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Thermochemical Pathways for Green Hydrogen Production from Biomass: Current Trends and Challenges

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Abstract

The growing demand for sustainable energy has intensified research into green hydrogen production, particularly from biomass via thermochemical pathways. Traditional fossil-fuel-based hydrogen generation is associated with high carbon emissions, necessitating environmentally friendly alternatives. This study explores the thermochemical conversion of biomass into hydrogen, focusing on pyrolysis, gasification, and liquefaction. Each method is analyzed based on its efficiency, product yield, and economic feasibility. The review identifies key challenges, including feedstock variability, process optimization, and catalyst development, while also highlighting emerging solutions. Findings suggest that gasification holds the highest potential for large-scale applications due to its superior hydrogen yield and integration potential with carbon capture technologies. The study concludes that advancing thermochemical hydrogen production requires continued improvements in process efficiency, cost reduction, and policy support to enhance industrial scalability.

Keywords: Green hydrogen production; biomass thermochemical conversion; pyrolysis; gasification; hydrothermal liquefaction

INTRODUCTION

The global energy crisis and rising greenhouse gas emissions have accelerated the transition toward sustainable energy. Many countries have set ambitious carbon neutrality targets, driving innovations in green energy, particularly hydrogen production. The European Union aims for carbon neutrality by 2050, with a 55% emission reduction target by 2030 (Addai et al., 2023). China targets peak carbon emissions before 2030 and neutrality by 2060, while Japan plans a 46% reduction by 2030 and neutrality by 2050 (Horiuchi, 2024). These commitments

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highlight the urgent need for clean hydrogen as a fossil fuel alternative. Despite its potential, 96% of hydrogen production still relies on fossil fuels, mainly Steam Methane Reforming (SMR) and coal gasification, leading to high emissions (Hwang et al., 2023). Developing sustainable alternatives, such as biomass-derived hydrogen, is essential for reducing the sector's carbon footprint. Biomass is an abundant, renewable feedstock sourced from agricultural waste (Reddy et al., 2023), wood residues (Chani, 2024), and municipal waste (Berenguer et al., 2023). Additionally, integrating biomass hydrogen production with Carbon Capture and Storage (CCS) could achieve carbon neutrality or even negative emissions (Zhao et al., 2017).

Among various production methods, thermochemical pathways—pyrolysis, gasification, and hydrothermal liquefaction—offer high hydrogen yields, cost competitiveness, and scalability. These methods enable flexible biomass processing (Lepage et al., 2021) and potential CCS integration (Anand et al., 2025), enhancing their industrial viability. However, challenges persist regarding conversion efficiency, by-product management, and economic feasibility (Mota et al., 2024). Production costs remain higher than fossil-based hydrogen due to additional purification steps (Nemitallah et al., 2024). Moreover, infrastructure limitations and policy frameworks must support large-scale adoption (Balat, 2009). Although thermochemical processes hold great potential, research remains fragmented, with limited industrial-scale studies. Comparative analyses on efficiency, by-products, and CCS integration are crucial for identifying the optimal pathway. This study aims to assess the efficiency, economic viability, and industrial applicability of pyrolysis, gasification, and hydrothermal liquefaction, addressing key challenges and opportunities for large-scale hydrogen production.

RESEARCH METHODOLOGY

This study employs a narrative review by analyzing research articles and review papers from the Scopus database (2016–2025). Literature selection is based on relevance to biomass-based hydrogen production, research novelty, and contributions to understanding conversion mechanisms, efficiency, and industrial challenges. The review focuses on thermochemical pathways—pyrolysis (bio-oil cracking and H_2 reforming), gasification (syngas reforming), and hydrothermal liquefaction (biocrude-to-H_2 conversion)—evaluating their technical, economic, and sustainability aspects. This study compares biomass-to-hydrogen conversion efficiency, by-product characteristics, and production costs while assessing key challenges such as catalyst requirements and gas purification optimization to enhance process feasibility. Inclusion criteria for literature selection include studies published between 2016 and 2025, peer-reviewed articles, and those focusing on thermochemical processes for biomass-based hydrogen production. Exclusion criteria involve studies not related to thermochemical conversion processes, studies without experimental data, or papers that focus on unrelated biofuel production processes. Validation of the selected literature is performed through cross-referencing with other high-impact sources, and the consistency of findings is verified by comparing outcomes with

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established research benchmarks in the field.

