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A comparative review for hydrogen production from biomass using steam and supercritical water gasification technologies

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مراجعة مقارنة لإنتاج الهيدروجين من الكتلة الحيوية باستخدام تقنيات البخار وتغويز الماء فوق الحرج

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Abstract:
Biomass gasification has emerged as a promising technology for sustainable hydrogen production, offering a renewable pathway to meet global energy demands while reducing greenhouse gas emissions. This review provides an in-depth analysis of biomass gasification technologies, focusing on steam gasification and supercritical water gasification. It critically evaluates the influence of operating conditions, such as temperature, pressure, and feedstock characteristics, on hydrogen yield and syngas quality. The role of advanced catalysts in enhancing process efficiency and mitigating tar formation is also discussed in detail, with emphasis on transition metals, bimetallic catalysts, and novel composite materials. Challenges such as high capital costs, tar management, scalability, and competition with alternative hydrogen production methods are addressed, along with potential technological innovations to overcome these barriers. By integrating recent advancements and identifying critical research gaps, this manuscript aims to guide future studies toward achieving cost-effective and sustainable hydrogen production via biomass gasification. The review underscores the importance of techno-economic analyses, sustainability assessments, and large-scale implementation strategies to ensure the viability of biomass-derived hydrogen as a green energy carrier.

Keywords: Biomass gasification, Hydrogen production, Steam gasification, Supercritical water gasification, Catalysts.

الملخص
برز تغويز الكتلة الحيوية كتقنية واعدة لإنتاج الهيدروجين المستدام، مُوفرًا بذلك مسارًا متجددًا لتلبية الطلب العالمي على الطاقة مع خفض انبعاثات غازات الاحتباس الحراري. تُقدم هذه المراجعة تحليلًا مُعمّقًا لتقنيات تغويز الكتلة الحيوية، مع التركيز على التغويز بالبخار والتغويز بالماء فوق الحرج. وتُقيّم هذه المراجعة بشكل نقدي تأثير ظروف التشغيل، مثل درجة الحرارة والضغط وخصائص المواد الخام، على إنتاج الهيدروجين وجودة الغاز الاصطناعي. كما تُناقش بالتفصيل دور المحفزات المتقدمة في تعزيز كفاءة العمليات والحد من تكوّن القطران، مع التركيز على المعادن الانتقالية، والمحفزات ثنائية المعدن، والمواد المركبة الجديدة. وتُعالج هذه المراجعة تحديات مثل إدارة القطران، وقابلية التوسع، والمنافسة مع طرق إنتاج الهيدروجين البديلة، إلى جانب الابتكارات التكنولوجية المُحتملة للتغلب على هذه العوائق. من خلال دمج أحدث التطورات وتحديد الثغرات البحثية الحرجة، يهدف هذا البحث إلى توجيه الدراسات المستقبلية نحو تحقيق إنتاج هيدروجين فعال من حيث التكلفة ومستدام عبر تغويز الكتلة الحيوية. وتؤكد المراجعة على أهمية التحليلات التقنية والاقتصادية، وتقييمات الاستدامة، واستراتيجيات التنفيذ واسعة النطاق لضمان جدوى الهيدروجين المشتق من الكتلة الحيوية كناقل للطاقة الخضراء.

الكلمات المفتاحية: تحويل الكتلة الحيوية إلى غاز، إنتاج الهيدروجين، تحويل البخار إلى غاز، تحويل الماء إلى غاز فوق الحرج، المحفزات.

