

Review on Advance Catalyst for Biomass Gasification

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Abstract

The production of renewable energy from biomass waste is a recent innovative approach attracting significant attention. In this field, gasification technology has become an important method, enabling the transformation of biomass into bio-syngas for wide applications, such as electrical power, transportation fuel, cooking fuel, and chemicals. Bio-syngas containing hydrogen, carbon monoxide, carbon dioxide, and methane, are considered a clean and nontoxic fuel. To achieve an effective and efficient gasification process, capable of producing a fuel grade syngas, the use of the catalyst has been reported as the most practical approach. Although this concept is currently in development, it has captured the interest of numerous investigations. The current challenge is the development of a catalyst that can reduce tar, enhance H₂ yield at a relatively low temperature, capture CO₂, and maintain an extended active lifespan. Therefore, this research aimed to review the novel catalysts discussed in the latest literatures with the ability to produce the highest hydrogen product by using an effective process. The catalysts included natural minerals containing alkali metals, metals, carbon, and composites. Additionally, here also suggested the potential materials should be explored more intensively for gasification catalysts. This review would help to promote and accelerate the research and application of biomass gasification using local existing feedstock. Since the future of energy depended on renewable sources, producing syngas became one of the best options to support energy demand using biomass waste in Indonesia.

Keywords: Biomass, Catalyst, Gasification, Renewable energy, Syngas

1 Introduction

Biomass-based power and hydrogen production plants are becoming more popular recently. The extraction of syngas from various biomass-based feedstock has become the dominant approach in producing renewable

energy and minimizing the negative effect on the environment simultaneously [1], [2]. Several research works have been carried out to convert biomass into valuable energy through biochemical and thermochemical transformation. However, the thermochemical process shows a greater significance due to its rapid process,

simple technology, and ability to transform low-grade biomass into high-grade fuel.

There are three main thermochemical methods, namely combustion, pyrolysis, and gasification [3], [4]. The gasification process includes all the first two processes, combustion (complete and partial oxidation) and pyrolysis, besides drying and reduction, thereby offering a greater potential for higher gas production. Moreover, bio-syngas refers to syngas produced from biomass.

Traditionally, syngas has been predominantly procured from fossil fuels such as coal, natural gas, residual oil, and petroleum. However, the environmental implications of this practice, particularly regarding carbon emissions, have ignited ongoing debate. To overcome this issue, renewable resources-based hydrogen production would be a significant alternative.

High-quality syngas derived from biomass is critical for improving the efficiency of combustion engines and reducing emissions, due to its carbon-neutral nature [2], [5]. The most popular feedstock for syngas production is lignocellulosic biomass derived from agro-industrial and wood residues. It is highly available [3], [6] and can be efficiently converted into hydrogen and carbon monoxide through thermochemical processes. Moreover, utilizing this feedstock can significantly reduce waste accumulation and mitigate potential environmental issues.

Biomass waste available in each area depends on the natural resources and agricultural activities. The use of locally sourced biomass is crucial to reduce material transportation costs. Due to the specific characteristics of each biomass waste, there is a need to identify the physical and chemical properties through proximate and ultimate analysis. Subsequently, the proper reactor, gasifying medium, and appropriate catalyst will be selected according to the biomass characteristics, desired gas product, and capital investment.

The most significant problem in the gasification process is tar formation as well as the high temperature required to obtain feedstock-medium gasification reaction and promote water-gas shift reaction. To address this issue, the use of the catalyst has been reported to reduce tar concentration in gas products, lower the reaction temperature, and release more combustible gases. However, the catalyst materials and preparation have a crucial impact on the gasification effectiveness and feasibility. The biomass catalytic

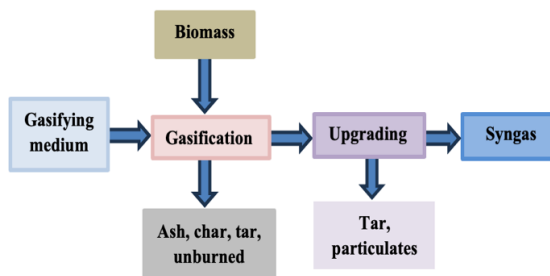


Figure 1: General gasification scheme.

gasification with the prospective catalyst suggestion to overcome the main problems associated with biomass gasification was extensively discussed in this paper.

