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 Msc

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Chapter 1

INTRODUCTION

Nearly 84.5% of the world's energy needs are still met by fossil fuels. In 2023, oil accounted for 32.78% of global energy use, followed by natural gas at 23.96% and coal at 27.79%. Consequently, energy-related greenhouse gas emissions are predicted to reach 378.3 Gt CO₂ in 2024 representing a year-over-year increase of approximately 1% (357 Mt CO₂) [1,2]. As fossil fuel reserves become scarcer, prices increase, and the environmental effects of increasing energy demand escalate, researchers are exploring alternatives to fossil fuels such as low-carbon alternatives and renewable energy resources [3].

The renewable energy industry is regarded today as being one of the cleanest forms of energy available, almost emission-free, because it draws its energy from natural phenomena such as wind, sunlight, biomass, geothermal heat, ocean currents, and hydropower, which are replenished on human timescales and produce significantly lower greenhouse gas emissions than fossil fuels. Globally, final energy demand is divided into four primary sectors: industry, transportation, buildings, and agriculture [4]. In comparison to fossil energy, renewable energy has lower local air pollution burdens, significantly lower lifecycle greenhouse gas emissions, an inexhaustible primary resource base, and often lower operating expenses. The diversification of renewable energy sources also strengthens energy security by reducing dependency on imported fuels. Due to the fact that these technologies are available across most geographies, nearly every nation can deploy some combination of them [5].

Within this landscape, bioenergy is distinctive and can also serve as a feedstock for low-carbon hydrogen, enabling decarbonization beyond the power sector [6]. Hence, renewable forms of energy are the most promising alternative in the coming years. Figure 1 summarizes the principal renewable modalities and typical implementations.

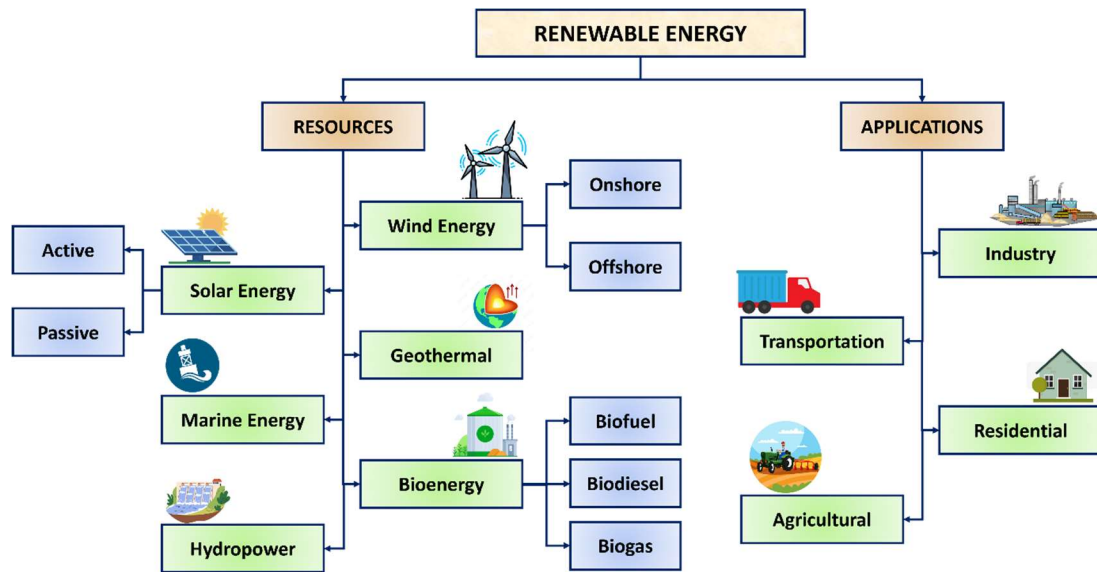


Figure 1: Overview of renewable energy types and their practical implementations.

1.1 Background and Motivation: Global Status of Renewable Energy

The status of primary energy consumption (includes both renewable and non-renewable energy sources) across multiple regions from 2021 to 2024 is presented in Figure 2. The primary energy consumption is highest for Asia Pacific in the world. The regional distribution for consumption of primary energy Asia Pacific (279.24 EJ) > North America (111.75 EJ) > Europe (71.66 EJ) > Middle East (41.43 EJ) > Commonwealth Independent States (41.07 EJ) > Central and South America (26.04 EJ) > Africa (21.03 EJ) in 2024. Global primary energy consumption has exhibited a steady upward trend. Asia Pacific region has recorded an increase of nearly 40 EJ since 2015.

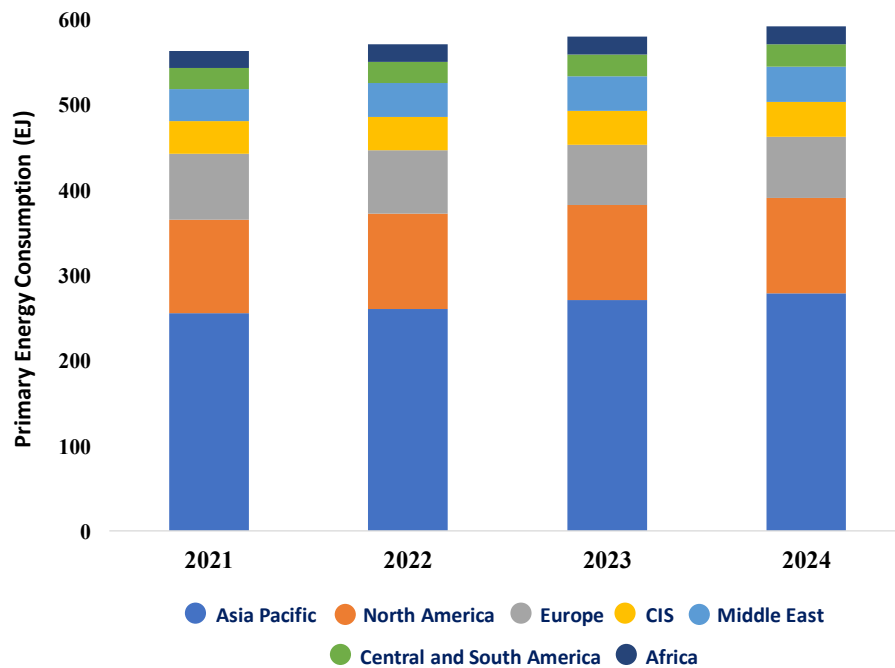


Figure 2: Status of renewable energy and tradable energy consumption across multiple regions from 2021 to 2024.

While the renewable sources include wind energy, solar energy, bioenergy, and geothermal power. The data presented in Figure 3-5 shows a steady annual increase in renewable energy consumption and generation. Renewable energy consumption and generation are highest in the Asia Pacific across all years. The order for renewable energy consumption is Asia Pacific (17.22 EJ) > Europe (10.14 EJ) > North America (8.44 EJ) > South and Central America (3.35 EJ) > Africa (0.47 EJ) > Middle East (0.18 EJ) > Commonwealth of Independent States (0.10 EJ).

With approximately 11.32 EJ, China is the leading consumer of renewable energy in the Asia-Pacific region. This is followed by India (1.79 EJ) and Japan (1.32 EJ). As expected, a similar trend is observed for renewable energy generation. The order of renewable energy generation in 2021 is Asia Pacific (1690.1 TWh) > Europe (946.5 TWh) > North America (714 TWh) > South and Central America (229.3 TWh) > Africa

(49.0 TWh) > Middle East (18.5 TWh) > Commonwealth of Independent States (9.6 TWh).

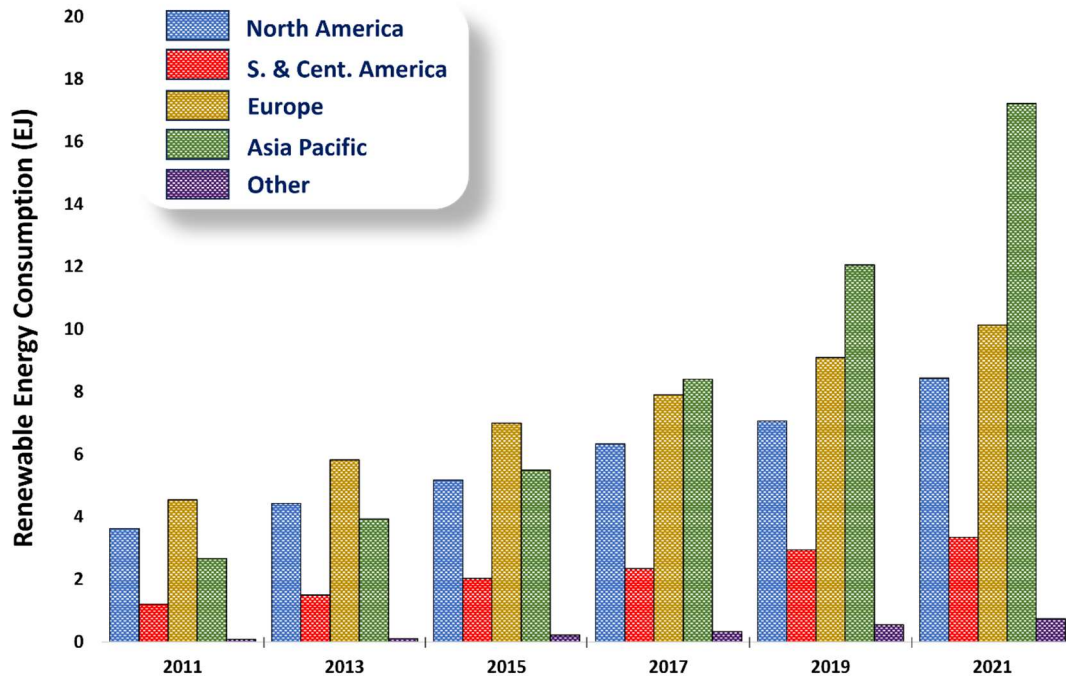


Figure 3: Statistics of renewable energy consumption in different regions. ‘Other region’ includes CIS, the Middle East, and Africa.