RESULTS

Biomass is a promising renewable energy source for sustainable hydrogen production (He et al., 2025). Unlike conventional methods such as steam methane reforming (SMR), which depend on fossil fuels and emit high carbon levels (Awadh, 2023), biomass-derived hydrogen can be carbon-negative when integrated with Carbon Capture and Storage (CCS) technology (Yuan et al., 2021). Thus, efficient biomass-to-hydrogen conversion technologies are critical in green energy research.

Thermochemical Pathways for Hydrogen Production

Thermochemical processes convert biomass carbon into hydrogen-rich gas at high temperatures. Key methods include gasification, pyrolysis, and liquefaction. Gasification partially oxidizes biomass to produce hydrogen-rich syngas (Demirbas, 2016). Pyrolysis thermally decomposes biomass into bio-oil, which can be further reformed into hydrogen (Al, 2024). Supercritical water gasification (SCWG) efficiently processes wet biomass under supercritical conditions (Demirbas, 2016). Temperature and catalysts significantly impact hydrogen yield. Higher temperatures enhance production efficiency, with optimal steam gasification occurring around 950 K (Inayat et al., 2010). Nickel-based catalysts are widely used due to their cost-effectiveness, while Rh/CeO_2 and Rh/Al_2O_3 catalysts improve reforming efficiency and stability (Dou, 2019).

Gasification is highly efficient for hydrogen production due to its versatility in biomass feedstocks, though optimizing conditions and catalysts is crucial (Salaudeen, 2024). However, its high temperature and pressure requirements pose challenges (Cao et al., 2020). Pyrolysis, particularly when combined with the water-gas shift reaction, offers high hydrogen yields but requires effective catalysts to minimize by-products. Liquefaction converts biomass into biocrude, which undergoes catalytic reforming for hydrogen production. While it accommodates high-moisture biomass, it demands substantial energy input and purification processes (Buffi et al., 2022).

Table 1. Comparison of thermochemical pathways for hydrogen production from biomass

Pathway	Process	Advantages	Challenges
Pyrolysis Bio-oil cracking & H_2 Reforming	Therman decomposition of biomass to bio-oil, followed by steam reforming	High hydrogen yield, especially with steam reforming	High temperature, efficient catalysts needed

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Gasification → Syngas Reforming	Conversion of biomass to syngas, followed by reforming	Efficient, handles various feedstocks, produces hydrogen-rich syngas	Optimization of conditions and catalysts, high temperature and pressure
Liquefaction → Biocrude-to-H_2 conversion	Conversion of biomass to biocrude, followed by catalytic reforming	Utilizes various biomass types, can integrate with other technologies	Significant energy input, efficient catalysts, hydrogen separation

Table 1 compares various thermochemical pathways for hydrogen production from biomass. The first pathway, pyrolysis followed by bio-oil cracking and hydrogen reforming (H2), involves thermally decomposing biomass into bio-oil, which is then reformed with steam. This pathway offers high hydrogen yield, especially with steam reforming. However, challenges include the need for high temperatures and efficient catalysts. The second pathway, gasification followed by syngas reforming, converts biomass into syngas, which is then reformed to produce hydrogen. Its advantages include high efficiency, the ability to handle various feedstocks, and the production of hydrogen-rich syngas. Challenges include optimizing conditions and catalysts, as well as the requirement for high temperatures and pressures. The third pathway, liquefaction followed by biocrude-to-hydrogen conversion, converts biomass into biocrude, which is then catalytically reformed. This pathway can utilize various biomass types and can integrate with other technologies. However, it faces challenges such as significant energy input, the need for efficient catalysts, and hydrogen separation issues.

Pyrolysis and reforming of Bio-Oil

The pyrolysis process involves the thermal decomposition of biomass in the absence of oxygen, with its efficiency and product distribution significantly influenced by temperature and pressure. The optimal temperature varies depending on the desired product. Lower temperatures (300-500°C) favour biochar production, medium temperatures (500-650°C) maximize bio-oil yield, while higher temperatures (700-1100°C) enhance pyrolytic gas production (Tan et al., 2024). Studies suggest that temperatures around 500-700°C are particularly effective, with 700°C producing a bio-gas with a high heating value (Abou et al., 2023). While pyrolysis is generally conducted at atmospheric pressure, increased pressure (up to 2 MPa) can affect product yield and composition, particularly in coal pyrolysis (Park, 2017).

The type of biomass used in pyrolysis also plays a crucial role in determining the efficiency and quality of the products. Lignocellulosic biomass, which includes forestry (Mulligan, 2014) and agricultural residues, paper, cardboard, organic municipal waste, and sewage sludge, is widely

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used due to its availability and composition (Adhikari et al., 2018). Additionally, exotic biomass sources such as coffee grounds and cotton shells have also demonstrated suitability for pyrolysis (Fahmy et al, 2020). Specific examples, such as malt waste from the brewing industry and oak wood chips, have been studied for their potential in bioenergy applications (Silva et al., 2022).