The primary objective of this research is to thoroughly examine the catalysts utilized in biomass gasification; specifically focusing on the latest technological advancements. Through careful analysis, the results obtained from using these catalysts were identified and comprehensively compared. Furthermore, this study delves into discussing the necessary future work that needs to be undertaken and emphasizes the importance of conducting in-depth investigations on prospective catalysts. By providing a comprehensive review of these catalysts, it would establish a solid foundation of knowledge for further studies. This will greatly contribute to developing and preparing the most effective catalyst for optimal performance in biomass waste gasification processes within Indonesia's burgeoning industry.

2 Biomass to Bio-syngas

Bio-syngas is the syngas produced from biomass as raw material. Previous reports showed that biomass-based fuel is a promising solution to replace natural gas and other fossil fuel functions. However, the technology for biomass conversion still possessed technical problems concerning a high tar formation during production, necessitating further research both in the present and the future.

The gasification process includes the conversion of a solid organic feedstock into a gas phase (syngas), a solid phase (char), and a condensable phase (tar) using a gasifying medium under a certain temperature. Biomass gasification occurred through the chemical reaction of lignocellulosic materials under partial oxidation with a gasifying medium. In this process,

solid by-products, such as ash, char, tar, and unburned materials are commonly generated, while the gas outlet goes through another line to the upgrading process before leaving as a syngas fuel, as shown in Figure 1. The main reactions inside a reactor are outlined in Table 1.

The Boudouard and water-gas reactions are endothermic and dominate the process. In general, the gasification temperature is 1000 °C or more, but catalytic gasification is operated at a lower temperature, typically around 650 °C [7].

The quality of gas products is significantly affected by the type of biomass, operational parameters, such as type of reactor, working temperature, equivalence ratio (ER), steam to biomass ratio (S/B) [3], [8] and upgrading method. Additionally, the use of specific catalysts has been investigated to improve the syngas properties and yield significantly.

Table 1: Procedure and chemical reaction in gasification [7], [9]–[12]

Process and Reaction	Chemical Reaction Mechanisms	ΔH^0_{298K} (kJ/mol)
Drying:	Biomass + heat \rightarrow dry feedstock + H ₂ O	
Pyrolysis:	Carbon + heat \rightarrow volatile + char	
Solid to gas reaction (heterogenous)		
Oxidation: Partial oxidation	C + O ₂ \rightarrow CO ₂	-394
	C + ½O ₂ \rightarrow CO	-123
	H ₂ + ½O ₂ \rightarrow H ₂ O	-242
	CO + ½O ₂ \rightarrow CO ₂	-283
	NH ₃ + ¾O ₂ \rightarrow ½N ₂ + 3/2H ₂ O	-383
Reduction: Water-gas	H ₂ S + 3/2O ₂ \leftrightarrow SO ₂ + H ₂ O	-563
	C + H ₂ O \rightarrow CO + H ₂	+131
	C + 2H ₂ O \rightarrow CO ₂ + 2H ₂	+77
Boudouard	C + CO ₂ \rightarrow 2CO	+173
Methanation	C + 2H ₂ \rightarrow CH ₄	-75
Gas-to-gas reaction (homogenous)		
Water-gas shift	CO + H ₂ O \rightarrow CO ₂ + H ₂	-41
Steam reforming	CH ₄ + H ₂ O \rightarrow CO + 3H ₂	+206

3 The Function of Gasification Catalyst

The presence of high tar content in the gas product constitutes a critical challenge in biomass gasification. The removal of tar through the thermal method is not recommended due to the huge energy consumption. Carbon dioxide is also another gas impurity that should be reduced in syngas. Meanwhile, several investigations have explored the application of a wide range of catalysts to overcome these obstacles.

Catalyst plays an important role in gasification technology. It triggers the effective gasification process for optimum production of syngas. Catalyst works on lowering operational temperature, maximizing hydrogen and carbon monoxide production by stimulating further tar conversion [2], [7], and adsorbing CO₂ from the gas product. The use of appropriate catalysts is crucial in improving the gasification rate and controlling the certain components production in syngas [13].

4 Catalytic Gasification

The production of syngas requires a high temperature to support the complex reactions occurring in the reactor. Generally, the operating condition exceeds 873K to increase H₂ purity [14], indicating a high operational cost [15]. In this context, an effective catalyst plays a crucial role in reducing the activation energy and accelerating the reaction to obtain the desired products [16]. Catalytic gasification is a novel technology for increasing the effectiveness of gasification for syngas production.