With approximately 1,152.5 TWh, China is the leading renewable energy producer in the Asia-Pacific region. This is followed by India (171.9 TWh) and Japan (130.3 TWh). Wind power accounts for the highest share of renewable electricity production, estimated at approximately 1,596.4 TWh in 2020 and 1,861.9 TWh in 2021 [7]. This is followed by solar energy estimated at about 846.2 TWh in 2020 and 1032.5 TWh in 2021 [8].

Therefore, among low-carbon alternatives including renewable electricity (solar, wind, hydro, geothermal), nuclear power, sustainable bioenergy, direct electrification with batteries, and carbon capture, utilization, and storage, “Hydrogen” is a key to a Carbon neutral future.

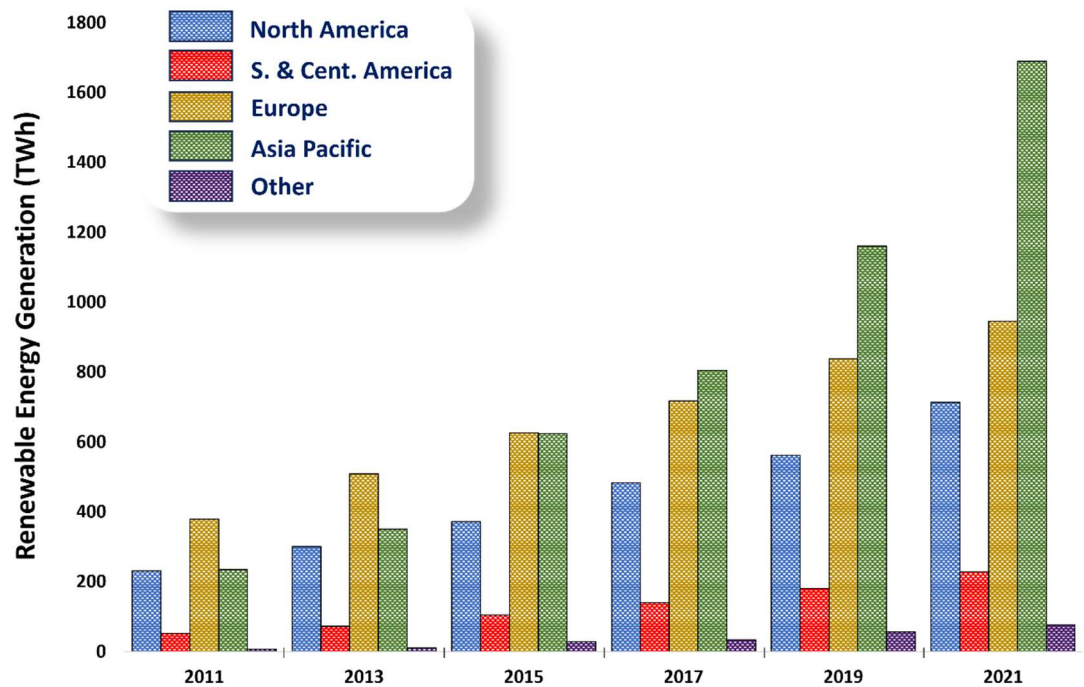


Figure 4: Statistics of renewable energy generation in different regions. ‘Other region’ includes CIS, the Middle East and Africa.

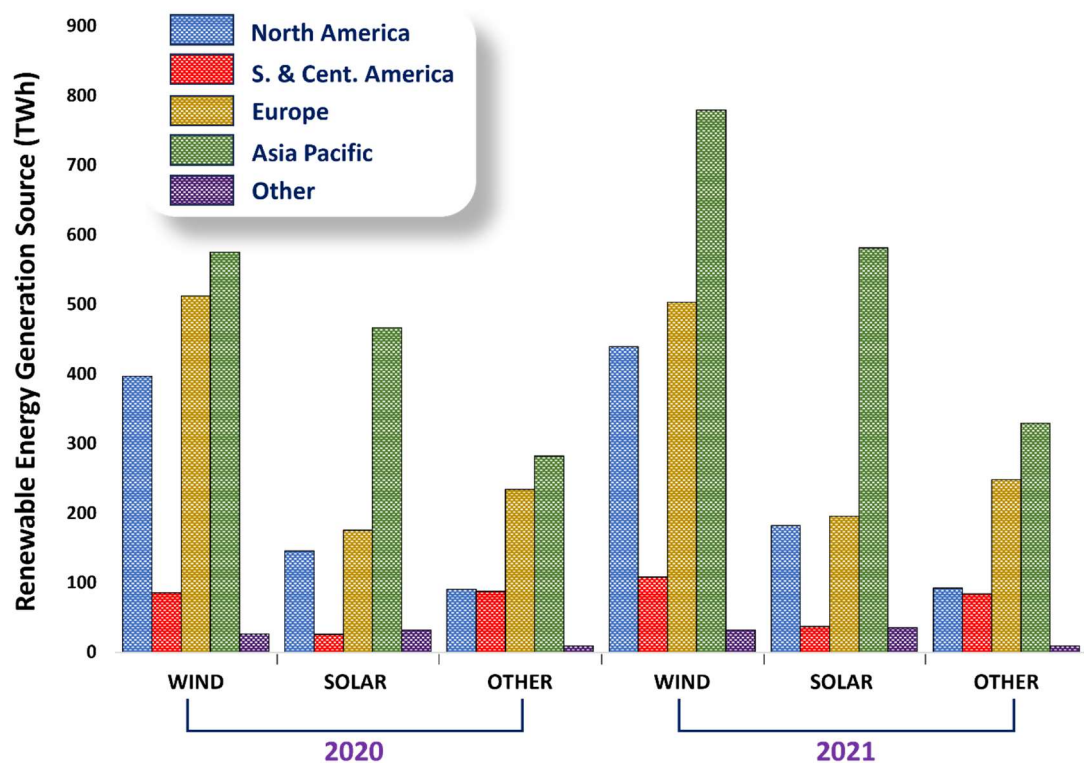


Figure 5: Statistics of renewable energy generation sources in different regions. ‘Other region’ refers to the CIS, the Middle East and Africa.

It stands out as a versatile energy carrier for hard-to-abate sectors that can be produced from diverse resources and is amenable to storage and long-distance transport [9]. At the point of use, hydrogen conversion (in fuel cells or via combustion) emits no CO₂; life-cycle emissions depend on the production pathway. When produced by water electrolysis powered by renewable electricity (“green hydrogen”), the life-cycle CO₂ can approach a net-zero carbon footprint, positioning hydrogen as a promising option for decarbonization, as the CO₂ released during combustion is absorbed by plants during photosynthesis [10,11].

This review gives a detailed assessment of the biomass-to-hydrogen value chain. It encompasses feedstock characteristics, preprocessing strategies, thermochemical and biochemical conversion pathways, technology readiness levels (TRLs), and techno-economic considerations. Recent studies are systematically compared across gasification, pyrolysis, dark fermentation, and photo fermentation. Performance indicators such as reactor configuration, catalyst selection, operating conditions, hydrogen yield, gas yield, and tar generation are compared. Additionally, detailed mechanistic pathways for hydrogen generation in both thermochemical and biochemical processes are discussed. Insights regarding reaction behaviour and the determinants of hydrogen production are presented. The study integrates process performance, mechanistic understanding, and commercialization readiness. This review provides the opportunities, limitations, and prospects of biomass-based hydrogen production technologies.

1.2 Advantages of hydrogen over Conventional Fuels

Hydrogen is considered a zero emission source as it burns cleanly and produces water vapour only [12]. The physical and chemical characteristics make it attractive for clean

energy systems. Hydrogen escapes and disperses into the air at a much faster rate in outdoor accidents. As a result it is less likely to accumulate. It remains manageable under controlled conditions despite its wide flammability range (from 4% to 77% by volume) in air [13]. It burns quickly and has a low impact on nearby objects owing to its low heat radiation during combustion. This chemical has a wider explosive range at higher concentrations. Although with the increasing concentration combustion transitions to deflagration rather than a violent explosion [14].

It has a higher energy density due to its lower mass density and heating value of 120 MJ/kg. Hydrogen has a flame propagation rate of approximately 346 cm^{-1} . This is significantly faster than most conventional fuels [15]. Overall hydrogen is a key element in the worldwide decarbonization strategy due to its excellent gravimetric energy density, low carbon footprint in combustion, wide flammability range, and extensive applicability [16].

1.3 Hydrogen Production

The production of hydrogen can be performed using fossil fuels or renewable feedstocks [17].

1.3.1 Fossil fuel-based: Hydrogen can be produced from natural gas, oil and coal where pyrolysis or steam reforming of hydrocarbons takes place. Different methods are available to achieve steam reforming like partial oxidation of methane (POX), methanol steam reforming (MeSR), methane steam reforming (MSR), and sorption-enhanced methane steam reforming (SE-MSR) [18].

1.3.2 Renewable resources-based: Water splitting and biomass processing are the two conversion techniques employed for renewable resource based hydrogen production. Several methods are available for splitting water including thermolysis, photolysis and

electrolysis [19]. **Biomass processing can be biological such as** glycerol steam reforming (GSR) or thermochemical [20]. It includes bio-photolysis and fermentation [21,22]. **Thermochemical processes:** They include pyrolysis, gasification, and liquefaction [23].

One of the most environmentally friendly and economically viable routes to sustainable hydrogen production is biomass-derived hydrogen, which can be produced using waste biomass and renewable carbon sources [24].

Chapter 2

BIOMASS RESOURCES AND FEEDSTOCK CHARACTERIZATION

2.1 Feedstock overview

Biomass is now regarded as an innovative renewable feedstock for producing hydrogen. It can be broadly classified based on origin and composition [25]. This strongly influences their suitability for hydrogen production. Figure 6 presents a flowchart of the main biomass categories. These are forest biomass, agricultural residues, energy crops, industrial and municipal waste, and algal and microbial biomass. Additionally, it presents their characteristic composition and the most suitable hydrogen production pathways.