Pyrolysis produces three main products: bio-oil, biochar, and pyrolytic gas. Bio-oil is a liquid that can serve as a substitute for fuel oil and contains various organic compounds, including phenols, hydrocarbons, ketones, aldehydes, and furans. Biochar, a solid by-product, is primarily produced at lower temperatures and is commonly used as a soil amendment, adsorbent, or in energy storage applications (Zhang, 2023). Meanwhile, pyrolytic gas, consisting of hydrogen, carbon monoxide, methane, and carbon dioxide, serves as a valuable renewable fuel source, contributing to sustainable energy production (Abou et al., 2023). Reforming bio-oil into hydrogen involves a series of key chemical reactions, primarily steam reforming (SR) and the water-gas shift (WGS) reaction. In steam reforming, bio-oil reacts with steam to produce hydrogen and carbon monoxide, a process that commonly utilizes Ni-based catalysts due to their cost-effectiveness and high activity. The water-gas shift reaction follows steam reforming, converting carbon monoxide and water into additional hydrogen and carbon dioxide, further enhancing hydrogen yield (Liu et al., 2019).

Reaction of Steam Reforming:

$$C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{m}{2}\right)H_2$$

Reaction of Water-Gas Shift:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (1)$$

Catalysts are essential in the reforming process, with Ni-based catalysts favored for their cost-effectiveness, while noble metals like Rh and Ru offer superior activity but at higher costs (Liu et al., 2019). Bimetallic catalysts, such as Ni-Cu and Ni-Co, enhance performance and mitigate coke formation (Xie et al., 2015). However, catalyst deactivation remains a key challenge due to carbon deposition, metal sintering, and sulfur poisoning from bio-oil contaminants (Garcia et al., 2022). Scaling bio-oil reforming to an industrial level is hindered by feedstock variability and reactor design constraints, which affect stability and efficiency (Valle et al., 2018). Economic feasibility is also a concern due to high catalyst costs and the need for process integration (Pafili et al., 2021). Optimizing hydrogen production requires precise process control. Yields of up to 88% can be achieved at 650°C, with sorption-enhanced reaction processes (SERP) further improving conversion (Wu et al., 2016). However, high temperatures (>700°C) accelerate coke formation and catalyst deactivation. Feedstock pre-treatment and periodic catalyst regeneration are crucial for long-term efficiency (Garcia, 2022).

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a. Conversion efficiency in the pyrolysis process:

- 300-500°C: At this temperature range, pyrolysis mainly produces more biochar, with conversion efficiency around 27.39% to 35%. Efficiency varies depending on the biomass used, such as agricultural waste like rice straw, which can achieve higher efficiency at lower temperatures (Chen et al., 2022).
- 500-650°C: At this temperature, bio-oil becomes the dominant product. Conversion efficiency of bio-oil can reach 45-53%. Research shows that lignocellulosic feedstocks like wood and rice husk have better conversion around 550°C.
- 700-1100°C: Higher temperatures increase pyrolytic gas production, with gas conversion efficiency reaching 55-70%, but with lower bio-oil yield (around 25-30%) and biochar around 10-15%. Studies show increased hydrogen and methane content in pyrolytic gas, which can be used as renewable fuel (Wang et al., 2022).

b. Effect of Pressure on Conversion Efficiency:

- Atmospheric pressure (0.1 MPa): This is the standard condition in most pyrolysis experiments. Conversion efficiency for bio-oil at this pressure can reach 40-50%, depending on the feedstock.
- High pressure (up to 2 MPa): Using high pressure increases gas conversion efficiency. Research by Xie *et al.,* (2022) indicates that at 2 MPa, pyrolytic gas can reach 62-68%, while bio-oil yield slightly decreases to around 30-35%.

c. Effect of Biomass Type on Conversion Efficiency:

- Lignocellulosic Biomass (Wood, Rice Husk, Agricultural Waste): Lignocellulosic biomass produces good conversion in pyrolysis, with bio-oil conversion efficiency between 40-55% and pyrolytic gas between 25-35% (Cen et al., 2023).
- Organic Biomass (Municipal Waste, Paper Waste): Pyrolysis of organic waste produces bio-oil with an efficiency of around 35-45%, with pyrolytic gas around 30-40%. Organic waste generates more methane, improving gas efficiency (Saletnik et al., 2022).