1. Introduction

Hydrogen is increasingly recognized as a key energy carrier due to its high energy density and zero carbon emissions during combustion [1]. Biomass gasification, a thermochemical process that converts organic materials into syngas (a mixture of hydrogen, carbon monoxide, methane, and other hydrocarbons), has gained significant attention as a renewable route for hydrogen production [2]. Biomass contains approximately 6% hydrogen by mass, equivalent to 0.672 m^3 of gaseous hydrogen per kilogram of biomass [3]. Gasification offers a versatile platform for producing not only hydrogen but also other valuable chemicals and fuels [4]. When combined with carbon capture and storage (CCS), biomass gasification can achieve negative carbon emissions, aligning with global climate goals [5]. The thermochemical conversion of biomass into hydrogen involves several stages: drying, pyrolysis, oxidation, and reduction. During pyrolysis, biomass decomposes into volatile gases, char, and tar at elevated temperatures (typically 400–800°C). In the subsequent oxidation stage, oxygen or steam is introduced to partially combust the biomass, generating heat and reactive intermediates such as CO and H_2 [6]. The reduction zone facilitates reactions like the water-gas shift reaction and methanation, which play a critical role in enhancing hydrogen yield [7]. Two primary gasification technologies have emerged as particularly promising for hydrogen production: steam gasification (SG) and supercritical water gasification (SCWG). Steam gasification maximizes hydrogen production through steam reforming reactions and operates at atmospheric to moderate pressures (1-30 bar) with temperatures ranging from 700-900°C. SCWG achieves near-complete gasification of wet biomass at supercritical conditions ($T > 374°C$, $P > 221$ bar), eliminating the need for biomass drying and enabling processing of high-moisture feedstocks [8]. Despite its promise, biomass gasification faces several challenges that hinder its widespread adoption. One of the most significant issues is tar formation, which reduces syngas quality and clogs downstream equipment [9]. Tars are complex hydrocarbon compounds that require additional processing steps, such as catalytic cracking or thermal decomposition, to mitigate their impact [10]. Another challenge is the high capital and operational costs associated with gasification plants, which limit their economic feasibility, particularly for small-scale applications [11]. Additionally, scaling up laboratory-scale processes to industrial levels remains a major hurdle, as does optimizing the composition and stability of catalysts under harsh operating conditions [12]. To address these challenges, researchers are exploring innovative strategies and technological advancements. For instance, advanced catalysts based on transition metals such as nickel (Ni), cobalt (Co), and ruthenium (Ru) have shown great potential in enhancing hydrogen production and mitigating tar formation [13]. Bimetallic catalysts, such as $Ni\text{-}Co/Al_2O_3$ and $Ru/CeO_2\text{-}ZrO_2$, exhibit superior performance at low temperatures and steam-to-carbon ratios, making them ideal candidates for commercial applications [14]. Novel reactor designs, including circulating fluidized beds and entrained-flow reactors, offer improved heat distribution and mixing, enabling higher hydrogen yields and better process control [15]. Moreover, integrating biomass gasification with complementary technologies, such as Biorefineries concepts and CCS, can enhance resource efficiency and environmental benefits [16].

This comprehensive review synthesizes recent advancements in biomass gasification for hydrogen production, comparing two mainstream technologies: steam gasification (SG) and supercritical water gasification (SCWG). It discusses the roles of operating conditions, advanced catalysts, and reactor designs in optimizing hydrogen yield and product quality. Furthermore, challenges and prospects for improving process efficiencies are explored to inform future research directions.

2. Fundamentals of Biomass Gasification

Process Mechanisms and Thermodynamics

The gasification process employs thermochemical reactions to convert carbonaceous feedstocks including biomass, coal, and waste into synthesis gas (syngas). This combustible mixture is dominated by hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4) [17]. The process involves complex interactions between multiple chemical reactions, heat and mass transfer phenomena, and fluid dynamics [18]. The principal reactions in gasification are endothermic, requiring energy input, which is typically supplied through partial oxidation of the feedstock. This can occur via autothermal or allothermal processes. In **autothermal gasification**, the gasifier is internally heated through partial combustion of the feedstock. If air is used as the oxidizing agent, the resulting syngas contains significant nitrogen. For higher-quality syngas production, pure oxygen (in entrained flow reactors) or oxygen-steam mixtures (in fluidized bed reactors) are preferred. Autothermal gasification offers a major efficiency advantage through direct internal heating, significantly enhancing energy utilization [19, 20]. In contrast, **allothermal (indirect) gasification** separates heat production from heat consumption. This method typically employs two interconnected reactors: the first for biomass gasification and the second for combusting residual char or product gas to generate heat for the first reactor. Heat transfer is achieved through circulating bed materials or heat exchangers. The gasification mechanism occurs through four sequential stages (Figure 1):