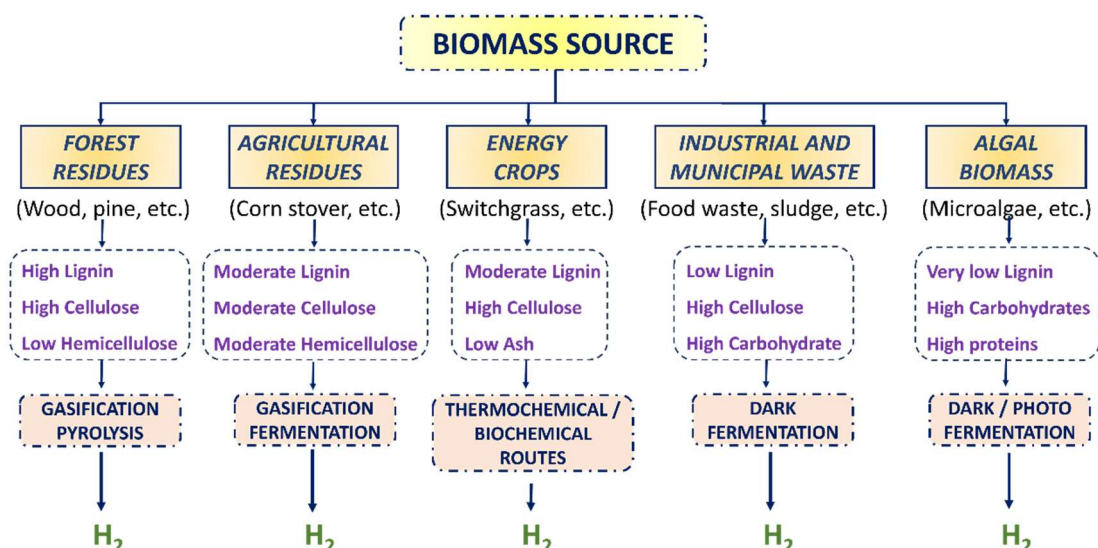


Figure 6: Biomass classification, composition and its suitability for hydrogen production pathways.

Lignin-rich biomass is generally preferred for thermochemical routes such as gasification and pyrolysis. While carbohydrate-rich and low-lignin biomass is more favourable for biochemical processes such as dark and photo fermentation. Therefore, forest biomass and energy crops favour thermochemical processes. Industrial and municipal waste favour biochemical fermentation. Algal and microbial biomass are ideal for dark and photo fermentation.

9 Biomass is considered to have a neutral carbon footprint, as the CO₂ released during its production is counteracted by the CO₂ absorbed during growth [26]. The pollution-free nature of this method makes it superior to other methods of hydrogen production. Despite these challenges, cultivar selection, growth period, harvesting, shipping, and pre-treatment costs must be considered. There are a variety of chemical or biological reactions that can occur in biomass sources, resulting in a variations in the production rate and quality of hydrogen [27]. With low sulphur content, agricultural residues and bio-waste offer a cost-effective solution and may become key energy crops for hydrogen generation. In addition, since energy crops don't interfere with food crop production, they are excellent options for generating hydrogen via physicochemical or biological routes. A wide range of sources supply lingo-cellulosic biomass. These include agricultural residues, food wastes, forest byproducts, marine residues, and energy crops. It is estimated that approximately 4.6 billion tons of lignocellulosic biomass are produced from agricultural residues every year, and about 7 billion tons are produced from forest residues [28].

2.2 Agricultural residues and biowastes

They are inexpensive and sustainable feedstocks due to their low sulfur content and wide availability [29]. Additionally, they can be cultivated on marginal land without interfering with food production. Specialized energy crops provide an excellent alternative for hydrogen production via physicochemical and biological conversion pathways [30, 31]. For example forest leftovers, marine biomass, agricultural residues, food and agro-industrial waste and crops cultivated for energy are all sources of lignocellulosic biomass [30]. An estimated 4.6 billion tonnes of lignocellulosic biomass are produced each year globally from agricultural wastes, while an estimated 7 billion tonnes come from forest resources [30, 31]. Globally, it is estimated that approximately 4.6 billion tonnes of lignocellulosic biomass are generated annually from agricultural residues, while around 7 billion tonnes originate from forest resources [31,32]. Figure 7 shows the schematic representation of biomass sources.

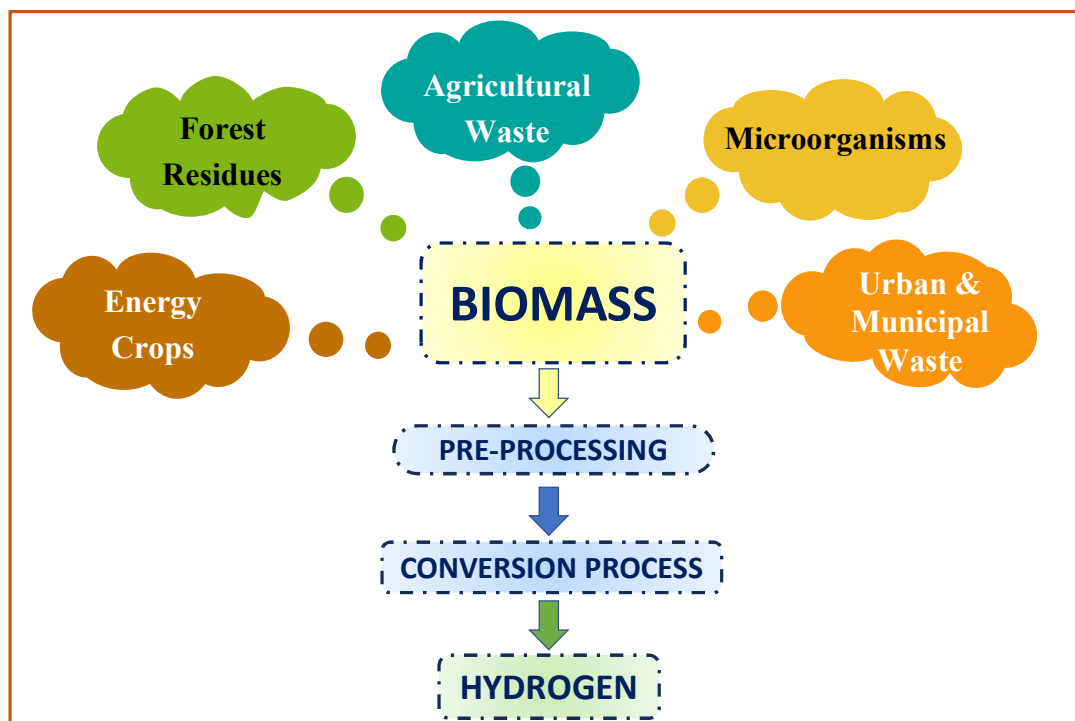


Figure 7: Schematic presentation of hydrogen production using different sources of biomass.

2.3 Critical Properties of Biomass Feedstocks

The chemical properties of biomass can vary widely from one feedstock to another, and these differences become especially important when multiple feedstocks are used in the same conversion process. Therefore, the heating value of a biomass sample reflects the amount of lignin present in it. A higher lignin content generally means a higher energy potential. This is due to its highly aromatic and carbon-rich structure. Lodgepole Pine (30.50%) has the highest and Sorghum (16.01%) contains the least lignin content. High lignin content increases thermal resistance. It promotes char formation during pyrolysis. This leads to higher fixed carbon yield and enhanced production of gas-phase products under gasification conditions. The aromatic structure of lignin also contributes to higher energy density. It influences syngas composition including hydrogen formation under steam gasification. This conveys that lignin rich materials such as Lodgepole Pine are more suitable for combustion due to higher energy density [33]. However, the chemical composition of biomass is not determined by species alone. Environmental factors such as climate, soil characteristics and local agricultural conditions also effect biomass quality. Ash content, structural carbohydrate and moisture levels are also affected by variation temperature and rainfall.

Harvesting practices further contribute to these differences. Properties of biomass are influenced by season, equipment used, and timing of harvest. Lower moisture content improves thermochemical processes like co-firing and pyrolysis. Strategic harvest timing can also help maximize carbon content and reducing ash formation at the same time. This trade-off is important to consider. Lower ash is beneficial for combustion

but may not be as favourable for biological processes like fermentation as carbon availability is critical in these cases [34].

Ash content varies significantly across feedstocks. Sugarcane bagasse contains the highest ash content (10.6%) and Hybrid Poplar contains the lowest ash content (0.9%). The method of collection is also important. Biomass harvested manually tends to contain less soil and therefore less ash than biomass collected using large-scale mechanical equipment. To better understand these differences, both manual and commercial harvesting methods should be evaluated especially to quantify the soil uptake during large-scale operations. Table 1 shows an analysis of different parameters using biomass feedstocks.

Table 1: Proximate, ultimate, and calorimetric properties of selected lignocellulosic biomass feedstocks relevant to biohydrogen production.

Attribute → Biomass ↓	Proximate analysis (%)			Ultimate analysis (%)		Calorimetry (kcal/kg)	
	Volatile matter	Ash	Fixed carbon	Hydrogen	Carbon	HHV	LHV
Corn Stover	79.0	4.3	16.7	5.7	48.7	7990	6614
Switchgrass	80.2	4.2	15.6	5.7	47.2	8077	6749
Miscanthus	85.5	1.4	13.1	5.8	50.6	8493	7073
Sorghum	77.8	7.8	14.4	5.6	45.6	7880	6554
Wheat Straw	77.0	9.1	13.9	5.9	45.0	7742	6333
Hybrid Polar	86.5	0.9	12.6	6.0	49.4	8746	7370
Lodge Pole Pine	84.5	1.1	14.4	6.1	50.1	8760	7371
Sugarcane Bagasse	76.0	10.6	13.4	5.4	45.2	7829	6499

2.4 Impact of Biomass Collection on Contamination Level

The mode of collection has a direct impact on the purity of the feedstock. Biomass harvested manually tends to have lower ash and soil content. Material harvested using large-scale commercial machinery can elevate ash levels due to soil intrusion during mechanical cutting and transport. Hence, a combined evaluation of manual and mechanized harvesting systems is crucial for accurately assessing soil contamination and optimizing feedstock handling protocols for sustainable bioenergy production.