The catalytic mechanism reported in [7] showed that the rate-determining step was attributed to the diffusion of catalyst particles, rather than the adsorption of the gasification medium or the reaction of adsorbed components with the carbon. Direct catalysis was also discussed, where the gasification medium was absorbed, and the reaction took place in the catalyst-carbon interface. Subsequently, the catalyst was divided into ‘pitting’ and ‘edge-recession’ categories based on its affinity to the carbon. During gasification, the catalyst spread on the surface and created channels, which further increased the surface area and reaction rate. There were also improved gasification systems and products, which facilitated specific reaction rates by increasing burnout, concentration, and availability of the carbon remaining. The reaction rate will also increase by the significant catalytic activity due to the enhancement of the ratio catalyst to carbon [17]. Moreover, increasing the reaction rate means obtaining gas products in a shorter time to enhance productivity as well as reduce operational energy demand and cost.

5 Type of Catalyst

The catalyst for gasification is generally loaded into a gasifier (*in situ*) to control tar production by further

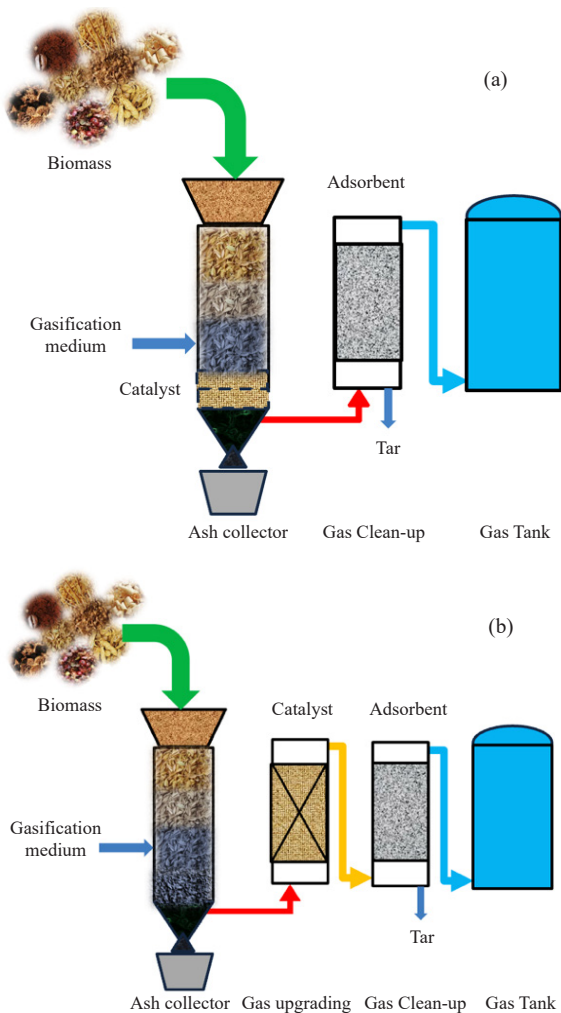


Figure 2: Gasification using (a) *in situ* (b) *ex situ* catalytic reactor mechanism.

reaction and produce more flammable gas components. The scheme of *in situ* catalytic gasification mechanisms is shown in Figure 2.

The catalyst can also be located outside the gasifier (*ex situ*) in a catalytic reactor to reduce the operating temperature and enhance the thermal cracking of tar [18], [19]. *Ex situ* catalytic gasification provides the catalyst in another unit outside the gasification reactor. Although this method can make the catalyst free of the ash and other impurities produced from the gasification, it requires higher capital investment for the catalytic reactor.

According to Ren *et al.* [3], catalysts commonly

used in gasification include natural minerals, alkali metals, and Ni-based, which have activity for biomass gasification. The selection of the appropriate loading method and type of catalyst is based on the feedstock type, product desired, technology, and capital investment.

5.1 Natural mineral-based catalyst

Natural minerals including dolomite, zeolite, bentonite, olivine, and limonite, have shown their efficacy as catalysts in biomass gasification. These mineral catalysts typically contain oxides, such as Al_2O_3 , Fe_2O_3 , MgO , CaO , AlO_4 and SiO_4 [20].

Dolomite and olivine have been proven to reduce tar content and enhance the hydrogen in syngas in the gasification of coal and pine sawdust blends, as reported by Ma *et al.* [21]. The use of these catalysts led to increase H_2 yield from 52.9–55.5 g/kg-fuel and 47.5–52.1 g/kg-fuel, respectively. Consequently, the tar content decreased from 5.4–0.4 (g/Nm³) and 7–0.8 g/Nm³. Aprianti *et al.* [22] applied 12.5% natural zeolite for fine coal gasification at 750 °C, leading to an increase in temperature. The resulting syngas comprised 32 vol% H_2 , 30.1 vol% CO, 27.7 vol% CH_4 and 5.1 vol% CO_2 , with the HHV of 18.97 MJ/Nm³.