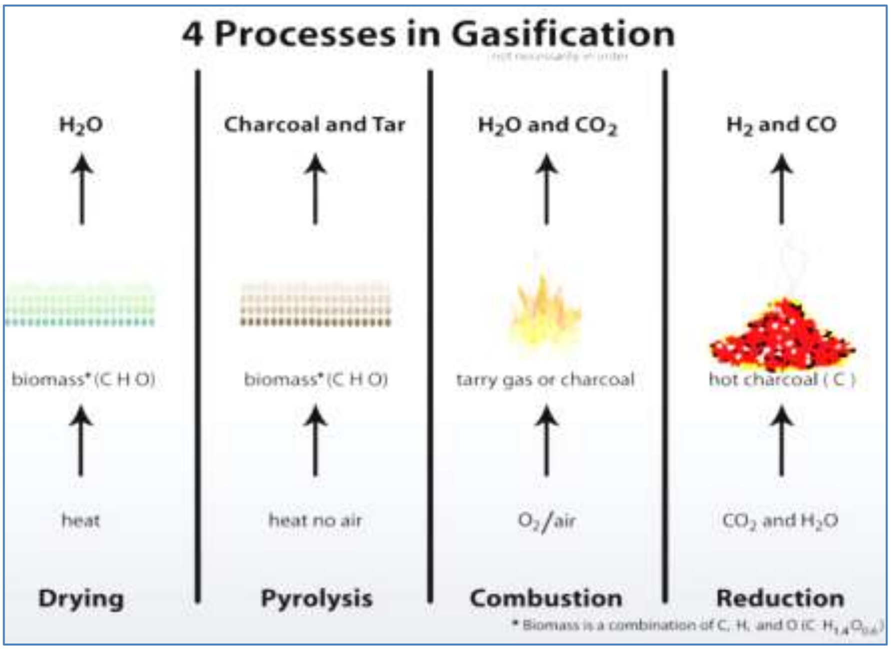

Figure (1): Steps of the gasification process.

I. Drying (Endothermic Stage): Moisture in the biomass is evaporated at temperatures of 100–200°C, reducing moisture content to below 5%. No chemical reactions occur during this phase due to the low temperatures.

II. Pyrolysis (Endothermic Stage): In the absence of oxygen, dry biomass decomposes into volatile compounds, solid char, and tar. This stage requires heat, which is often supplied by combustion in adjacent zones.

III. Oxidation (Exothermic Stage): Partial oxidation of the feedstock provides the thermal energy needed to sustain endothermic reactions and maintain operating temperatures. This step occurs under oxygen-deficient conditions to avoid complete combustion.

IV. Reduction (Endothermic Stage): The gas mixture and char from previous stages react to form syngas. Temperature plays a critical role in syngas composition, with higher temperatures reducing tar formation but increasing ash sintering risks. Typical gasification temperatures range from 800–1100°C, or 500–1600°C when oxygen is used.

3. Kinetics of Gasification

Gasification reactions proceed to varying degrees depending on temperature, pressure, and feedstock. Typically, only one-fifth to one-third of the oxygen required for complete combustion is used. This limited oxidant generates sufficient heat to gasify the remaining feedstock. Biomass gasification involves thermochemical conversion processes that produce hydrogen, carbon monoxide, methane, and other gases. Steam gasification utilizes water vapor as a gasifying agent to convert biomass into combustible gases. Supercritical water gasification occurs above the critical point of water ($(T > 374\,℃\ and\ P > 221\ bar)$ [4] where water exhibits unique solvent properties. Catalysts enhance hydrogen selectivity and improve carbon gasification rates under steam gasification conditions. Supercritical water acts as both solvent and reactant, yielding high hydrogen concentrations without tar or coke. The main reactions involved in the biomass gasification process are the followings [21]:

$$\text{Carbon gasification:} \qquad C + H_2O_{(g)} \rightarrow\ CO + H_2 \ldots\ldots\ldots\ldots \Delta H = +131.3\ \frac{kJ}{mol} \ldots\ldots (1)$$

$$\text{Water} - \text{gas shift reaction: } CO + H_2O_{(g)} \rightarrow\ CO_2 + H_2 \ldots\ldots \Delta H = -41.2\ \frac{kJ}{mol} \ldots\ldots (2)$$

$$\text{Methane reforming: } CH_4 + H_2O_{(g)} \rightarrow\ CO + 3H_2 \ldots\ldots\ldots\ldots \Delta H = 205.8\ \frac{kJ}{mol} \ldots\ldots (3)$$

$$\text{Methanation for } CO\text{:}\quad CO + 3H_2 \rightarrow\ CH_4 + H_2O_{(g)}\ \ldots\ldots\ldots \Delta H = -205.8\ \frac{kJ}{mol} \ldots\ldots (4a)$$

$$\text{Methanation for } CO_2\text{:}\quad CO_2 + 4H_2 \rightarrow\ CH_4 + 2H_2O_{(g)} \ldots\ldots \Delta H = -164.7\ \frac{kJ}{mol} \ldots\ldots (4b)$$

4. Factors Influencing Hydrogen-Rich Syngas

The efficiency and output of hydrogen-rich syngas in biomass gasification are governed by a multitude of operational and feedstock-related factors. Understanding these parameters is critical for optimizing the gasification process, enhancing hydrogen yield, and minimizing undesirable byproducts such as tar. Below, are some important indicators in detail, supported by a summary table (1) and an illustrative diagram, Figure (2).

