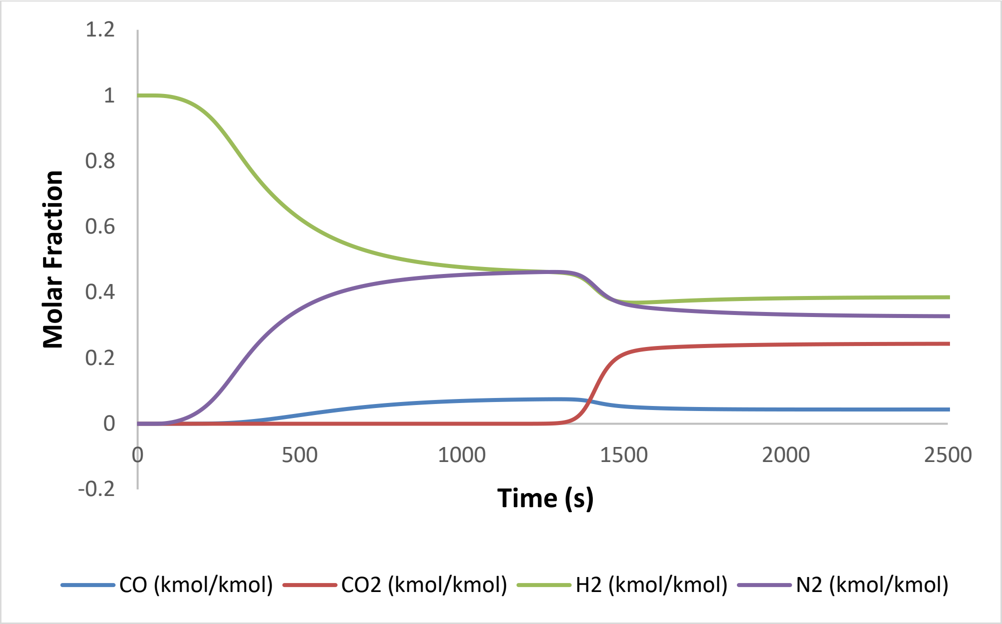


Figure 4.10(b): Breakthrough curve at feeding flowrate 0.00792582 kmol/hr and pressure 35bar

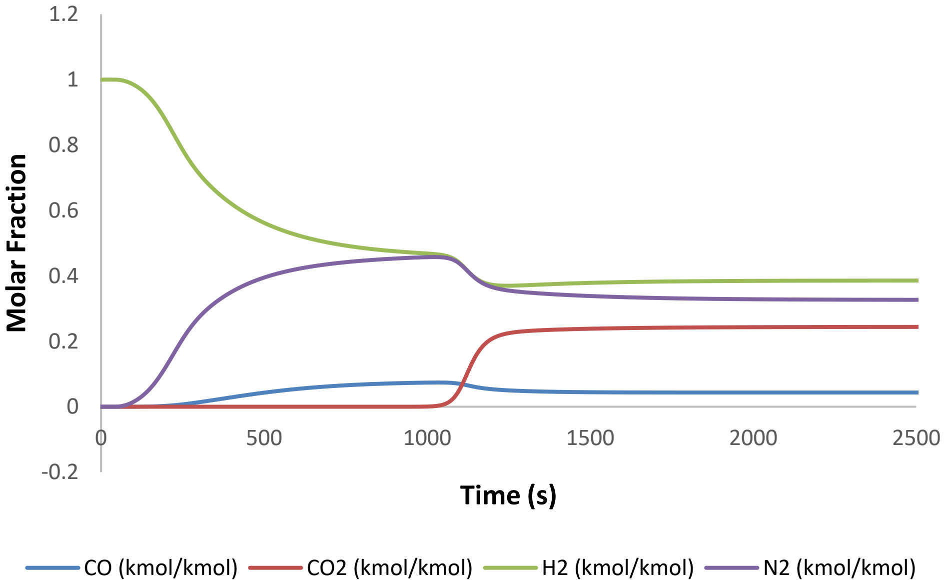


Figure 4.10(c): Breakthrough curve at feeding flowrate 0.00992582 kmol/hr and pressure 35bar

Figure 4.11 (a, b, c) illustrates the breakthrough curves for H_2, CO_2, CO, and N_2 at three different adsorption pressures (15 bar, 25 bar, 35 bar), aiming to examine their influence on hydrogen purification performance. It is noticeable that a higher adsorption pressure leads to a delayed breakthrough due to the increased adsorption capacity of the adsorbent.

