

Review

Lignin Gasification: Current and Future Viability

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Abstract: The consumption of fossil fuels is one of the main drivers of climate change. Lignin derived from biomass is a carbon-neutral raw feedstock, and its conversion into fuels is gaining much attention. The gasification of biomass aims to transform heterogeneous feedstocks into syngas and heat that could be used for various purposes. Lignin is a biomass feedstock of special interest due to its particular properties and its ability to be obtained in abundant quantities as a side product from the paper pulp industry as well as the growing cellulosic ethanol industry. This review explores the existing works regarding lignin gasification from different perspectives and compares the results obtained with other existing thermochemical processes, in addition to providing a perspective on the long-term fate of gasification as a technology compared to other emerging technologies. The analysis indicates that while lignin gasification may grow in importance in the near future due to increased interest in hydrogen production, its potential in emerging applications indicates that lignin may be too valuable to be used purely for energy generation purposes, and applications that take advantage of its inherent chemical compounds are expected to take priority in the long-term.

Keywords: lignin; gasification; hydrogen; syngas; biomass



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1. Introduction

The improved understanding of the drivers of climate change is forcing society to move towards more environmentally friendly and less CO₂-intense sources of energy to power society. In light of this, considerable progress has been achieved over the course of the past four decades in terms of renewable energy technologies, such as the development of solar photovoltaic cells and wind turbines to generate renewable electricity. However, in spite of this progress, society still needs fossil fuels to power much of our infrastructure, and they are also required for the manufacture of many goods that require hydrocarbons as precursors, such as plastics, dyes, and chemicals [1].

Biomass could potentially be used to replace fossil fuels, and amongst the different types of biomass resources, lignocellulosic biomass is the most feasible replacement, as it is the most abundant source of carbon in nature, in addition to being renewable [2]. Inspired by this fact, significant progress was accomplished in the conversion of certain kinds of biomass, such as cellulose [3], sugars [4], and fatty acids [5]. Sadly, one of the major components of lignocellulosic biomass (8 to 30% by weight), lignin, is underused compared to cellulose due to its recalcitrancy compared to cellulose and its technical limitations but also the limited development of technologies that use it [6]. Lignin is a three-dimensional organic polymer composed of repeating aromatic structures that contain a large variety of chemical bonds. This represents a great opportunity, as there are no other renewable sources of aromatic chemical structures found in nature available in such large quantities. Depolymerizing lignin has been the subject of extensive research in the past decades through a variety of methods that could mostly be divided into biological and thermochemical processes [7]. Among these, biological methods exhibit great selectivity towards specific aromatic products but suffer from slow conversion [8]. As a result, thermochemical methods, including solvolysis, pyrolysis, gasification, and hydrogenolysis, compose the

majority of the research conducted in recent years. The focus of these thermochemical studies has mainly been on the production of “bio-oil”, a liquid mixture of hydrocarbons with a high oxygen content, intended to be used for fuel purposes for upgrading [9] and minimizing the formation of solid residues or char and non-condensable gas products. The exceptions to this are gasification processes, which focus entirely on the production of a mixture of syngas, principally composed of CO and H₂, and a smaller fraction of methane and CO₂, with the concentration of CO₂ being highly dependent on the ratio of the oxidant to biomass used in the process [10].

Recently, there was a strong push towards the inexpensive production of H₂ as an energy source and carrier, highlighting its potential for decarbonizing many sectors of industry and its potential role in a CO₂-neutral society [11], with the Japanese government establishing that H₂ would play a large role in its future energy mix [12]. This bolsters research in biomass conversion to H₂, and particularly lignin, as it could be reliably obtained as a side-stream from industrial pulping processes and more recently from cellulosic ethanol production resulting in an abundance of lignin as a feedstock and it being available without the need for collection, resulting in a potentially easy integration into pulping processes or cellulosic ethanol biorefineries [13]. This increased interest could be seen from the available statistics on the number of studies relating to “lignin gasification OR black liquor gasification”, as shown in Figure 1, where the yearly number of studies related to this search string has increased consistently over the years and is expected to continue.