- **Particle Size of Feed Material:**
  - Smaller particles (<3 mm) increase the surface area for reactions, accelerating devolatilization and char gasification. This results in higher hydrogen (H_2) and carbon monoxide (CO) concentrations.
  - Larger particles hinder diffusion, reducing gas yield and promoting tar formation [22].
- **Gasification Temperature**
  - Elevated temperatures (800–900°C) favor endothermic reactions (e.g., Boudouard reaction, steam reforming), boosting H_2 and CO production.
  - Methane (CH_4) and heavier hydrocarbons crack at higher temperatures, further enriching syngas quality [23].
- **Equivalence Ratio (ER)**
  - ER (ratio of actual air to stoichiometric air) impacts oxidation and combustion.
  - Low ER (0.2–0.4) optimizes gasification by balancing heat generation and syngas quality. Excessive ER reduces H_2 yield due to combustion of flammable gases [24].
- **Gasification Agents**
  - Steam: Maximizes H_2 production via water-gas shift reactions.
  - Oxygen: Yields medium-calorific syngas but is costly.
  - Air: Introduces nitrogen, diluting syngas and lowering heating value [25].

- **Steam-to-Biomass Ratio (S/B)**
  - Higher S/B ratios (1.5–2) enhance H_2 production by promoting steam reforming and tar cracking.
  - Excessive steam lowers process efficiency and increases CO_2 content [26].

Table 1: Summary of Factors Influencing Hydrogen-Rich Syngas.

Factor	Optimal Range	Impact on H_2 Production	Remarks
Particle Size	0.5–3 mm	↑ H_2 and CO; ↓ tar	Smaller particles improve reaction kinetics.
Temperature	800–900°C	↑ H_2 (up to 24.7 vol%); ↓ CH_4	Endothermic reactions dominate at high temperatures.
Equivalence Ratio (ER)	0.2–0.4	Moderate ER maximizes H_2 yield	High ER oxidizes H_2, reducing syngas quality.
Gasification Agent	Steam > Oxygen > Air	Steam yields ~47.5% H_2; air yields ~12–20% H_2	Steam avoids nitrogen dilution, enhancing calorific value.
S/B Ratio	1.5–2	↑ H_2 yield (up to 34.28 mol/kg)	Excess steam raises energy costs and CO_2 emissions.

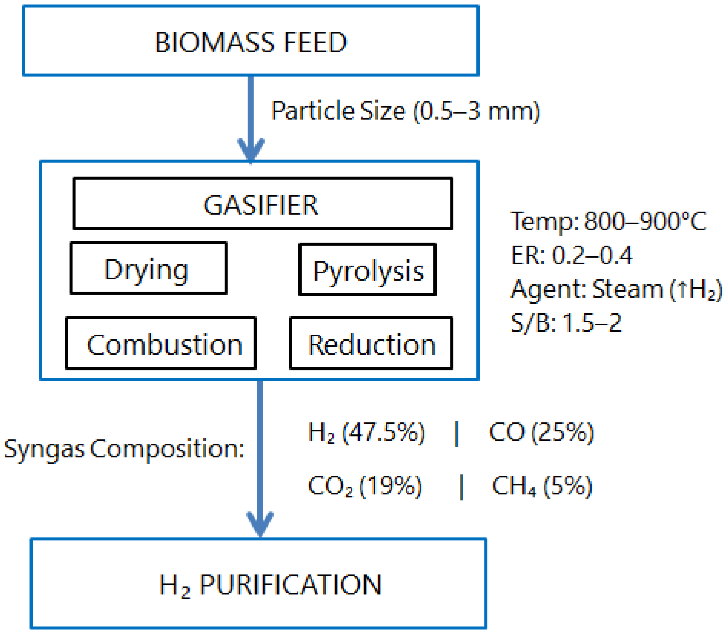

Figure (2): Influence of some important indicators on Hydrogen Yield in Biomass Gasification.