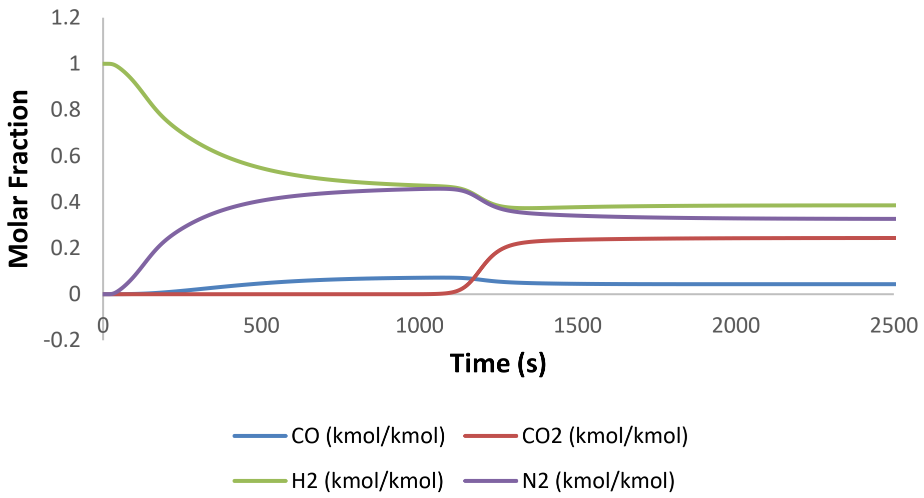


Figure 4.11(a): Breakthrough curve at pressure 15bar and feeding flowrate 0.00792582 kmol/hr

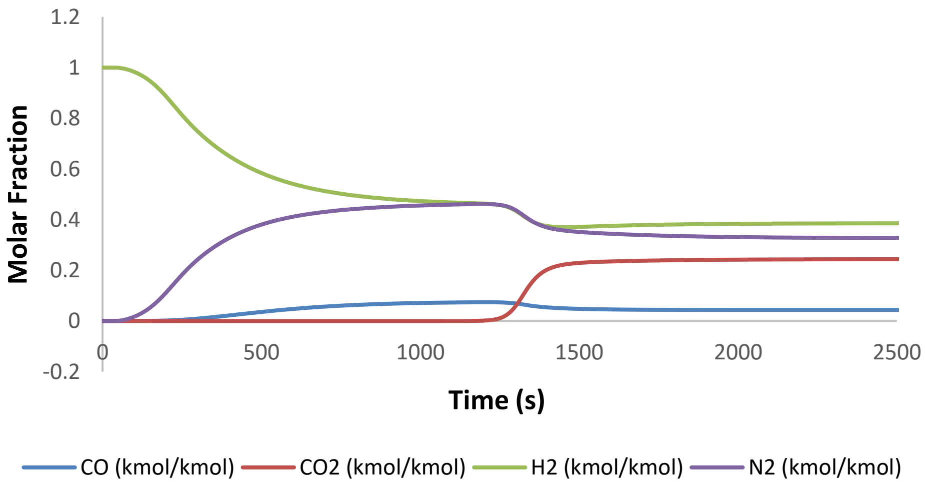


Figure 4.11(b): Breakthrough curve at pressure 25bar and feeding flowrate 0.00792582 kmol/hr