A specific preparation technique is imperative for better gasification efficiency. Some reported the direct use of the catalyst, while the others performed several treatments. Calcination through the thermal process is the most common procedure found in the literatures. It substantially enhances the fundamental characteristics of the materials. Adding any other materials through physical or chemical processes is another interesting preparation method to modify catalysts. Waluyo *et al.* [23] used modified natural zeolite in the steam gasification of palm kernel shells at 750 °C, resulting in a significant reduction of tar content up to 98%, and 52–64% hydrogen composition in the syngas. Bentonite was used by Aprianti *et al.* [24] in the gasification of palm empty fruit bunch using updraft steam gasification at 550 °C. The syngas obtained contained 27.74% H_2 and 20.43% CO, with the HHV up to 12.79 MJ/Nm³. Lahijani *et al.* [16] prepared ash of palm empty fruit bunch for gasification of palm shell char. The results showed that loading 10% of the ash content delivered the highest gasification reactivity, with an activation energy of 158.75 kJ/mol.

Catalysts play a crucial role in promoting the

gasification reaction and removing CO₂ resulting from the gasification reaction through adsorption, as shown in Table 1. These actions significantly contribute to the increase in the quality of the syngas produced. The use of catalysts with CO₂ capture ability is a promising technology for producing syngas with high yields of CO and H₂ [25]–[27]. Chandarin *et al.* [28] reported the modification of Al₂O₃ with Mg-Zr oxide for the gasification catalyst. The introduction of Mg-Zr oxide to alumina resulted in a 1.4-time larger capacity for CO₂ adsorption compared to bare alumina. Zhao *et al.* [25] investigated the CaO-based catalyst integrated CO₂ capture in the gasification process. The CO₂ adsorption energy increased on the 10% Ni/CaO surface compared to the CaO. This indicated that the 10% Ni/CaO favored *in situ* CO₂ capture in biomass thermochemical process. Furthermore, Zamboni *et al.* [29] explained that the CaO-Ca₁₂Al₁₄O₃₃/olivine bifunctional catalyst had sorption stability at 700 °C, leading to a higher H₂ production compared to olivine at 800 °C and CO₂ sorption. At 700°C, sorbent addition allowed to halve tar content and eliminate the heaviest tar. Lan *et al.* [30] also used CaO as the catalyst in the steam gasification of sawdust, where the increase in temperature from 650–850 °C enhanced H₂ and CO production but decreased CO₂ and CH₄ content. The use of steam as a gasifying agent also increased H₂ up to 48%. Moreover, increasing CaO from 0–50% led to the enhancement of H₂ content from 40–68%.

CaO has proven to be exceptional for CO₂ capture in bare CaO or modification with metals. However, modifying CaO with metals or other materials significantly improved the catalyst capacity and performance. The CO₂ captured by CaO follows the carbonation reaction as expressed in Equation (1), leading to a reduction of CO₂ under gasification conditions. This phenomenon also drives the water gas-shift reaction, as expressed in Equation (2) to increase H₂ yield. Subsequently, CaO is recovered through calcination under a certain temperature to remove CO₂, as expressed in Equation (3). The efficiency of these reactions varies depending on the S/B ratio, temperature, pressure, and CaO loads [31].



5.2 Alkali metal and metal-based catalyst

Alkali metal catalysts belong to Group IA in the periodical table, including Li, Na, K, Rb, etc., which are categorized as the primary catalysts to elevate the biomass gasification reaction. Although these metals cannot be used directly for tar reforming, their application as an additive and mixture in the gasification feedstock is significant [3].

The metal-based catalyst seems to be more attractive compared to natural-based. This is because metal catalysts are mostly mixed or impregnated onto other materials such as natural minerals, to facilitate their use in the gasifier. The combination of the metal and other materials also escalates the functional characteristics of the catalyst.