Figure 8 presents compositions of various biomass.

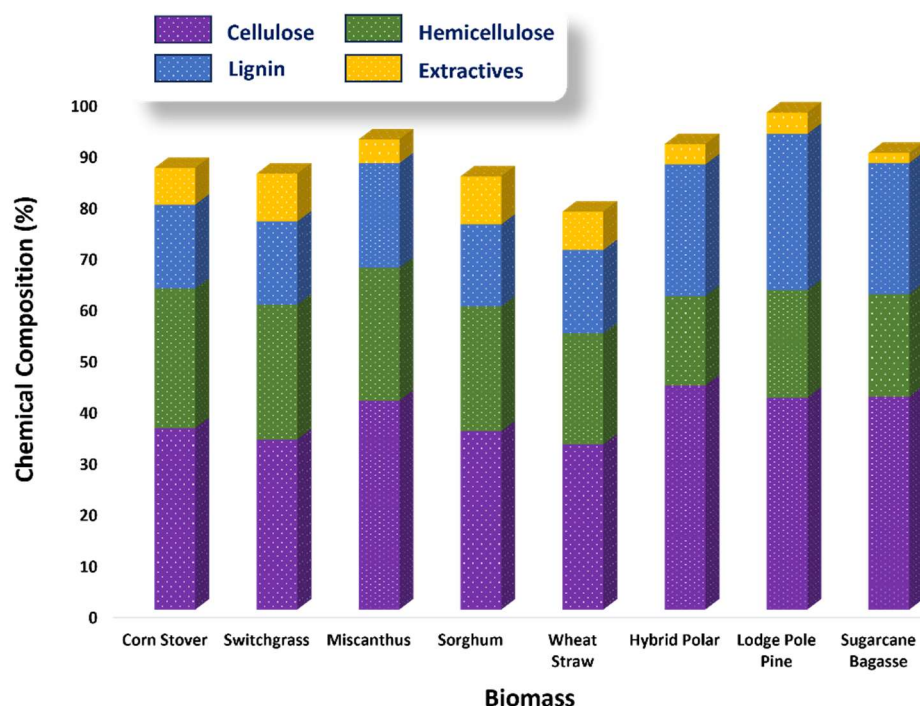


Figure 8: Overview of chemical composition of various biomass.

2.5 Preprocessing of Biomass

Substrate selection and conversion technology are key factors that affect the rate of hydrogen production. Among various sources of energy [35]. The biomass-based sustainable fuels stand out as the most viable strategy for achieving sustainable energy

[36]. One of the key stages in the efficient production of biohydrogen from biomass is substrate pretreatment. Physical, chemical, biological, and hybrid pretreatment methods have been employed for efficient hydrogen production [37,38]. Figure 9 presents the classification of preprocessing techniques.

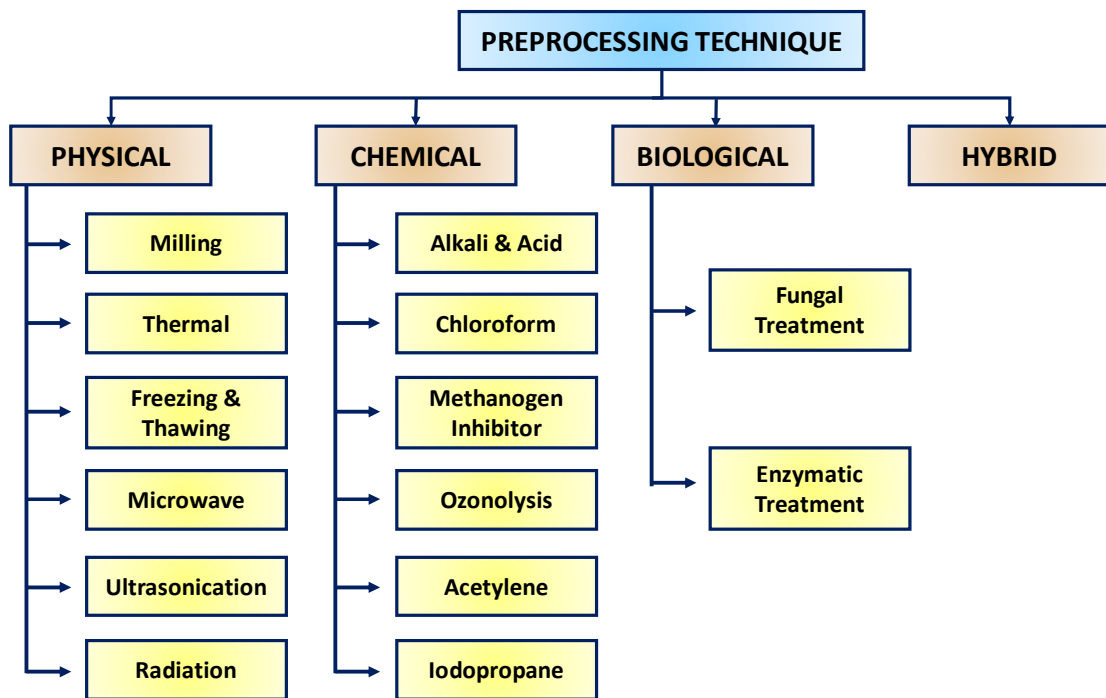


Figure 9: Classification of preprocessing techniques.

2.3.1 Physical Pretreatment

Physical pretreatment includes mechanical milling, heating, freeze–thaw cycles, microwave exposure, ultrasonic treatment, and irradiation. The pretreatment process starts with milling to increase the molecular surface area of the substrate [34]. Milling is carried out before applying chemical, enzymatic, or physicochemical preprocessing. Techniques such as two-roll, hammer, bead, colloid, and disc milling are used in the milling of biomass for hydrogen production [39].

- **Thermal treatment** supports the growth of hydrogen-producing bacteria and simultaneously hinders the activity of methanogens. Time and temperature are critical

factors during pre-treatment optimization. Brief pretreatments at controlled temperatures may effectively inhibit hydrogen-consuming microbes [39,40].

- **Freezing and thawing** processes includes high-pressure or dehydro-freezing, application of antifreeze proteins, induction of ice nucleation and thawing by high-pressure microwave heating [41]. During freezing the temperature is lowered causing a phase shift from liquid to solid while thawing generally occurs at a slower rate than freezing.
- **Microwave radiation** is commonly employed as a preprocessing technique for lignocellulosic feedstocks. The method may be preferred for its ability to operate conveniently, facilitate cellulose breakdown, generate heat rapidly, produce limited inhibitors and reduce energy consumption.
- **Ultrasound treatment** accelerates the process while cutting down on the amount of enzymes or chemicals needed. It is regarded as an innovative and sustainable method providing strong capacity for intensification. This is considered the optimal approach for pre-processing activated sludge for hydrogen production during dark fermentation. The structural damage to lignin and cellulose in biomass is induced by gamma radiation through free radical formation.
- **Irradiation Pretreatment:** The gamma radiation from the radioisotope Cobalt-60 has been utilized to treat substrates for hydrogen generation. Pretreatment of seed sludge with ionizing radiation resulted in peak hydrogen production performance [42].

2.3.2 Chemical preprocessing

The chemical agents employed for biomass pre-processing encompass alkalis, acids, inhibitors of methanogens, chloroform, ozonolysis, acetylene and iodopropane [43].

Alkaline and acidic preprocessing are the most popular adopted strategies for

16 enhancing hydrogen production efficiency. This is primarily due to their ability to exploit the pH sensitivity of non-sporulating hydrogen-consuming microorganisms [32, [44]. This process facilitates the delignification of biomass, enhances the release of fermentable sugars, and supports efficient generation of biohydrogen. Alkaline treatment disintegrates the crystalline structure of lignocellulosic material by saponifying ester bonds. This results in more efficient hydrolysis. In contrast, acid treatment aids in dissolving hemicellulose but fails to efficiently separate lignin from biomass [45,46]. Preprocessing with a dilute alkali enhances the effectiveness of enzymatic hydrolysis. It also improves the conversion of residual polysaccharides. This enhancement is because of partial delignification and cleavage of ester linkages.

21 It increases the accessibility of cellulose and hemicellulose to hydrolytic enzymes. Additionally disruption of the rigid lignocellulosic structure reduces crystallinity. This allows more efficient enzyme penetration and substrate enzyme interaction.

Methanogen inhibitors allow for the targeted and effective removal of hydrogen consuming methanogens [47,48]. Methanogen inhibitors such as chloroform, iodopropane and acetylene are frequently utilized to suppress the targeted hydrogen consuming methanogens [47].

Chloroform inhibits methanogenesis. It disrupts corrinoid (vitamin B12-dependent) enzymes. These enzymes are involved in key methyl-transfer reactions within methanogenic pathways. This represents an enzymatic level inhibition. Here the activity of corrinoid-dependent proteins is suppressed. This leads to reduced methane formation. Thus lowers hydrogen consumption by methanogens. Hydrogen-producing fermentative bacteria are independent of these methanogen-specific corrinoid-dependent enzymes. Therefore hydrogen production proceeds with limited impact.

Iodopropane acts as a corrinoid (vitamin B12) cofactor antagonist [48]. It interferes directly with the function of B12-containing methyl-carrier systems [41]. These systems are fundamental to methyl transfer processes in methanogenic pathways. Thus iodopropane blocks the cofactor-mediated transfer steps [49]. This results in suppression of methanogenic hydrogen utilization.

Thus hydrogen-producing fermentative bacteria continue to be unaffected. This is because their metabolic pathways for formation of hydrogen does not involve corrinoid (vitamin B12)-dependent methyl-transfer systems targeted by these inhibitors [50]. Acetylene serves as an economical and effective methanogenesis inhibitor in preprocessing and help in hydrogen production [51].

Ozonolysis breaks down lignin and thereby facilitates the hydrolysis of the enzyme into fermentable sugars. It is applied under controlled optimal thermal and pressure settings. It aims at preventing the formation of harmful by-products and supporting sustainable operation [52,53]. Biomass moisture content is the key factor affecting ozone pretreatment as higher moisture levels reduce lignin oxidation [44].