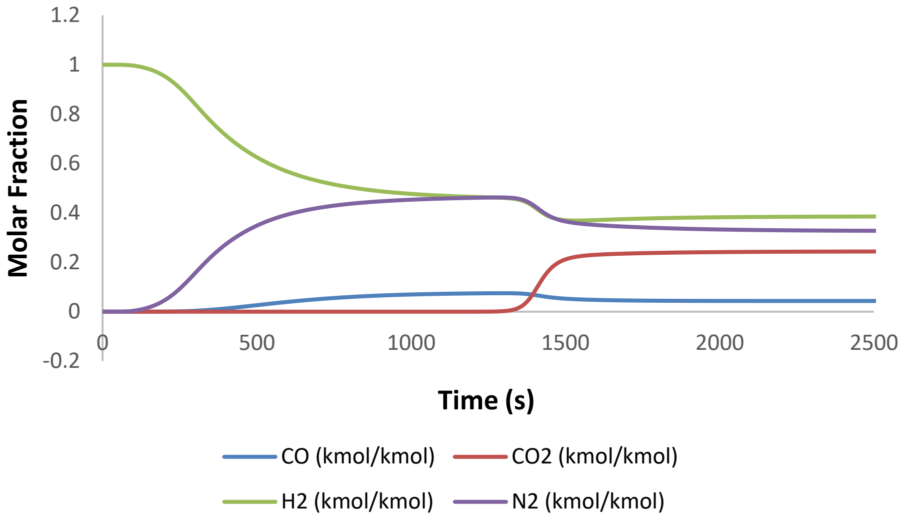


Figure 4.11(c): Breakthrough curve at pressure 35bar and feeding flowrate 0.00792582 kmol/hr

SUMMARY OF RESEARCH WORK

In this study, we conducted a comprehensive numerical investigation into the process of integrated biohydrogen production through gasification, utilizing sugarcane bagasse as a biomass source. To simulate and analyze the various processes involved in hydrogen production, including gasification, hydrogen enrichment, and hydrogen purification, we employed Aspen Plus/Hysys/Adsorption software. Process modeling and simulation play a crucial role in predicting system behavior under different operating conditions and exploring the impacts of parameter variations.

To obtain the desired product gas, the biomass residue was fed into a steam-blown circulating fluidized bed gasifier. Through sensitivity analysis of the gasification process, we discovered that increasing the temperature and steam-to-biomass ratio had a positive effect on hydrogen production. Conversely, an increase in gasifier pressure negatively impacted hydrogen production.

Subsequently, the product gas was directed into the hydrogen enrichment process, where it underwent processing to eliminate hydrocarbon content and underwent the water-gas shift reaction to generate hydrogen-rich synthesis gas. The parametric analyses conducted on the enrichment process revealed that a lower inlet temperature for the water-gas shift reactor and a higher steam flow rate were found to be beneficial for effective hydrogen enrichment.

Finally, the synthesis gas was introduced into the pressure swing adsorber, which facilitated the production of hydrogen with a purity exceeding 99%. Through a parametric analysis of the purification process, we determined that higher adsorber pressure and lower syngas flow rate resulted in delayed breakthrough points.

CHAPTER 5: CONCLUSIONS AND FURTURE RECOMMENDATION

This chapter discusses the conclusion and future recommendations.

5.1 Conclusion

The objective of this study was to use Aspen Plus™ to simulate various sugarcane bagasse gasification scenarios. Specifically, this study focuses on the impact of operating parameters, such as temperature, pressure, steam-to-biomass ratio, and moisture content, on the composition of product gas. Sensitivity analyses were conducted to analyze these effects. The results demonstrated the significant impact of temperature (T) on increasing CO content and reducing CO_2 formation, particularly within the temperature range of 750-950°C for the CFB steam-only scenario. Conversely, the steam-to-biomass ratio (S/B) was identified as a key parameter for adjusting the H_2/CO ratio of the syngas. Although moisture content (MC) is a form of water, its effect was found to be less significant compared to S/B due to its lower reactivity. The circulating fluidized bed technology was used to obtain product gas, which consisted of H_2 (52.6%), CH_4 (6.2%), CO (21.1%), N_2(0.084%) and CO_2 (20%).

This research involved the development of an integrated chemical process simulation model using Aspen HYSYS software to enhance hydrogen production from the gasification process. The simulations were conducted under steady-state conditions. The study focused on examining the impact of key parameters, including the temperature of the water-gas shift (WGS) reactor and steam flow rate, on the concentrations of hydrogen-rich syngas, reaction conversions, and the H_2/CO ratio.