The interplay of these factors determines the viability of biomass gasification for hydrogen production. For instance, combining steam gasification (high S/B ratio) with optimized temperature and particle size can achieve H_2 concentrations exceeding 40 vol%. However, challenges like tar formation and energy-intensive steam generation necessitate trade-offs, underscoring the need for integrated process design and advanced catalysts [25, 26].

5. Reactor Technologies

Gasification is the process of converting organic material into a syngas through high-temperature reactions, which is composed of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4). Biomass gasifiers are reactors designed to convert biomass through thermochemical processes such as pyrolysis, partial oxidation, and reduction. There are various gasifiers technologies designed to suit different feedstocks, scales, and applications. Gasification of biomass offers a great potential of possible product gas applications and there are various gasification technologies available for biomass. The main difference is the used gasification agent and related to this the way of heat supply. Depending on the designed heating system, gasifiers can be operated either autothermally (adiabatic) or allothermally (isothermal). Other difference is the reactor design, which distinguishes between fixed bed, fluidized bed, and entrained flow reactors and the used gasification agent [27].

i. **Fixed Bed Gasifiers** are the most commonly used type of biomass gasifier. In this case, biomass is fed into a stationary bed within the gasifier, where it undergoes thermal decomposition. The gasification process occurs as the biomass moves downward through the reactor. The hot gases flow upward through the bed, and the resulting syngas is collected at the top (by Updraft Gasifier) or flow downward through the reactor and exits through the bottom (by Downdraft Gasifier) [28]. Fixed-bed gasifiers are structurally simple but face limitations such as generating low-calorific gas with elevated tar levels. The produced gas typically comprises 40–50% nitrogen (N_2), 15–20% hydrogen (H_2), 10–15% carbon monoxide (CO), 10–15% carbon dioxide (CO_2), and 3–5% methane (CH_4), yielding a net calorific value (CV) of 4–6 MJ/Nm³. When air is used as the gasifying agent, the high nitrogen content doubles the gas volume, necessitating larger downstream gas cleaning systems. To enhance gas CV, biomass feedstock moisture must remain below 15–20%, which often demands pre-drying prior to processing [29].

ii. Fluidized bed (FB) gasifiers are generally used for uniform mixing of the feedstocks and gases and utilize a bed of inert materials (usually sand or alumina) that are fluidized by a stream of gas. The two primary types of fluidized bed gasifiers are the Bubbling Fluidized Bed (BFB) and the Circulating Fluidized Bed (CFB). Both reactors can operate at atmospheric conditions and temperature distribution along the gasifiers is better in comparison to that of the fixed bed reactor. Fluidized-bed (FB) gasifiers face significant operational challenges, primarily bed material slagging caused by biomass ash content, particularly due to alkali metals prevalent in herbaceous annual feedstocks. While reducing bed temperature mitigates slagging, it raises char loss through ash removal. The resultant gas contains impurities including particulates, tars, nitrogen compounds, sulfur compounds, and alkali compounds [30]. The required gas purification level depends on its end application, achievable via two approaches: hot-gas cleaning, which maximizes energy recovery but involves technical complexity, or cold-gas cleaning, a simpler method generating tar-contaminated wastewater with disposal challenges.

iii. Entrained flow gasifiers operate at higher temperatures (approximately 1500 °C) compared to fixed bed and fluidized bed gasifiers, which allows for a higher throughput of feedstocks [30]. The syngas produced by entrained flow gasifiers exhibits a high purity and minimal impurities such as tar.

6. Role of Catalysts

Several research groups have actively developed metal catalysts for the steam reforming (SR) of biomass tar. In 2008, He et al. [31] utilized the deposition-precipitation method to prepare a supported nano-NiO/γ-Al_2O_3 catalyst. This catalyst demonstrated high activity for tar removal within a bench-scale combined fixed bed reactor during biomass pyrolysis, achieving a tar removal efficiency of 99% at 1073 K. Separately, Wang et al. (2006) [32] reported a highly stable NiO-MgO catalyst synthesized via co-precipitation. This NiO-MgO formulation exhibited excellent reducibility and maintained stable activity for reforming raw fuel gas without requiring pre-reduction. Sricharoenchaikul et al. (2016) [33] found that employing NiO-loaded calcined dolomite catalysts resulted in a reduced formation rate of both tar and char, alongside a 30% increase in total product gas yield. Furthermore, char-supported Ni catalysts, prepared and reported by Jiang et al. (2017) [34], were also shown to be effective for tar steam reforming. Subsequent catalyst development has progressed through diverse approaches, with two particularly significant aspects being the exploration of novel catalyst supports and the refinement of preparation methods.