2.3.3 Biological preprocessing

Biological preprocessing lowers energy demand, resulting in superior performance. It is environmental friendly compared to other traditional approaches (physical or chemical) [44]. It facilitates faster hydrolysis by disrupting the lignocellulose substrates [54]. This preprocessing method includes both fungal and enzymatic methods. Various fungal strains, including brown, white, and soft-rot fungi, are used to degrade lignin and hemicellulose [55]. Hydrolysis by an enzyme bypasses the need for fungi by utilizing enzymes to perform the hydrolysis process.

Chapter 3

BIOMASS CONVERSION PATHWAYS

Biomass serves as a promising renewable source for hydrogen generation. It is beneficial for biofuel production because it can improve carbon neutrality. It can be converted into hydrogen either by thermochemical routes or biochemical routes.

3.1 Thermochemical Route

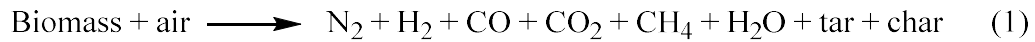
Biomass serves as a promising renewable source for hydrogen generation. It is beneficial for biofuel production because it can improve carbon neutrality. It can be converted into hydrogen either by thermochemical routes or biochemical routes [56,57].

Liquefaction can be classified into solvolysis, hydropyrolysis, and hydrothermal. It is suitable for biomass with a moisture content up to ten folds higher [58]. It is a comparatively unattractive alternative owing to demanding operating conditions and restricted productivity [59]. The ability to tune operating parameters allows pyrolysis to valorise variety of biomass [60].

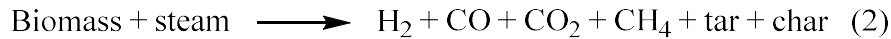
3.1.1 Gasification technique

It involves thermochemical conversion of biomass into gases like hydrogen, carbon dioxide, carbon monoxide and methane. This outcome is possible when oxygen or steam is introduced under optimised conditions during high-temperature heating of the biomass. It can be air gasification, steam gasification or oxygen gasification. The overall reactions involved are given in equations 1-3 [61,62].

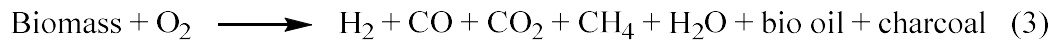
Air gasification:



Steam gasification:

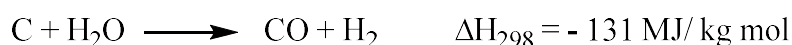


Oxygen gasification:

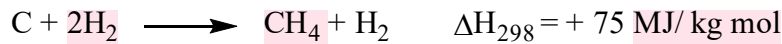
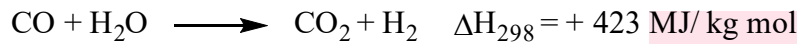


The dry biomass requires less energy for gasification than wet feedstock. There are various phases of gasification that occur at different temperatures, including drying, pyrolysis, reduction, and combustion [63]. Wet feedstock is dried (250 °C) in the gasifier, releasing water in the process. This is followed by pyrolysis (250-500°C), where gaseous chemicals, such as carbon dioxide and carbon monoxide, and tar are liberated. Here biomass decomposes into char, tar and gaseous compounds such as carbon monoxide and carbon dioxide. These gases subsequently participate in gasification and reforming reactions. Hydrogen is then produced via the reduction process (800-600°C). This is primarily through char-steam gasification and water-gas shift reactions. These convert carbonaceous intermediates and carbon monoxide into hydrogen-rich syngas. Finally the remaining char is subjected to the combustion process (800-1000°C) [64]. Thus, it provides the heat required to sustain the endothermic gasification reactions. Figure 10 represents the working of the reactor.

Reduction Process:



5



Combustion Process:

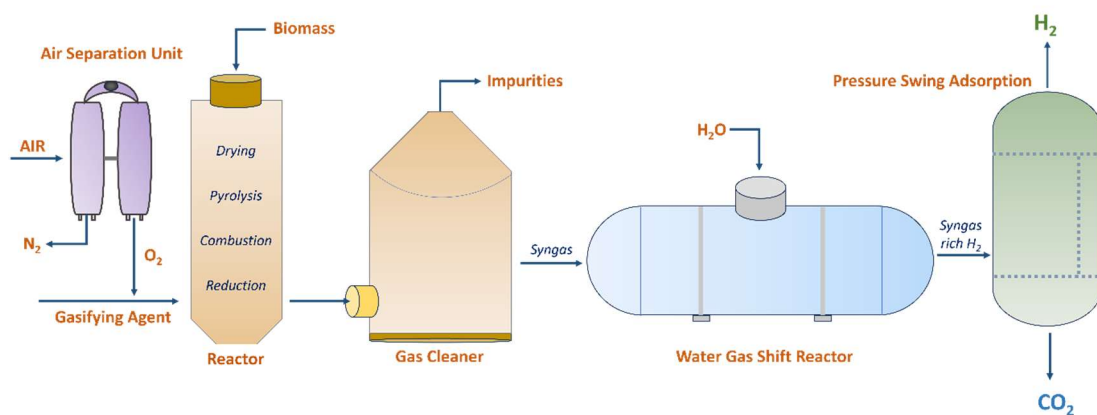


Figure 10: Working Flow Chart of Gasification Techniques

The rise in temperature makes gasification an endothermic process requiring substantial energy input. The type of oxidizer determines it as air, oxygen or steam gasification [65]. Generally, air is used as an oxidizer in fixed-type bed reactors resulting in low hydrogen generation due to the presence of a considerable amount of carbon dioxide and nitrogen. Removal of nitrogen reduced the heating value of the fuel [66]. This drawback is overcome by the oxygen gasification process. However, pure oxygen is quite expensive, which limits its use as an oxidizer [67]. Steam gasification is adopted as an alternative that lies between air and oxygen gasification [21]. Steam gasification generally yields higher hydrogen concentrations. This is because steam participates directly in char-steam gasification and water-gas shift reactions. Both of these promote additional hydrogen formation. The hydrogen level in syngas is strongly

influenced by the type of biomass and the gasification parameters, including temperature, the ratio of steam to biomass, heating rate, type of oxidizer, and reaction time [68]. Table 2 represents hydrogen production using different biomass with its key parameters including reactor configuration, catalysts, gas yield, etc [69].

Table 2: Hydrogen Production with Different Biomass using Gasification routes.

Biomass	Reactor configuration	Catalyst	Operating conditions	H ₂ production (wt %)	Gas Yield (Nm ³ /kg _{biomass})	Tar content (g/Nm ³)	Ref.
Pine wood	Downdraft fixed bed	-	T = 850 °C	6.2	1.4	-	[70]
Waste wood	Fluidized bed	Silica sand	T = 900 °C S/B = 1	5.9	1.22	12.5	[71]
Wood pellets	Dual fluidized bed	Olivine	T = 815 °C S/B = 0.84	0.76	2.2	4.4	[71]
Pine wood pellets	Dual fluidized bed	Silica sand	T = 820 °C S/B = 2	1.8	0.82	10.3	[68]
Almond shells	Fluidized bed	Olivine : Dolomite (9:1)	T = 820 °C S/B = 0.72	7.3	1.58	2.13	[72]
Sewage sludge	Dual fluidized bed	Silica sand	T = 820 °C S/B = 1.5	3.6	0.85	122	[73]
Pine needles	Bubbling fluidized bed	CaO	T = 850 °C S/B = 1.6	12.4	1.98	-	[73]
Torrefied woodchips	Bubbling fluidized bed	-	T = 800-900 °C S/B = 0.32	1.12	0.89	-	[74]
Corn straw	Downdraft fixed bed	Blast furnace gas ash	T = 850 °C	5.6	3.01	-	[75]
Palm kernel shell	Fluidized bed	Ni powder	T = 750 °C S/B = 2	49 mol/kg	-	-	[76]
Beech wood	Cavity-type solar reactor	-	T = 1100-1300 °C S/B = 2	6.8	0.85	-	[77]
<i>Enteromorpha intestinalis</i> (algae)	Tubular batch reactor	Fe-Ni-Ru/γ-Al ₂ O ₃	T = 440 °C	12.28 mol/kg	30.16 mol/kg	-	[78]

2

3.1.2 Pyrolysis Technique

Pyrolysis is a process that thermally decomposes biomass in the absence of oxygen, resulting in the production of gases such as carbon dioxide, carbon monoxide, hydrogen, and methane, as well as solid char and fumes [74]. It offers benefits such as cost-effective process, easy storage and transportation, along with suitability for containers, appliances, turbines, and incinerators. It decomposes major macromolecules, such as cellulose, protein, carbohydrates, hemicellulose, and lipids, into simpler structures of vapours and gases. It can be grouped into fast pyrolysis (450-600 °C), slow pyrolysis (450 °C), and flash pyrolysis depending on the operating temperature [75]. The overall reaction involved is given by equation 4 [76].



(4)

The pyrolysis process includes complex primary and secondary reaction pathways.

This is illustrated in Figure 11.