The results of the study revealed that higher temperatures in the water-gas shift (WGS) reactor led to a slight decrease in hydrogen content. The thermodynamic equilibrium conversion of carbon monoxide (CO) showed a decreasing trend between 200°C and 320°C. Similarly, the H_2/CO ratio at the outlet stream of the WGS reactor exhibited a decrease within the same temperature range. Based on the initial findings from the conceptual process simulation model using Aspen HYSYS, the composition of the hydrogen-rich gas was determined to be approximately 0.8% H_2O, 61.7% H_2, 12.3% CO, 24% CO_2, 1.1% CH_4, and 0.06% N_2.

The Aspen Adsorption module was utilized to purify hydrogen-rich gas, resulting in hydrogen with a purity exceeding 99%. Our study involved a parametric analysis of breakthrough curves. In the breakthrough curve simulations, we employed three distinct pressures and gas feeding rates, which revealed that lower pressure and faster feeding flow rates led to earlier breakthrough points.

5.2 Future work

The future holds promising opportunities for utilizing different biomasses in the production of biohydrogen through the implementation of gasification technology. Gasification is a thermochemical process that converts solid biomass into a mixture of gases, including hydrogen, carbon monoxide, and methane. By harnessing this technology, Pakistan can tap into its abundant biomass resources, such as agricultural waste, forestry residues, and energy crops, to generate clean and sustainable biohydrogen.

Biohydrogen production through gasification offers several advantages. Firstly, it provides an alternative to fossil fuels, reducing greenhouse gas emissions and mitigating the impact of climate change. Secondly, biomasses are renewable resources, which ensures a continuous and sustainable supply for biohydrogen production. Moreover, the utilization of biomass residues helps manage waste and promotes the efficient use of available resources.

To establish an effective hydrogen economy structure in Pakistan, it is crucial to develop a strategy for hydrogen storage and transportation. Hydrogen has low energy density, making its storage and transportation challenging. However, various methods can be explored, such as compressed gas storage, liquid hydrogen storage, and solid-state hydrogen storage. Each method has its advantages and limitations, and a comprehensive cost and benefit analysis can help determine the most suitable approach for Pakistan's specific needs and infrastructure.

Furthermore, the transportation of hydrogen requires careful planning and infrastructure development. This includes establishing hydrogen refueling stations, upgrading pipelines or implementing alternative transportation methods like hydrogen fuel cell vehicles. Assessing the costs and benefits associated with different transportation options will enable policymakers to make informed decisions regarding the most efficient and economically viable strategies.

Conducting a thorough cost and benefit analysis is crucial in designing a robust and sustainable hydrogen economy structure for Pakistan. It allows policymakers and stakeholders to evaluate the economic feasibility, environmental impact, and potential social benefits of implementing biohydrogen production, storage, and transportation systems. Additionally, it helps identify any potential challenges or barriers and provides insights into necessary policy frameworks, incentives, and investment opportunities.

By embracing gasification technology for biohydrogen production and employing a well-designed strategy for hydrogen storage and transportation, Pakistan can unlock the potential of its biomass resources while contributing to a cleaner and more sustainable energy future. This will not only reduce dependence on fossil fuels but also stimulate economic growth, create employment opportunities, and foster innovation in the renewable energy sector.

REFERENCES

[1] Sun H, Ebadi AG, Toughani M, Nowdeh SA, Naderipour A, Abdullah A. Designing framework of hybrid photovoltaic-biowaste energy system with hydrogen storage considering economic and technical indices using whale optimization algorithm. Energy 2022;238:121555. https://doi.org/10.1016/j.energy.2021.121555.

[2] Qyyum MA, Dickson R, Ali Shah SF, Niaz H, Khan A, Liu JJ, et al. Availability, versatility, and viability of feedstocks for hydrogen production: Product space perspective. Renew Sustain Energy Rev 2021;145:110843. https://doi.org/10.1016/j.rser.2021.110843.

[3] Meher Kotay S, Das D. Biohydrogen as a renewable energy resource-Prospects and potentials. Int J Hydrogen Energy 2008;33:258–63. https://doi.org/10.1016/j.ijhydene.2007.07.031.

[4] Rathore D, Singh A, Dahiya D, Nigam PS. Sustainability of biohydrogen as fuel: Present scenario and future perspective. AIMS Energy 2019;7:1–19. https://doi.org/10.3934/energy.2019.1.1.