Syngas Gasification and Reforming

Gasification operates optimally at 700–1000°C, enhancing syngas yield and quality (Rumbino et al., 2018). The gasification medium significantly influences syngas composition: air is widely used but lowers heating value due to nitrogen dilution, while pure oxygen improves efficiency (Ali et al., 2017). Steam gasification enhances hydrogen-rich syngas production and reduces tar formation (Zhou et al., 2024). The main gasification products are hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4). Hydrogen yield

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increases with higher temperatures and steam addition, while CO production is also temperature-dependent (Choung et al., 2024). CO_2 levels can be managed by optimizing gasification conditions, and methane formation is influenced by feedstock type (Duan et al., 2016). Syngas reforming relies on key reactions, including gasification ($C + H_2O$ ⍰ $CO + H_2$) and the water-gas shift ($CO + H_2O$ ⍰ $CO_2 + H_2$), which boost hydrogen output (Pinto et al., 2023). Nickel- and iron-based catalysts are commonly used, with nickel favoured for its high activity but prone to sintering and carbon deposition. Innovations, such as ultra-small Ni nanoparticles, improve catalyst stability (He et al., 2025). Fe-Ni bimetallic catalysts also enhance hydrogen yield while minimizing carbon accumulation (Zhang et al., 2017). Scaling up syngas reforming faces challenges, including tar formation, catalyst poisoning by sulphur, and residual carbon deposition (Smith et al., 2012). Carbon capture technologies, such as CaO-based CO_2 adsorption and sorption-enhanced steam reforming (SESR), improve hydrogen yield and process efficiency (Quan et al., 2024). These advancements support cleaner hydrogen production.

Liquefaction and Conversion of Biocrude to Hydrogen.

Hydrothermal liquefaction (HTL) operates at 10–25 MPa and 250–400°C, efficiently converting wet biomass into biocrude without requiring drying (Wang et al., 2024). Biocrude must undergo deoxygenation and hydrodesulfurization (HDS) to produce hydrogen, necessitating highly active catalysts (Muangsuwan et al., 2021). NiMo catalysts are preferred for their superior performance in hydrodeoxygenation (HDO) and HDS, reducing oxygen and sulfur content while improving fuel properties. CoMo catalysts are also effective but exhibit lower stability and activity (Yang et al., 2022). Liquefying hydrogen on an industrial scale presents challenges due to high energy consumption, particularly for maintaining cryogenic temperatures and ortho-para hydrogen conversion, increasing energy demand by ~15% [57]. Cost reduction strategies include integrating high-speed centrifugal compressors and optimizing cryogenic components (Tamarona et al., 2024). However, energy-intensive liquefaction and regasification reduce overall supply chain efficiency (Incer et al., 2023).

Biocrude-to-hydrogen conversion faces multiple obstacles, including carbon loss in the aqueous phase, necessitating biocrude upgrading. Coupling HTL with aqueous phase reforming (APR) can enhance hydrogen recovery and process viability (Tito et al., 2023). High oxygenated compound levels require catalytic HDO to improve biocrude quality (Badoga et al., 2023). Scaling from laboratory to industrial production involves addressing heat management, process recovery, and waste treatment (Lee et al., 2016). The high cost of refining biocrude limits large-scale adoption. Upgrading processes like solvent extraction and catalytic hydrotreating reduce oxygen content but increase costs (Zhao et al., 2024). Additionally, biocrude instability affects storage, transport, and upgrading. Factors like distillation temperature and storage conditions influence aging and quality degradation, necessitating improved stabilization techniques (Si et al., 2024).

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Comparison of Efficiency, Yield H_2, By-Products, and Costs

Hydrogen conversion efficiency differs across pyrolysis, gasification, and liquefaction, depending on process conditions and biomass type. It is commonly assessed using the solar-to-hydrogen (STH) efficiency formula, which represents the ratio of hydrogen's energy content to the total solar energy input. Below is an example calculation using this approach.

$$\eta_H = \left(\frac{Energy\ content\ of\ produced\ hydrogen}{Energy\ content\ og\ the\ input\ biomass}\right) \text{ x } 100\% \quad (2)$$