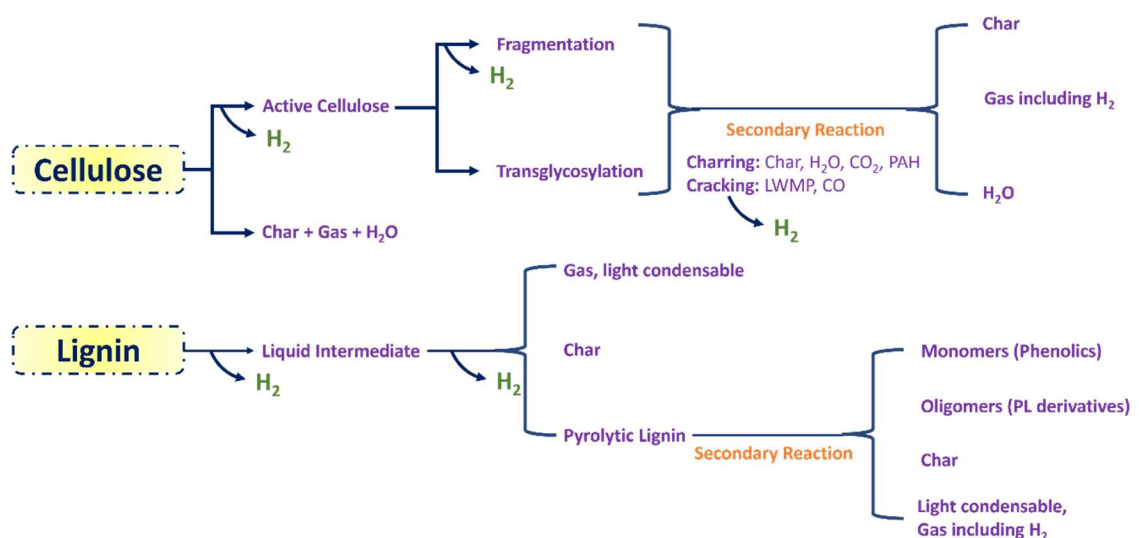


Figure 11: Mechanistic pathways of hydrogen formation during biomass pyrolysis.

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In primary pyrolysis lignocellulosic biomass decomposes under heat. It produces char, condensable vapours (bio-oil) and non-condensable gases. These primary products subsequently participate in secondary reactions. Secondary reactions include thermal cracking and reforming. Hydrogen, carbon monoxide and carbon dioxide are produced as result. The final hydrogen yield and gas composition are strongly influenced by the extent of these secondary reactions. The working of pyrolysis reactor is presented in Figure 12.

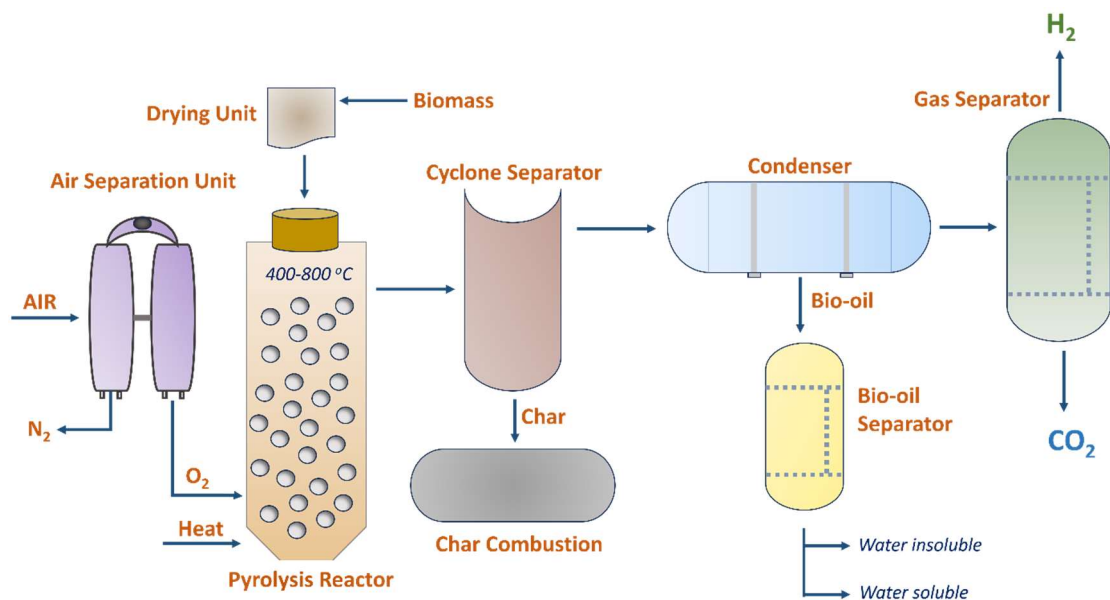


Figure 12: Schematic Representation for Pyrolysis.

The process begins with drying the biomass, and then it is directed towards the pyrolysis unit. It is then sent to the cyclone separator, the combustion system, and finally the condenser. The combustion system burns off the remaining char, which is used during the drying process of biomass. The condenser yields gaseous products and bio-oils. These are then purified and separated into usable products and side products. Bio oil is a heterogeneous fluid similar to tar and can be categorised into water-soluble and insoluble fractions (olefins, xylene, toluene, and benzene). They consist of furan,

phenols, organic acids, alcohols, and ash. The characteristics of bio-oil are influenced by parameters of pyrolysis, the type of reactor, and the type of biomass employed.

Some of the biomass is presented in table 3.

Table 3: Different Biomass used in Hydrogen Production via Pyrolysis.

Biomass	Reactor configuration	Catalyst	Operating conditions	H ₂ production (wt %)	Ref.
Poplar wood/Pine	Fixed bed	Ni/Mg-Al with Ce	T = 650 °C	14.7	[84]
Pine sawdust	Fixed bed/Fluidized bed	Ni/La ₂ O ₃ -Al ₂ O ₃	T = 500 °C	7.0	[85]
Coconut shell	Fixed bed	Fe/Olivine	T = 800 °C	17.9	[86]
Corn cob	Fixed bed	Ce-Ni/Co-Al ₂ O ₃	T = 650-850 °C	11.7	[87]
Wood sawdust	Fixed bed	Nano Fe-Zn/Al ₂ O ₃	T = 500 °C	1.9	[88]
Wood sawdust	Fixed bed	Ni/CaAlO _x	T = 800 °C	3.1	[89]
Wood sawdust	Fixed bed	NiZnAlO _x	T = 535 °C	4.0	[90]
Wood sawdust	Fixed bed	Ca/Ni-Mg-AlO _x	T = 550 °C	4.3	[90]
Wood pellets	Fixed bed	Acid treated tyre char	T = 500 °C	6.1	[91]
Cellulose	Fixed bed	Ni/Al ₂ O ₃	T = 800 °C	5.9	[92]
Rice husk	Fixed bed	RHC Ni	T = 750°C	24.3 (vol %)	[93]
Corn cob	Fixed bed	Ni-lignite char	T = 900 °C	12.2	[94]
Corn cob	Fixed bed	Ni-exchanged resin char	T = 900 °C	12.3	[95]
Corn cob	Fixed bed	Limonite	T = 900 °C	14.8	[96]
Pine wood sawdust	Spouted bed/Fluidized bed	Ni/Al ₂ O ₃	-	11.0	[97]

It has several limitations, like poor heating value, high oxygen and moisture content, dense and viscous, and a strong corrosive nature [75]. These limitations cause chemical instability and deterioration during storage. Despite the drawbacks, it is a promising alternative for producing hydrogen. Pyrolysis of biomass has been shown to enhance energy recovery during hydrogen production [78, 79].

3.2 Biochemical route

3.2.1 Dark fermentation

Dark fermentation begins when economical anaerobic microbes (obligatory and facultative) are kept without light at operating temperatures over 25 °C [98]. Species of *Clostridium*, *Enterobacter*, *Bacteroides* and *Ruminococcus* are the most prevalent microbes used during the process [99,100]. The various gases produced based on the substrate being converted during the process are hydrogen, carbon dioxide, carbon monoxide, hydrogen sulphide, and methane. Catalysis of carbohydrates is the central process during this technique. Only a small amount of hydrogen is generated since other gases are also produced during the process [101,102]. It is necessary to implement an efficient method for isolating and purifying gases. The presence of by-products in the reaction further alters hydrogen production levels. With one mole of glucose, two moles and four moles of hydrogen are produced when butyric acid and acetic acid are the byproducts, respectively [103]. The overall reactions involved are presented in equations 5 and 6.



The microbial strain employed and the sugar content of the substrate influence the efficiency. Partial pressure of gas and pH are among other parameters that impact hydrogen generation [104]. Biomass-based hydrogen production by dark fermentation using different substrate with different parameters are presented in table 4 [107].

Table 4: Different substrate with hydrogen yield and other parameters via Dark Fermentation.

Substrate	pH	Temp (°C)	Microbe	Reactor	Hydrogen yield	Ref.
Washing wastewater from beverages	5.5	40	Mixed cultures (wastewater treatment plant)	-	0.30 mol/mol hexose	[108]
Food waste	-	36	Mixed culture from aerobic sludge	Batch	70.34 cm ³ /gVS	[109]
Raw cassava starch	-	35	Facultative anaerobic bacteria	Batch	1.44 mol/mol glucose	[110]
Pumpkin and potato waste	7.5	35	Anaerobic sludge	Batch	135.6 cm ³ /VS	[111]
Palm oil mill effluent	6.8	35	Mixed cultures	Upflow column bioreactor	0.52 mol/mol glycerol	[112]
<i>Jatropha curcas</i> (biodiesel industry residue)	5.5	37	Mixed cultures	Continuous stirred tank reactor	148 cm ³ /g carbohydrate 324 mmol/mol glycerol	[113]
Cassava starch wastewater	5.5	30	Mixed cultures	Batch	1.58 mol/mol hexose	[114]
Palm oil decanter cake with glycerin	7	55	Mixed cultures	Semi continuous	-	[115]
Barley hulls	-	60	<i>Clostridium thermocellum</i>	Batch	1.07 mmol/g substrate	[116]
Cornstalk	7.5	55	<i>Clostridium sartagoforme</i>	Batch	6.38 mmol/g substrate	[117]
Cornstalk	6.5	35	<i>Thermoanaerobacterium</i>	Batch	87.2 cm ³ /g substrate	[118]
Corn staw	6.5	37	<i>Ethanoligenes harbinense</i>	Batch	72 cm ³ /g	[119]
Rice husk	7	35	Mixed cultures (sewage sludge digester)	Batch	1.25 mol/mol substrate	[120]
Pine tree wood	7	35	Mixed cultures (sewage sludge digester)	Batch	0.99 mol/mol substrate	[120]
Cheese wey powder	-	55	Mixed cultures from sugarcane stillage T	-	3.67 mol/mol lactose	[121]

Dark fermentation offers the benefit of generating hydrogen using cellulosic and lignocellulosic feedstocks, such as garbage [105,106]. Therefore, it potentially enables the integration of energy with waste management. Despite the benefits of dark fermentation, one issue is that both the production speed and hydrogen yield are inferior to those achieved by thermochemical techniques. Owing to the structural complexity of ligno-cellulosic and agricultural waste, the substrate must be fermentable through enzymatic processes. Such an extra procedure, being both expensive and slow, limits progress toward large-scale implementation. The metabolic pathways involved in dark fermentation are illustrated in figure 13.