[5] Kothari R, Singh DP, Tyagi V V., Tyagi SK. Fermentative hydrogen production - An alternative clean energy source. Renew Sustain Energy Rev 2012;16:2337–46. https://doi.org/10.1016/j.rser.2012.01.002.

[6] Grey, blue, green – the many colours of hydrogen explained | World Economic Forum n.d. https://www.weforum.org/agenda/2021/07/clean-energy-green-hydrogen/ (accessed October 15, 2021).

[7] Levin DB, Pitt L, Love M. Biohydrogen production: Prospects and limitations to practical application. Int J Hydrogen Energy 2004;29:173–85. https://doi.org/10.1016/S0360-3199(03)00094-6.

[8] Pan A, Liu J, Liu Z, Yang Y, Yang X, Zhang M. Application of Hydrogen Energy and Review

of Current Conditions. IOP Conf Ser Earth Environ Sci 2020;526. https://doi.org/10.1088/1755-1315/526/1/012124.

[9] Community Research and Development Information Service, CANEBIOFUEL Report Summary, (2018) n.d.

[10] Food and Agriculture Organization of the United Nations, Crops, http://www.fao. org/faostat/en/#data/QC/visualize, (2018) , Accessed date: 1 January 2018 n.d.

[11] Motta IL, Miranda NT, Maciel Filho R, Wolf Maciel MR. Sugarcane bagasse gasification: Simulation and analysis of different operating parameters, fluidizing media, and gasifier types. Biomass and Bioenergy 2019;122:433–45. https://doi.org/10.1016/j.biombioe.2019.01.051.

[12] Daood SS, Munir S, Nimmo W, Gibbs BM. Char oxidation study of sugar cane bagasse, cotton stalk and Pakistani coal under 1% and 3% oxygen concentrations. Biomass and Bioenergy 2010;34:263–71. https://doi.org/10.1016/j.biombioe.2009.10.014.

[13] Naqvi SR, Jamshaid S, Naqvi M, Farooq W, Niazi MBK, Aman Z, et al. Potential of biomass for bioenergy in Pakistan based on present case and future perspectives. Renew Sustain Energy Rev 2018;81:1247–58. https://doi.org/10.1016/j.rser.2017.08.012.

[14] Singh H, Sapra K, Sidhu BS. Evaluation and Characterization of Different Biomass Residues through Proximate & Ultimate Analysis and Heating Value. Asian J Eng Appl Technol 2013;2:6–10.

[15] Garivait S, Chaiyo U, Patumsawad S, Deakhuntod J. Physical and Chemical Properties of Thai Biomass Fuels from Agricultural Residues. Sustain Energy Environ 2006;048:48–1.

[16] Balaji RK, Rajan KP, Ragula UBR. Modeling & optimization of renewable hydrogen production from biomass via anaerobic digestion & dry reformation. Int J Hydrogen Energy 2020;45:18226–40. https://doi.org/10.1016/j.ijhydene.2019.08.209.

[17] Ghimire A, Frunzo L, Pirozzi F, Trably E, Escudie R, Lens PNL, et al. A review on dark fermentative biohydrogen production from organic biomass: Process parameters and use of by-products. Appl Energy 2015;144:73–95. https://doi.org/10.1016/j.apenergy.2015.01.045.

[18] Energy Report 2011. World energy council Turkish national committee (in Turkish). 2011 n.d.

[19] Cannon J. Clean hydrogen transportation: a market opportunity for renewable energy. REPP Issue Brief No 1997;7:20e1 n.d.

[20] Ersöz A, DurakÇetin Y, Sarıoğlan A, Turan AZ, Mert MS, Yüksel F, et al. Investigation of a novel & integrated simulation model for hydrogen production from lignocellulosic biomass. Int J Hydrogen Energy 2018;43:1081–93. https://doi.org/10.1016/j.ijhydene.2017.11.017.

[21] I.L. Motta, N.T. Miranda, R. Maciel Filho, M.R. Wolf Maciel, Biomass gasification in fluidized beds: a review of biomass moisture content and operating pressure effects, Renew. Sustain. Energy Rev. 94 (2018) 998–1023, https://doi.org/10.1016/j.rser. 2018. n.d.