Hydrogen conversion efficiency varies by method. In pyrolysis, the steam-iron process achieves 53% efficiency at 800°C (Bleeker et al., 2010), while other studies report 27.39% efficiency (Zhao et al., 2024). Gasification efficiency ranges from 33% to 70%, depending on conditions and system centralization (Abuadala, 2010). Liquefaction exhibits exergy efficiencies between 31.4% and 45.5%, influenced by technology and operations (Naquash et al., 2022). Hydrogen yield also differs. Pyrolysis achieves 43.58–75.96 g H_2/kg biomass (Ma et al., 2014). while steam gasification can yield 40–190 g H_2/kg biomass, with wheat straw steam gasification reaching 55%. By-products vary across methods. Pyrolysis generates bio-oil, tar, and char. Gasification produces syngasbut also tar as a challenge. Liquefaction yields liquid hydrocarbons superior to pyrolysis bio-oil and gases like CO_2 and CH_4. Production costs fluctuate. Pyrolysis hydrogen costs \$1.25–\$2.20/kg, while air-steam gasification reaches \$2.69/kg. Air-blown gasification costs \$2.23/kg, whereas ballasted gasification reaches \$3.01/kg. Liquefaction costs range from \$0.979 to \$2.615/kg.

The production costs in Table 2 are calculated using the Levelized Cost of Hydrogen (LCOH), which determines the average hydrogen production cost over a facility's operational lifetime. The calculation formula is provided below.

$$LCOH_2 = \frac{ACC + OPEX_{total}}{mH_2} \quad (3)$$

where ACC represents the Annual Capital Cost, OPEX refers to the operational cost, and mH_2 denotes the amount of hydrogen produced per year (kg). While different methods have been compared for hydrogen yield, the interplay between these methods and potential scaling impacts need further exploration.

Table 2. Comparison of Hydrogen production methods: efficiency, yield, by-products, and costs

Method	Efficiency	H_2 Yield	By-products	Production Cost
Pyrolysis	27.39% -	43.58 – 75.96 g	Bio-oil, tar, char	\$ 1.25 - \$ 2.20/kg

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	53%	H_2/kg		H_2
Gasification	33% - 70%	40 -190 g H_2/kg	Syngas, tar	$ 2.69/kg H_2
Liquefaction	31.4% – 45.5%	-	High-quality liquid hydrocarbons, bio-oil, CO_2, CO, CH_4	$ 0.979 - $ 2.615/kg H_2

Challenges and Opportunities on An Industrial Scale

a. Challenges

The stability of non-precious-metal catalysts under extreme conditions remains a key industrial challenge. Encapsulation in 2D materials and platinum-based electrocatalysts improve performance, but reaction kinetics limit efficiency. Nanoporous electrocatalysts enhance energy conversion but face scalability issues. Similarly, CCS technologies encounter high costs and complex integration, despite advancements in solvent-based CO_2 capture. Gasification, pyrolysis, and liquefaction offer viable carbon capture pathways, yet catalyst deactivation and system integration hinder industrial adoption. In Cl_2 production from HCl, copper-based catalysts degrade over time, necessitating improved formulations like $Cu_{2.4}CeV_{0.5}Ox$. Catalytic membrane reactors (CMRs) enhance gas purification, but optimizing membrane flux and catalytic performance remains challenging. Advanced techniques such as coagulation-flocculation require further refinement for industrial use.

b. Opportunities in Technology Development

Perovskite-based catalysts offer promising applications in biomass thermochemical conversion, renewable energy integration, and CO_2 reforming. Their redox properties, ion mobility, and thermal stability enhance pyrolysis and gasification efficiency, with further optimization possible through ion substitution and structural modifications. Additionally, perovskite oxides exhibit high catalytic activity and stability in oxygen reduction and evolution reactions (ORR/OER), making them suitable for fuel cells and water splitting. In CO_2 reforming, perovskite catalysts facilitate methane conversion into hydrogen and syngas due to their oxygen mobility and resistance to reducing environments. Their integration into renewable energy systems supports sustainable fuel production by improving conversion rates and selectivity [86]. However, scalability remains a challenge, requiring surface engineering and doping to enhance stability and efficiency. Addressing these barriers is key to commercializing perovskite catalysts for sustainable energy applications.

CONCLUSIONS

This study evaluates the efficiency, economic viability, and industrial applicability of pyrolysis, gasification, and hydrothermal liquefaction for large-scale hydrogen production. The

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findings indicate that each method presents distinct advantages and challenges. Pyrolysis offers a viable route for bio-oil conversion into hydrogen, though catalyst performance and process optimization remain critical hurdles. Gasification achieves high hydrogen yields, yet syngas purification complexity limits its industrial deployment. Hydrothermal liquefaction demonstrates potential for biocrude-to-hydrogen conversion but requires further efficiency improvements and cost reductions for commercial viability. While these thermochemical pathways contribute to sustainable hydrogen production, addressing challenges related to efficiency enhancement, economic feasibility, and large-scale implementation is essential. Future research should focus on optimizing catalytic processes, integrating renewable energy sources, and developing cost-effective solutions to support the transition to a hydrogen-based energy system.

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