5.2.1 Ni-based catalyst

Ni-based catalyst has been extensively explored in the literature of gasification. This was due to the tremendous performance in tar cracking, methane reforming, and gasification temperature lowering [32]. Xu *et al.* [33] also compared the calcined dolomite, Ni/calcined dolomite, and Ni-modified dolomite catalyst to the catalytic activity in the gasification of sawdust. They found that the Ni-modified dolomite significantly increased the gasification performance compared to the use of calcined dolomite and Ni/calcined dolomite. Tarifa *et al.* [34] stated that using a 2Ni-Fe/MgAl₂O₄ catalyst in biomass gasification was a competitive and cost-effective material, delivering large amounts of CO in syngas with almost no coke deposition.

Aniruddha *et al.* [14] reviewed the autothermal gasification method and applied a composite catalyst with *in situ* CO₂ capture. The result showed that the Ni/CeO₂-ZrO₂-CaO catalyst exhibited the best performance, emitting 95% H₂ yield with a CO₂ capture capacity of 18 mmol/g at 823K. According to Gul *et al.* [35], Ni-based catalyst with CO₂ capture obtained 94% CH₄ conversion to H₂, rendering autothermal steam reforming with *in situ* CO₂ capture to be a more economical approach.

La₂O₃ has been used as a promotor to improve the active metal (Ni) dispersion, catalytic stability, and efficiency in attaining a high H₂ to CO ratio. This

compound also enhanced the CO₂ sorption by resisting carbon deposition. The application of 5% Ni/La₂O₃-biomass fly ash showed an increase in catalytic performance and high stability at 850 °C for 30 h with 85% methane conversion [36]. Consequently, Ni-CaO was considered the most effective catalyst to produce tar-free syngas with high H₂ content [37]. Compared to natural mineral and alkali metals, the Ni-based catalyst is easily deactivated due to carbon deposition high tar cracking activity, particle growth, thermal sintering, chlorine, and sulfur poisoning [3], [32], [38]. The low stability of the Ni-CaO catalyst also hindered its industrial application.

The novel metal composite catalyst possesses the potential to overcome the disadvantages of conventional catalysts. Ni can be modified with other materials through physical or chemical processes, such as mixing and impregnation [39] and other methods to promote the active site and enhance the thermal stability. Irfan *et al.* [37] explored the use of HfO₂ as a stabilizer and promoter for the Ni-CaO systems in municipal solid waste gasification. The results showed an increase in the H₂ content (597 mL/g) and a reduction in the tar content in syngas from 8.79–3.19% with Ni-CaO, and 2.81% with 20% HfO₂ promoted catalyst. Moreover, research on the feasibility of the promoter catalyst should be completely observed for large-scale production.

Khanchai *et al.* [40] simulated the biogas waste material to produce H₂ through a gliding plasma minireactor integrated with a Ni-based catalyst. They obtained that NiO/ZSM-5 able to convert methane up to 19.29%. Bimetallic Ni-Rh-based catalyst in the Ni-Rh/CeO₂eAl₂O₃ reported by Carrasco-Ruiz *et al.* [41] showed a higher reducibility compared to monometallic one. This observation indicated better redox and catalytic properties, preventing coke formation, improving sintering resistance, and achieving high conversion of methane to hydrogen. This is in accordance with the research of Piyapaka *et al.* [39], where the Ni-Co bimetallic catalyst has higher metal dispersion and smaller metal particle size than monometallic Ni catalyst.

Although the Ni-Rh and Ni-Co bimetallic catalyst has shown remarkable stability in converting biogas into hydrogen fuel, there is a lack of existing literature regarding its application in direct biomass gasification. Therefore, further investigation is required to

understand the role of the Ni-Rh and Ni-Co bimetallic catalysts in biomass gasification. This phenomenon presented a significant challenge in the development of gasification technology.

5.2.2 Nb-based catalyst

Niobium (Nb) compounds are fascinating materials for wide purposes including as catalysts for energy production [42]. These compounds exhibit the ability to promote the conversion of biomass into transportation fuels and fine chemicals. Generally, Nb is used in the composite form with other materials based on the target application. Razmgar *et al.* [43] prepared different Nb₂O₅/CeO₂ catalysts for CO₂ and H₂O gasification, where the presence of 12% Nb in Ce matrix enhanced the product gas at 600 °C up to 79% CO₂ conversion with 80% selectivity to syngas.

Niobium-based catalysts have great potential in biomass conversion, but their stability needs to be improved for industrial-scale application [44]. There is a lack of information on the application of niobium-based catalyst materials in biomass gasification in literature. This necessitates an in-depth investigation of the design and preparation of novel Nb catalysts for gasification in the future.