- **Metal Catalysts on Conventional Oxides**

Ni-based catalysts supported on conventional oxides, such as α-Al_2O_3, CeO_2, and ZrO_2, are widely studied for tar steam reforming. Adhikari et al. (2008) [35] compared Ni/α-Al_2O_3, Ni/ZrO_2, Ni/TiO_2, Ni/CeO_2, and Ni/MgO, finding that Ni/α-Al_2O_3 exhibited the highest activity (residual tar yield: 9.3%) but suffered severe coke deposition (12.7%). In contrast, Ni/CeO_2 showed lower coke yield (4.3%) due to CeO_2's redox properties, which enhance oxygen mobility and gasify carbon intermediates. Co-impregnation of CeO_2 with Ni on α-Al_2O_3 (Ni/CeO_2/α-Al_2O_3) further improved performance, achieving 8.6% tar yield and 5.6% coke, attributed to strong Ni-CeO_2 interaction and nanocomposite formation. Noble metal additives (e.g., Pt) enhanced Ni/CeO_2/α-Al_2O_3's self-activation and stability [36]. However, Pt/Ni/CeO_2/α-Al_2O_3 faced Ni particle aggregation, which was mitigated by MgO addition, forming NiO-MgO solid solutions [37]. MnO_2 addition to Ni/α-Al_2O_3 (Ni+MnO_2/α-Al_2O_3) outperformed CeO_2-modified catalysts, reducing coke via Mn's superior redox cycles. Alloying Ni with Fe (Ni-Fe/α-Al_2O_3) optimized at Fe/Ni=0.5 yielded high activity (syngas rate: 2,864 μmol·min^{-1}) and coke resistance, leveraging Fe's oxygen affinity to gasify carbon. Similarly, Ni-Co/α-Al_2O_3 (Co/Ni=0.25) showed synergy for oxygenate reforming, while Co-Fe/α-Al_2O_3 (Fe/Co=0.25) achieved the highest syngas yield (3,415 μmol·min^{-1}) among alloy catalysts [38].

- **Hydrotalcite-Derived Catalysts**

Hydrotalcite-like compounds (HTlcs) enable synthesis of highly dispersed, thermally stable catalysts. WANG et al. (2008) [39] developed Ni/Mg/Al catalysts from Ni-Mg-Al HTlcs, forming nanocomposites of Ni nanoparticles (~8.5 nm) and Mg(Ni, Al)O oxides (~11.5 nm). This structure enhanced metal-support interaction, achieving high activity (tar yield: 0.6%) and coke resistance (4.0%). Introducing Fe into HTlcs (Ni-Fe/Mg/Al) produced uniform fcc Ni-Fe alloy nanoparticles (Fe/Ni=0.25) with 3,594 μmol·min^{-1} syngas yield and 4.0%. These alloys outperformed MnO_2- or CeO_2-modified Ni/Al_2O_3 and Rh/CeO_2/SiO_2, maintaining regenerability via reversible oxidation-reduction cycles. Similarly, Ni-Cu/Mg/Al from Ni-Cu-Mg-Al HTlcs reduced coke tenfold compared to Ni/Mg/Al, attributed to Ni-Cu alloy stability [40]. Co-based HTlc-derived catalysts, like Co/Mg/Al (10/40/50), formed Co nanoparticles (~14 nm) on $MgAl_2O_4$ supports, achieving high activity (syngas yield: 2,449 μmol·min^{-1}) but gradual deactivation due to structural changes (Wang et al., 2014b). Co-Fe/Mg/Al (10-10/40/40) with bcc Co-Fe alloys showed superior activity (3,415 μmol·min^{-1}) and regenerability, though MgO support oxidation limited long-term stability [39].

Conclusion

Biomass gasification presents a viable and sustainable pathway for renewable hydrogen production, aligning with global decarbonization goals. Steam gasification and supercritical water gasification (SCWG) emerge as the most promising technologies, offering high hydrogen yields and efficient conversion of diverse feedstocks, including wet biomass (SCWG). Key operating parameters—temperature (800–900°C), steam-to-biomass ratio (1.5–2), equivalence ratio (0.2–0.4), and feedstock particle size (<3 mm)—critically influence hydrogen concentration and syngas quality.

Compliance with ethical standards

Disclosure of conflict of interest

The authors declare that they have no conflict of interest.

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