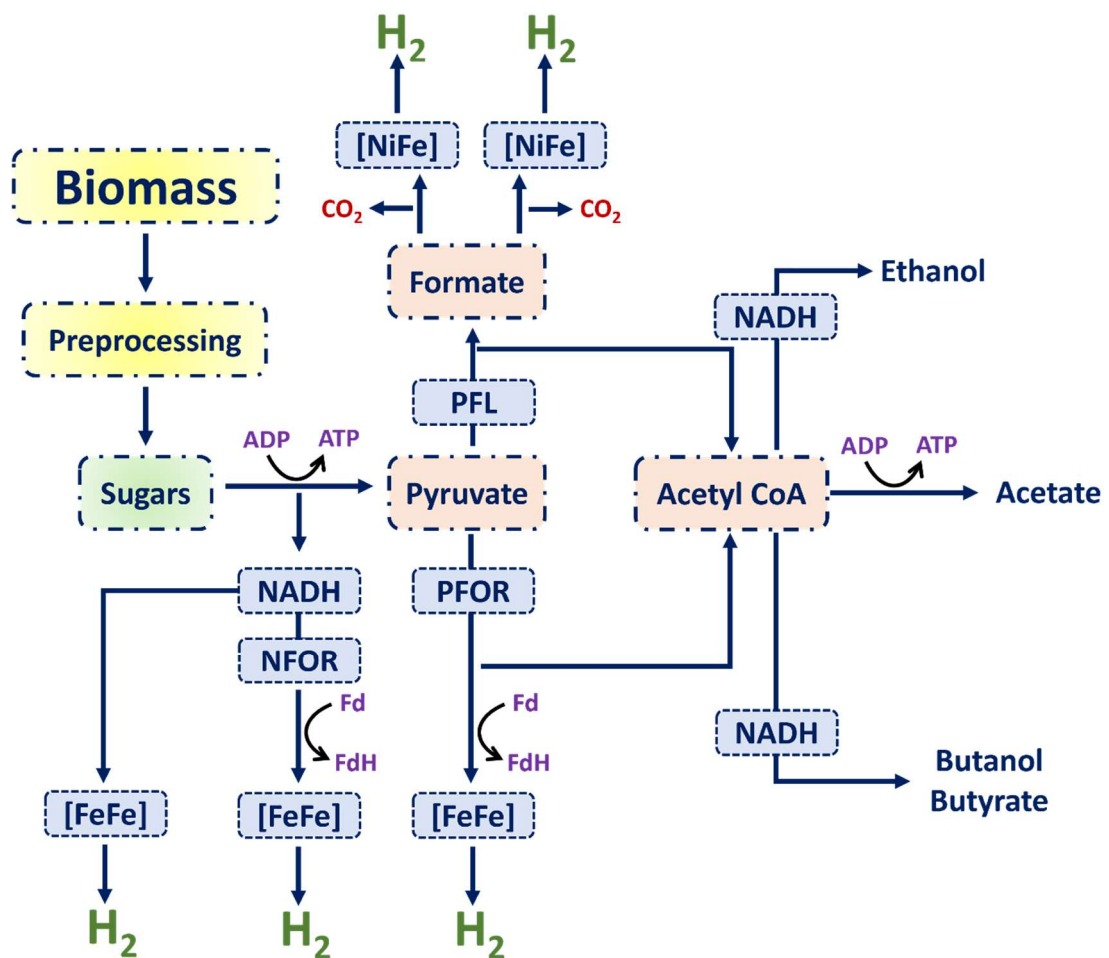
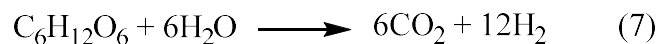


Figure 13: Process involved in Dark Fermentation.

Biomass-derived sugars are converted to pyruvate through glycolysis. This generates ATP and reducing equivalents (NADH/ferredoxin). Pyruvate is subsequently transformed into acetyl-CoA. The electrons released during these reactions are utilized by hydrogenase enzymes to produce H₂. The metabolic fate of acetyl-CoA influences hydrogen yield. The acetate pathway produces higher H₂ yields than the butyrate pathway. Therefore, operating conditions favouring acetate formation are usually preferred for enhanced biohydrogen production.

3.2.2 Photo fermentation

Photo fermentation relies on the nitrogenase enzyme to generate hydrogen from biomass using light energy in a nitrogen-deprived medium. The overall reactions involved are given in equation 7.



Organic acids undergo conversion to hydrogen and carbon dioxide via photosynthesis by the action of non-sulphur purple anaerobic bacteria [122]. The most common bacterial strains involved are *Rhodobium*, *Rhodobacter*, *Rhodospirillum*, and *Rhodopseudomonas* [123]. Oxygen is not produced in these conversions as it inhibits the nitrogenase enzyme [124].

The photo-fermentation process involves the oxidation of organic acids through the tricarboxylic acid (TCA) cycle. Reducing equivalents are generated in the form of NADH. These electrons are transferred via ferredoxin to the nitrogenase enzyme. ATP required for the reaction is supplied by light-driven cyclic photophosphorylation in purple non-sulphur bacteria. Under nitrogen-limited conditions, nitrogenase utilizes

the reducing power and ATP. This reduces protons and produces hydrogen. Carbon dioxide is released during substrate oxidation, as is illustrated in Figure 14.

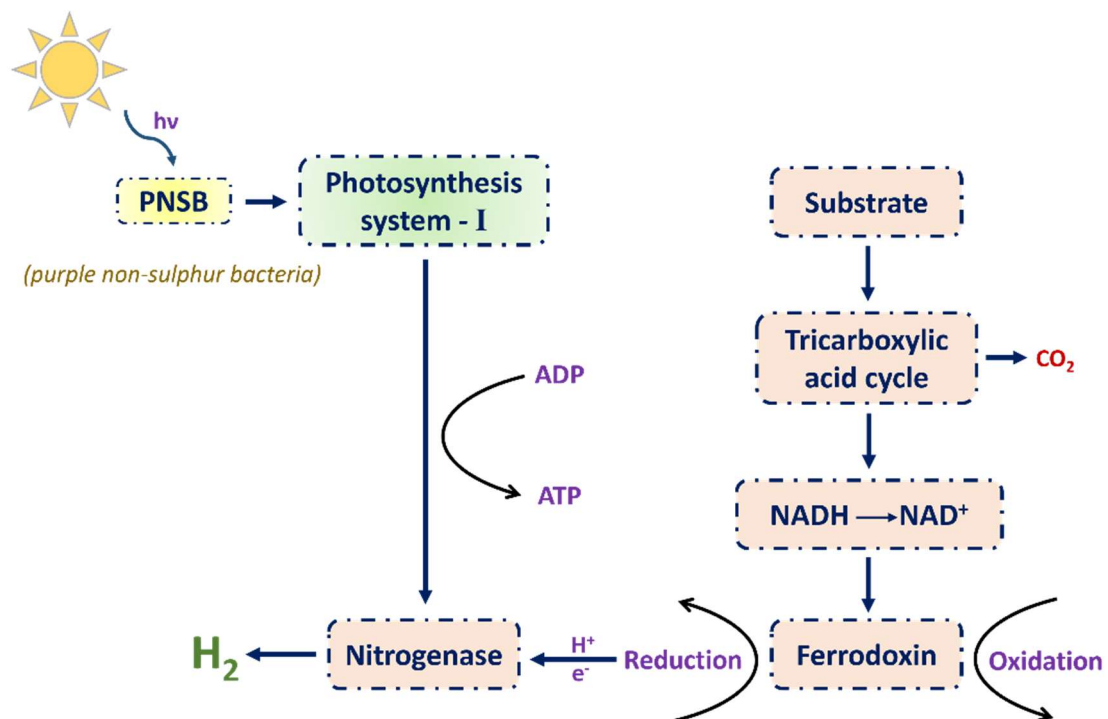
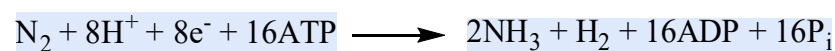
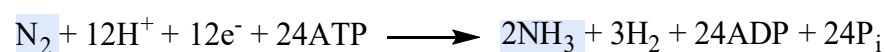


Figure 14: Flow chart for Photo-fermentation.

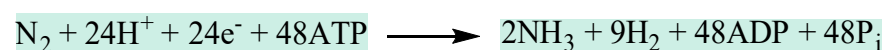
Mo-Nitrogenase



V-Nitrogenase



Fe-Nitrogenase



The process may follow either a single stage or a dual stage configuration. A single stage process setup is cost-effective to install but suffers from lower efficiencies [125].

The dual stage process uses dark fermentation beforehand to increase hydrogen

production by processing the organic acids generated first but this creates more complex operations. A peak hydrogen yield of 77.78 mL per litre per hour was reported for the photo-fermentation process [126]. The performance of this technique depends on preprocessing technique, bacterial engineering and configuration of the bioreactor. It is further affected by the choice of substrate, microbial species, and operational parameters [127]. The primary obstacle to industrial adoption of photo-fermentation is insufficient light intensity. Simply raising intensity of light does not solve the problem because excessive light hampers the growth of the bacteria and lower light conversion efficiency [128]. This issue is currently addressed by using shallow reactors to ensure that the substrate surface is exposed to the proper light [129].

Chapter 4

TECHNOLOGY ASSESSMENT AND ECONOMIC EVALUATION

4.1 Technology readiness level (TRL)

TRL assessment is a valuable method for identifying challenges and perspectives associated with technological innovation or new concepts [130]. It is a framework (level 1-9) that evaluates the maturity of a technology and allows a comparison between different technologies. Figure 15 represents the flow chart for TRL.