5.2.3 Fe-based catalyst

Similar to Ni-based, Fe-based catalyst was considered as an active metal in the water gas shift and dry reforming methane reactions, exhibiting a cost-effective advantage [34]. Zhou *et al.* [45] applied Fe-based composite catalyst in the steam gasification of biomass and found that a 10% Fe load produced 60.4% gas, 2.5% tar, and 37.1% char, with H₂ yielding up to 42.2% (27.65 g/kg). Tarifa *et al.* [34] found that the use of the bimetallic catalyst Ni-Fe/MgAl₂O₄ improved the catalytic function in the gasification, as mentioned in section 5.2.1.

Ruoppolo and Landi [46] described the promising option of using a hybrid Fe-based catalyst and monolith in biomass gasification, indicating a good tar conversion. However, further experiments should explore the wide range of operational conditions to investigate the possible catalyst deactivation as coke deposition. Cortazar *et al.* [19] confirmed that Fe/olivine catalyst improved the sawdust-steam gasification

according to the gas yield and composition, as well as carbon conversion and tar reduction. After 140 min, Fe oxidized to form Fe_2O_3 , leading to the deactivation of Fe-based catalyst as the reaction shifted from oxidation to reduction condition. This condition limited the use of Fe-based catalysts in the gasification, despite its status as the lowest-cost metal-based. Consequently, the pursuit of developing suitable conditions to prevent Fe oxidation in the gasification process would be imperative.

5.2.4 Co-based catalyst

The use of sepiolite played a significant role in the synthesis of Co/xLa-SEP catalyst for poppy seed gasification. The catalyst with 6% La loading showed the best performance, even at lower temperatures (650 °C), yielding 4.75 mol H_2 /kg poppy seed. Loading 10% La and gasification at 850 °C significantly reduced tar content and almost eliminated coke deposition [38]. Tian *et al.* [47] synthesized monolithic biochar-supported cobalt-based catalysts with unique long and through mesopores by impregnation and carbonization. The Co, Co-Fe, and Co-Ni alloy nanoparticles were uniformly dispersed on the carbon catalyst surface. The addition of Fe and Ni also increased the resistance of carbon deposition at 700 °C gasification. Co-Ni showed high activity in the decomposition of biomass pyrolysis up to 91% and the stability in a five-cycle test stayed excellent, improving the H_2 yield significantly.

5.2.5 Ce-based catalyst

Señorans *et al.* [15] investigated the Ce/Ni/pumice catalyst in biomass gasification and found 50% char conversion to H_2 at 640 °C, 642 °C, and 697 °C using Ce/pumice, Ni/pumice, and noncatalytic. Furthermore, it was discovered that the inclusion of pumice materials significantly increased the gasification rate.

5.2.6 Carbon-based catalysts

Carbon-based catalysts are mainly used as the basic material to impregnate the active metal on the surface. In this research, the discussion of carbon-based catalysts cannot be separated from the metal-based catalyst. The metal impregnated to the carbon surface primarily included Ni, Ce, Ca, Mg, Fe, etc.

Biochar-based nanocatalysts loaded with Ni/Ca/Fe nanoparticles reported by Yang *et al.* [48] showed a high H_2 yield and tar conversion. Ni and Fe particles also helped to maintain the stability of the carrier microporous structure. Furthermore, Fe-loaded biochar showed 87% tar conversion and 42.46 mmol/g H_2 production. Considering the influence of carrier consumption, the catalytic effect of Fe was also found to be higher in comparison to Ni and Ca. These findings highlight the potential of Fe-loaded biochar as a promising catalyst candidate for the production of hydrogen-rich syngas from biomass gasification.

Li *et al.* [32] prepared the catalyst from activated carbon, NiO active component, and calcined dolomite for sawdust gasification using a two-stage fixed-bed reactor. The result showed that the H_2 -rich syngas was significantly increased using carbon catalyst due to the catalytic properties and self-gasification. Moreover, optimal H_2 yield was achieved by using lower impregnation levels of carbon on the ZnCl_2 and H_3PO_4 . The NiO/ H_3PO_4 -activated carbon and calcite dolomite enhanced gasification with an H_2 yield of up to 62.54%. This was caused by synergetic CO_2 sorption and self-gasification of activated carbon.

Sun *et al.* [50] used biochar as the catalyst in a fluidized-bed gasifier. The result showed that using 0.2–0.4% O_2 levels maintained the catalytic efficiency of the carbon catalyst, yielding a tar conversion rate of up to 27%, and an H_2 yield of 0.523 L/g. Table 2 provides the summary of several catalysts used in gasification, operational characteristics and products obtained.