[22] Motta IL, Miranda NT, Maciel Filho R, Wolf Maciel MR. Sugarcane bagasse gasification: Simulation and analysis of different operating parameters, fluidizing media, and gasifier types. Biomass and Bioenergy 2019;122:433–45. https://doi.org/10.1016/j.biombioe.2019.01.051.

[23] A. Molino, S. Chianese, D. Musmarra, Biomass gasification technology: the state of the art overview, J. Energy Chem. 25 (2016) 10–25, https://doi.org/10.1016/j. jechem.2015.11.005 n.d.

[24] F. Monlau, A. Barakat, E. Trably, C. Dumas, J.-P. Steyer, H. Carrère, Lignocellulosic materials into biohydrogen and biomethane: impact of structural features and pretreatment, Crit. Rev. Environ. Sci. Technol. 43 (2013) 260–322, https://doi.org/ 10.1080/ n.d.

[25] J. Hrbek, Status report on thermal biomass gasification in countries participating in IEA Bioenergy Task 33, http://www.ieatask33.org/app/webroot/files/file/2016/ Status_report.pdf,

(2016) n.d.

[26] Z. Ud Din, Z.A. Zainal, Biomass integrated gasification-SOFC systems: technology overview, Renew. Sustain. Energy Rev. 53 (2016) 1356–1376, https://doi.org/10. 1016/j.rser.2015.09.013 n.d.

[27] R.L. Bain, K. Broer, Gasification, in: R.C. Brown (Ed.), Thermochem. Process. Biomass Convers. Into Fuels, Chem. Power, first ed., John Wiley & Sons, Chichester, 2011, pp. 47–77, , https://doi.org/10.1002/9781119990840.ch3 n.d.

[28] A. Demirbas, Thermochemical conversion processes, in: Springer (Ed.), Biofuels Secur. Planet's Futur, Energy Needs, Trabzon, 2009, pp. 261–304, , https://doi.org/ 10.1007/978-1-84882-011-1_6 n.d.

[29] A. Anukam, S. Mamphweli, P. Reddy, E. Meyer, O. Okoh, Pre-processing of su_garcane bagasse for gasification in a downdraft biomass gasifier system: a com_prehensive review, Renew. Sustain. Energy Rev. 66 (2016) 775–801, https://doi. org/10.1016/j.rser.201 n.d.

[30] Jayah TH. EVALUATION OF A DOWNDRAFT WOOD GASIFIER FOR TEA MANUFACTURING IN SRI LANKA 2002.

[31] National Energy Technology Laboratory. Gasification Technology R&D. World Gasification Database. ⟨http://energy.gov/fe/science-innovation/clean-coal_research/gasification⟩; 2010 [last accessed, December 2014] n.d.

[32] Sami M, Annamalai K, Wooldridge M. Co-firing of coal and biomass fuel blends. Prog Energy Combust Sci 2001;27:171–214. https://doi.org/10.1016/S0360-1285(00)00020-4.

[33] Surridge AD. Carbon sequestration leadership forum: South Africa status report. Report to the National Committee on Climate Change. Pretoria; 2004 n.d.

[34] Choi Y, Stenger HG. Water gas shift reaction kinetics and reactor modeling for fuel cell grade

hydrogen. J Power Sources 2003;124:432e9 n.d.

[35] Jiang Z, Pan Q, Xu J, Fang T. Current situation and prospect of hydrogen storage technology with new organic liquid. Int J Hydrogen Energy 2014;39:17442–51. https://doi.org/10.1016/j.ijhydene.2014.01.199.

[36] Singh S, Jain S, Ps V, Tiwari AK, Nouni MR, Pandey JK, et al. Hydrogen: A sustainable fuel for future of the transport sector. Renew Sustain Energy Rev 2015;51:623–33. https://doi.org/10.1016/j.rser.2015.06.040.

[37] W. Doherty, A. Reynolds, D. Kennedy, The effect of air preheating in a biomass CFB gasifier using ASPEN Plus simulation, Biomass Bioenergy 33 (2009) 1158–1167, https://doi.org/10.1016/j.biombioe.2009.05.004 n.d.