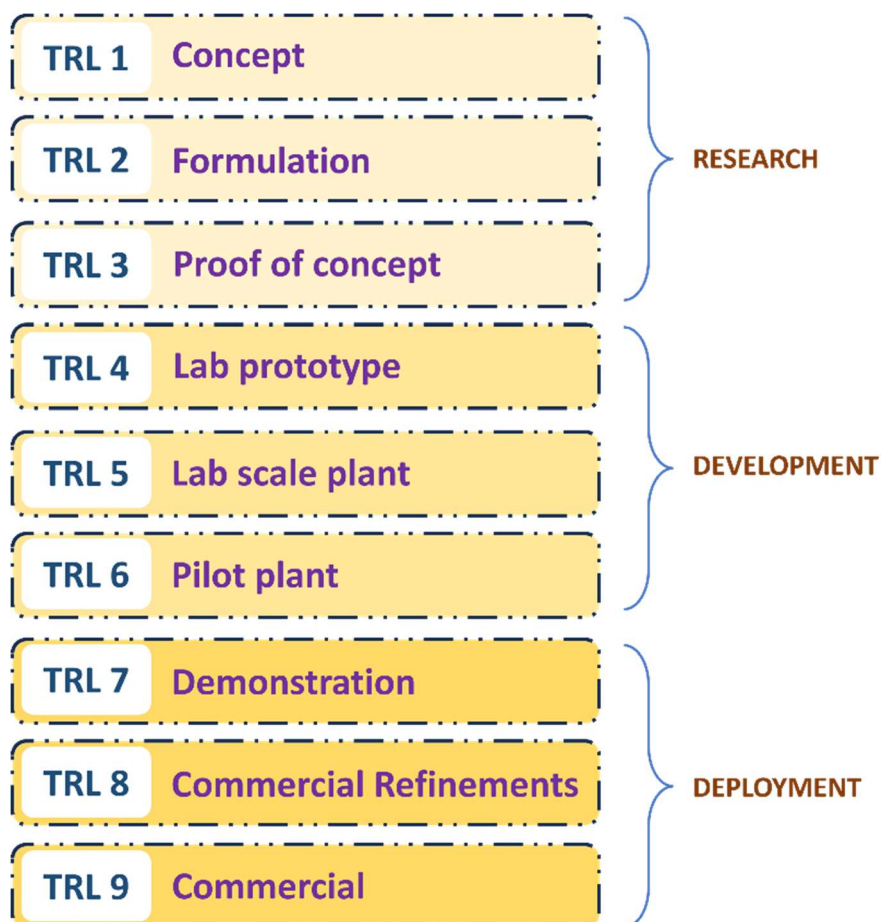


Figure 15: Flowchart for TRL

Industries worldwide have implemented TRL evaluations. Moving from lower to higher TRLs transforms a conceptual idea into a practical technology that can function in real industrial environments [131,132]. Level 1 through 3 indicate lab-scale research, 4 through 6 indicate pilot-scale developments, and 7 through 9 indicate technologies ready for industrial deployment [133]. Pyrolysis is evidently the primary method used for large-scale hydrogen generation. Liquid and gaseous biomass pyrolysis technologies are at TRL 4, while solid biomass pyrolysis has progressed to TRL 8 and is suitable for commercial use. Gasification of biomass has progressed to TRL level 6. Photo fermentation and dark fermentation are still in their early stages and call for extensive scientific advancements [134]. Table 5 presents the technology for TRL.

Table 5: The Technology and scale implement in TRL.

Technology	TRL	Scale	Efficiency (%)	Ref.
Gasification	4-7	Laboratory and bench scale	35-50	[135–137]
Pyrolysis	7	Bench	65	[135,138,139]
Dark fermentation	5	Laboratory scale	60-80	[59,123,137]
Photo fermentation	4	Laboratory scale	Light conversion efficiency 1-5	[59,123]

Technological maturity (TRL) and economic performance are important evaluation criteria. Along with these, environmental indicators like greenhouse gas emissions are assessed. This assessment enables a preliminary LCA-based comparison. The comparison focuses on different biomass-to-hydrogen conversion pathways.

4.2 Technoeconomic analysis (TEA)

A kinetic model was applied by Cook et al. to analyse the prospects of three separate biomass gasification units. The emission level in each plant fell between 2.92 and 3.15 kg of carbon dioxide per kg of hydrogen. Breakeven cost for hydrogen production fell between \$4.07-4.71 per kg of hydrogen in the absence of tax credits, while it fell between \$3.47-3.63 per kg of hydrogen in the presence of tax credits. Capital investment was identified as the dominant factor affecting hydrogen breakeven cost in the sensitivity results. It was further affected by the cost of the feedstock, length of the pipeline, and tax credits. Thus, these results show that the elements impose the strongest problem to scaling hydrogen gasification in industry [140].

Alam et al. in 2024 developed a process model in which wastewater sludge was used as the feedstock for dark fermentation. The production cost of hydrogen was \$11.4 per kg of hydrogen when the flow rate of feedstock was 23 tonnes per day. This cost reduced to \$5.9 per kg of hydrogen when the flow rate was increased to 500 tonnes per day. They also found that 17.5 kg of carbon dioxide was produced per kg of hydrogen. Capital investment and labour cost were identified as the dominant factors affecting hydrogen breakeven cost in the sensitivity results [141].

Genç et al. developed a process model in which dilute molasses was used as the feedstock for photo fermentation. The production cost of hydrogen was \$13.62 per kg of hydrogen when the production rate of hydrogen was 0.7 mmol per litre per hour. This resulted from the high costs of the cooling system and the bioreactor, making it economically nonviable. This suggests that research is needed to improve hydrogen production by the photofermentation technique [142]. Table 6 presents the cost analysis of the techniques.

Table 6: Cost and efficiency for different hydrogen production technologies.

Technique	Cost (\$/kg)	CO ₂ Emission	H ₂ recovery efficiency (%)	Ref.
Gasification	2	15%/kg syngas	48	[132,143]
Pyrolysis	1.47	1.5 kg CO ₂ /kg H ₂	42.5	[144]
Dark fermentation	2.57	47%/kg H ₂	22.5	[145]

The combined evaluation of TRL, techno-economic indicators and environmental emissions provide an integrated framework for assessing the sustainability of biomass-based hydrogen production technologies. Thermochemical pathways like gasification and pyrolysis are more economically feasible for production of hydrogen. They also result in moderate levels of carbon emissions. In contrast, biochemical pathways such as dark and photo fermentation are less technologically mature. They are associated with higher costs and environmental impacts. It is therefore important to examine the readiness of the process in technologies for producing hydrogen from biomass. Economic feasibility must be considered at the same time. Moreover environmental performance should be part of the assessment. Only by considering all these aspects together can truly sustainable pathways be identified.

Chapter 5

CONCLUSION AND FUTURE SCOPE

5.1 Merits and demerits of various techniques for the production of hydrogen from biomass

Various techniques were employed for the production of hydrogen production from biomass [123]. Table 7 represents merits and demerits for techniques.

Table 7: Merit and Demerit of several techniques.

Techniques	Merits	Demerits
Gasification	• Valorisation of industrial and forestry byproducts. • Adapt to existing industrial configuration • Eliminates the requirement for a costly oxygen supply • High productivity	• Carbon dioxide emission • Requires high temperatures (700-1000 °C) • Char and tar lead to deactivation of the catalyst • Reactor is costly
Pyrolysis	• Wide range biomass conversion (biochar, gas, bio-oil) • Uncomplicated method • Adapt to existing industrial configuration • Valorisation of industrial byproducts	• Carbon dioxide emission • Char and tar are produced • Catalyst needs to be regenerated • Reactor is costly
Dark fermentation	• Conversion of organic and biological waste into usable resources • Processes algal biomass • Requires mild pressures and temperatures	• Requirement of preprocessing • Low hydrogen production and low rate of yield • Byproducts are numerous
Photo fermentation	• Substrate conversion approaching completion • Conversion of organic and biological waste into usable resources • Requires mild pressures and temperatures	• Low hydrogen production and low rate of yield • Requirement of broad surface area • Requirement of bacteria • Requirement of high energy by the enzymes • Light conversion efficiency is low

It is apparent that both thermochemical techniques (gasification and pyrolysis) lead to carbon dioxide emission during production of hydrogen. However, these techniques have many advantages. It is useful in valorisation of industrial and forestry products and adapts easily to existing industrial configuration [104]. These techniques lower the requirement for oxygen and have comparatively higher hydrogen production efficiencies. Fermentation techniques being relatively new methods still require more research to make it economically and commercially more viable [8].

5.2 Conclusion

As the world transitions toward low-carbon energy systems, this article highlights the increasing importance of biomass as a practical and sustainable feedstock for hydrogen production. Since biomass has inherent adaptability, a variety of conversion methods are available, which can be used to convert it, with thermochemical and biological processes. It is evident that lignocellulosic and organic leftovers offer a rich resource capable of sustaining large-scale hydrogen generation without competing with food systems when starting with the basics of biomass availability and features. It involves the thermochemical methods, such as gasification and pyrolysis, which exhibit high conversion efficiency and comparatively advanced Technology Readiness Levels (TRLs), making them more feasible for commercial application. It covers preprocessing techniques and conversion pathways. Conversion routes include thermochemical and biological routes. It also includes TRL, a techno-economic assessment, and an evaluation of the merits of the biomass-based reactor for hydrogen production.

Overall, biomass-derived hydrogen is a viable alternative to fossil fuel-based production. It has potential for future clean energy systems. However, it faces many challenges regarding efficiency, scalability, and economics.

5.3 Future Scope

Even though significant progress in hydrogen production technologies several challenges still remain. These challenges include process efficiency, feedstock variability, scalability and economic viability. Future research should focus on the development of advanced catalysts. Integration of pretreatment and conversion systems along with process optimization should be the key focus. Techniques should be developed for integration of carbon capture. Improvements are necessary in reactor design as well as in feedstock logistics. Policy support mechanisms will be essential for accelerating commercialization. Additionally, hybrid thermochemical-biochemical approaches offer promising opportunities for hydrogen production. Further waste biomass utilization can improve the economic viability of hydrogen production.

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