6 Future Work

The preparation of feasible and low-cost catalysts for biomass gasification has attracted more attention recently. These catalysts are expected to meet the criteria of hastening water-gas shift reaction, reducing tar by further conversion into H_2 and CO, lowering reaction temperature, and simultaneously encapsulating CO_2 , including high stability and recovery. Current published literature has widely discussed the composite catalyst based on natural mineral modified, metal, and carbon materials. Moreover, the incorporation of several materials into the catalyst is supposed to increase the positive properties.

Table 2: Summary of several catalysts for gasification and the performance

No.	Catalysts	Fuels/Reactor/Medium	T(°C)	Result		Ref.
1.	Ce/Ni/pumice	Pennisetum Setaceum (PS)/simultaneous thermal Analyzer SDT650/N ₂	640, 642	CC 50%	-	[15]
2.	Dolomite 12% Olivine 12%	Pine sawdust & brown coal/bubbling fluidized bed/ steam	700–1000	TC 92.6% TC 88.6%	55.5 g/kg H ₂ 52.1 g/kg H ₂	[21]
3.	Zeolite 12%	Fine coal/ updraft/steam	750	CC 88.34%	32% H ₂ , 30.1% CO, 27.7% CH ₄ , 5.1% CO ₂	[22]
4.	Modified zeolite	Palm kernel shell/steam	750	TC 98%	64% H ₂	[23]
5.	Bentonite	Oil palm empty fruit bunch/ updraft/ steam	550	CC 85.49%	27.7% H ₂ , 20.4% CO	[24]
6.	CaO-Ca ₁₂ Al ₁₄ O ₃₃ /olivine	Miscanthus × giganteus/Bubbling fluidized bed/ steam	700	TC 54%	-	[29]
7.	CaO 50%	Sawdust/ fluidized bed/ steam	650–850	-	68.0% H ₂	[30]
8.	NiO/ H ₃ PO ₄ -activated carbon	Sawdust, corn stalk/ two-stage fixed bed/ steam	-	-	62.5% H ₂	[32]
9.	Ni/modified dolomite	Sawdust/fixed bed/ steam	800	-	50% H ₂	[33]
10.	2Ni-Fe/MgAl ₂ O ₄	CO, H ₂ , CH ₄ /fixed bed	700	-	No carbon deposition, high stability	[34]
11.	18 wt% Ni/Al ₂ O ₃ catalyst and CaO sorbent	CH ₄ /fixed bed/steam	477	MC 94%	92% H ₂	[35]
12.	Ni/La ₂ O ₃ -biomass fly ash	CH ₄ /downdraft reactor/O ₂	850	MC 85%	No carbon deposition, high stability H ₂ :CO ≈ 2	[36]
13.	Co/xLa-SEP catalyst 6% La 10%	Poppy seed	650, 850	Significant reduce TC	4.75 mol H ₂ /kg poppy seed, no coke deposition	[38]
14.	Biochar support Co, Co-Fe, Co-Ni	Toluene/steam	700	TC 91%	Stability up to 5x test for Fe-Ni loading	[47]
15.	Biochar nanocatalyst loaded Ni/Ca/Fe	Cotton stalk/steam	-	TC 87%	42.46 mmol/g H ₂	[48]
16.	Commercial catalyst: NaOH, KHCO ₃ , Na ₃ PO ₄ and MgO	Algal biomass/steam	700–900	TC 26% (NaOH catalyst)	Increase H ₂	[49]

Note: TC is tar conversion, CC is carbon conversion, and MC is methane conversion

According to Señorans *et al.* [15] the incorporation of Ce/pumice and Ni/pumice increased the syngas yield at lower temperatures, leading to relatively high stability and cost-effectiveness. The addition of catalyst promoters and stabilizers such as HfO₂ [37] also showed significant potential in enhancing stability. This mitigated the deactivation of the catalyst but required further investigation. Moreover, catalysts from local-based materials would be preferable to eliminate the cost of transportation, necessitating research on locally sourced materials. Several catalysts are commonly used in biomass gasification:

1) Natural mineral based. The natural minerals include zeolite, bentonite, olivine, dolomite, and ash

from biomass [16], [21]–[23], [25], [49], [51]–[54].

2) Alkali metal (Li, Na, K, Rb, etc.), and metal-based (Ni, Co, Ca, Ce, Nb, Mg, Fe, etc. [3], [7], [15], [33], [34], [37], [41], [43]–[46], [55]–[72].