[38] W. Doherty, A. Reynolds, D. Kennedy, Aspen plus simulation of biomass gasification in a steam blown dual fluidised bed, in: A. Méndez-Vilas (Ed.), Mater. Process. Energy Commun. Curr. Res. Technol. Dev. Formatex Research Centre, 2013, pp. 212–220 n.d.

[39] AspenTech, Getting Started Modelling Processes with Solids, (2013) n.d.

[40] W. Doherty, A. Reynolds, D. Kennedy, Process simulation of biomass gasification integrated with a solid oxide fuel cell stack, J. Power Sources 277 (2015) 292–303, https://doi.org/10.1016/j.jpowsour.2014.11.125 n.d.

[41] Liu K, Song C, Subramani V. Hydrogen and syngas production and purification technologies. Proc Natl Acad Sci 2010;94:1-13 n.d.

[42] Lin Lin., "Numerical Simulation of Pressure Swing Adsorption Process", China: Xidian University, 1997 n.d.

[43] Xiao J, Fang L, Bénard P, Chahine R. Parametric study of pressure swing adsorption cycle for hydrogen purification using Cu-BTC. Int J Hydrogen Energy 2018;43:13962–74.

https://doi.org/10.1016/j.ijhydene.2018.05.054.

[44] M. Niu, Y. Huang, B. Jin, X. Wang, Simulation of syngas production from municipal solid waste gasification in a bubbling fluidized bed using aspen plus, Ind. Eng. Chem. Res. 52 (2013) 14768–14775, https://doi.org/10.1021/ie400026b n.d.

[45] A. Sahoo, D.K. Ram, Gasifier performance and energy analysis for fluidized bed gasification of sugarcane bagasse, Energy 90 (2015) 1420–1425, https://doi.org/ 10.1016/j.energy.2015.06.096 n.d.

[46] R. Michel, S. Rapagnà, P. Burg, G. Mazziotti di Celso, C. Courson, T. Zimny, R. Gruber, Steam gasification of Miscanthus X Giganteus with olivine as catalyst production of syngas and analysis of tars (IR, NMR and GC/MS), Biomass Bioenergy 35 (2011) 2650–2 n.d.

[47] S. Hosokai, M. Sugawa, K. Norinaga, C. Li, J. Hayashi, Activity of mesoporous alumina particles for biomass steam reforming in a fluidized-bed reactor and its application to a dual-gas-flow two-stage reactor system, Ind. Eng. Chem. Res. 47 (2008) 5346–535 n.d.

[48] C. Franco, F. Pinto, I. Gulyurtlu, I. Cabrita, The study of reactions influencing the biomass steam gasification process, Fuel 82 (2003) 835–842, https://doi.org/10. 1016/S0016-2361(02)00313-7 n.d.

[49] H. Kitzler, C. Pfeifer, H. Hofbauer, Pressurized gasification of woody biomass_Variation of parameter, Fuel Process. Technol. 92 (2011) 908–914, https://doi.org/ 10.1016/j.fuproc.2010.12.009 n.d.

[50] F. Feng, G. Song, L. Shen, J. Xiao, Simulation of bio-syngas production from bio_mass gasification via pressurized interconnected fluidized beds, in: S. Qu, L. Zhang, X. Zhang, Z. Li (Eds.), Lect. Notes Electr. Eng. Springer-Verlag Berlin Heidelberg, Berl n.d.

[51] M. De Souza-Santos, A feasibility study of an alternative power generation system based on

biomass gasification/gas turbine concept, Fuel 78 (1999) 529–538, https://doi.org/10.1016/S0016-2361(98)00181-1 n.d.

[52] C. Berrueco, J. Recari, B.M. Güell, G. Alamo, Pressurized gasification of torrefied woody biomass in a lab scale fluidized bed, Energy 66 (2014) 849–859, https://doi. org/10.1016/j.energy.2013.12.035 n.d.

[53] T. Srinivas, a. V.S.S.K.S. Gupta, B.V. Reddy, Thermodynamic equilibrium model and exergy analysis of a biomass gasifier, J. Energy Resour. Technol. 131 (2009) 031801, , https://doi.org/10.1115/1.3185354 n.d.