3) Carbon-based. Biomass-based carbon in the form of activated carbon has been widely investigated as the catalyst [17], [32], [47], [48], [50], [57], [70].

The use of activated carbon-based catalysts works in synergy with metal catalysts prepared through impregnation to generate high activity and durability. Carbon can be obtained from the locally available biomass, with further preparation such as nanocatalysts [48], metal-impregnated carbon catalysts [47], [57], [70], and other possible methods.

The research on the catalyst for biomass gasification cannot be restricted to only the materials documented in the current literature. The new possibility is always vulnerable to unlimited materials and preparation methods, necessitating the adoption of the newest resources with promising materials and methods for better properties. Several materials that have not been fully explored as catalysts for biomass gasification are listed below:

1) Cerium-based catalysts: Cerium-based catalysts, such as ceria-zirconia or ceria-alumina, have shown promise in various catalytic applications. However, their potential as catalysts for biomass gasification has not been extensively studied. Meanwhile, only a limited number of papers discussed the catalyst application such as Señorans *et al.* [15] which investigated the Ce/Ni/pumice catalyst in biomass gasification. Cerium-based catalysts have high redox properties, oxygen storage capacity, proper surface acidity and abundant resource reserves [73], which can be beneficial for gasification reactions.

2) Transition metal carbides: Transition metal carbides, such as tungsten carbide or molybdenum carbide, have shown catalytic activity in other processes. These materials have high thermal stability and remain active even in the presence of impurities in biomass feedstock [74], which may make them potential materials for biomass gasification catalysis.

3) Phosphorus-based catalysts: Phosphorus-based catalysts, such as phosphates or phosphides, have shown versatile electrocatalytic activities [75] in other applications, such as hydrodeoxygenation. Phosphorus-based catalysts could potentially be explored for their ability to enhance the deoxygenation and tar removal reactions in biomass gasification.

4) Hybrid catalysts: Hybrid catalysts, consisting of multiple active components, have the potential to exhibit synergistic effects and improved catalytic performance [76]. For example, combining metal oxides with carbon-based materials or incorporating multiple metals in one catalyst may enhance the efficiency and selectivity of the gasification reactions.

5) Heterogeneous catalysts derived from biomass: Biomass itself can be used as a precursor to produce heterogeneous catalysts [77]. For instance, biochar generated from biomass pyrolysis can be subjected to further activation to produce carbon-based catalysts. Exploring the catalytic potential of these

biomass-derived materials in biomass gasification is an intriguing avenue for research.

Further research and development are needed to explore the potential of these materials as catalysts for biomass gasification. By investigating their catalytic activity, stability, and selectivity, we can advance our knowledge and potentially identify new and efficient catalysts for this process.

7 Conclusions

In conclusion, this overview successfully showed the significance of catalysts in a gasification process. Although biomass gasification offered a great prospect to fulfill the future green energy demand, the process was faced with a persistent challenge of tar generation during bio-syngas production. To overcome this problem, dedicated research into the feasible catalyst needed to be carried out.

According to the latest literature, several potential catalysts required in-depth exploration and analysis, including carbon-based, Fe-Co-Ni-Al-based, and CaO. Metal-based catalysts have been shown to significantly enhance gasification performance. Nevertheless, the issue of catalyst deactivation remains a challenging obstacle to overcome. The possibility of combining these materials as composite catalysts has also gained significant attention to obtain high stability. Carbon-based catalysts provide a significant improvement to the gas yield, but coke deposition hindered the further use. Metal loading to the carbon-based material was performed through impregnation to extend the catalytic lifetime.

Although this approach was previously preferable, the cost associated with metal loading posed a significant challenge. The addition of CaO material would provide the carbon dioxide capture site on the catalyst surface. Therefore, the desirable catalyst should have four criteria for catalytic activities, accelerating the gasification reaction, improving tar conversion, decreasing the required temperature for the gasification reaction, and capturing the excess carbon dioxide produced. The catalyst was also expected to be reusable and remain economically affordable. Finally, further research on potential catalysts from Ce-based, transition metal carbides, phosphorous, hybrid with multi-active components, and heterogeneous catalysts need to be intensely investigated.

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Author Contributions

Z.F.: conceptualization, investigation, reviewing, and writing original draft; I.R.: Reviewing original draft and funding acquisition; R.T.: Reviewing and analysis; F.T.: conceptualization and data curation; A.S. and A.D.: conceptualization and reviewing. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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