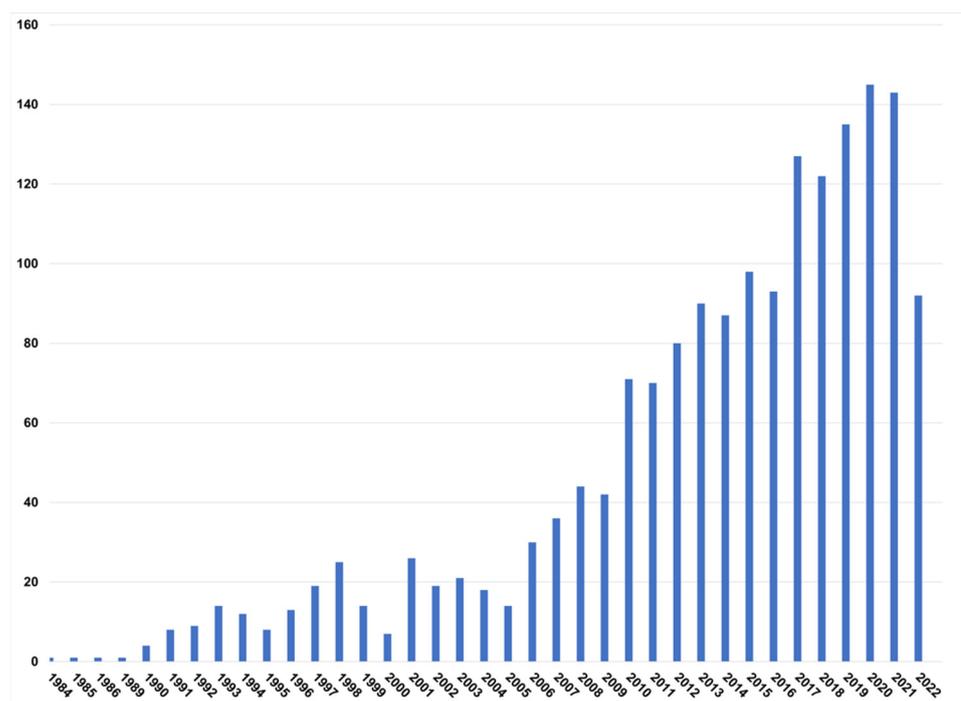


Figure 1. The number of studies published per year using the search string “black liquor gasification OR lignin gasification”, data obtained from the Web of Science.

In this review, we explore and analyze the existing research on the gasification of lignin from both quantitative and qualitative angles to understand better what the bottlenecks in the development of better lignin gasification processes are, as well as its long-term competitiveness compared to other available thermochemical conversion processes, in addition to commenting on the techno-economic pros and cons of these processes. The analysis provided here increases the awareness of the current limitations and future prospects of lignin gasification that would hopefully result in research in the future with greater impact.

1.1. Sources of Lignin

To access lignin, it must be first separated from the cellulose and hemicellulose that composes the polymer matrix of wood or other types of biomass. In industries, this is often seen during the various processes used to produce paper pulp, which is composed of cellulose. This requires the disruption of the cellulose-hemicellulose-lignin matrix that provides woody plants with structural rigidity and mechanical strength. Different kinds of lignocellulosic biomass contain different proportions of cellulose (38–50%), hemicellulose (23–32%), and lignin (12–25%), with herbaceous plants containing the least amount of lignin and hardwoods being the most abundant [14]. Moreover, lignin from different plants has different structures, with the overall structure being composed of three monolignols, p-coumaryl, coniferyl, and sinapyl alcohols [15]. These three monolignols are found in different proportions in different plants, resulting in a varying abundance of the chemical bonds found in lignin which are shown in Figure 2. This is important, as not all the bonds present in lignin are as easy to cut, resulting in varying degrees of recalcitrance that have to be considered when utilizing lignin depolymerization. Amongst these bonds, B-O-4 bonds are known to be relatively easy to cut compared to the 5'-5' carbon-carbon bond. This was highlighted in studies with model compounds [16].

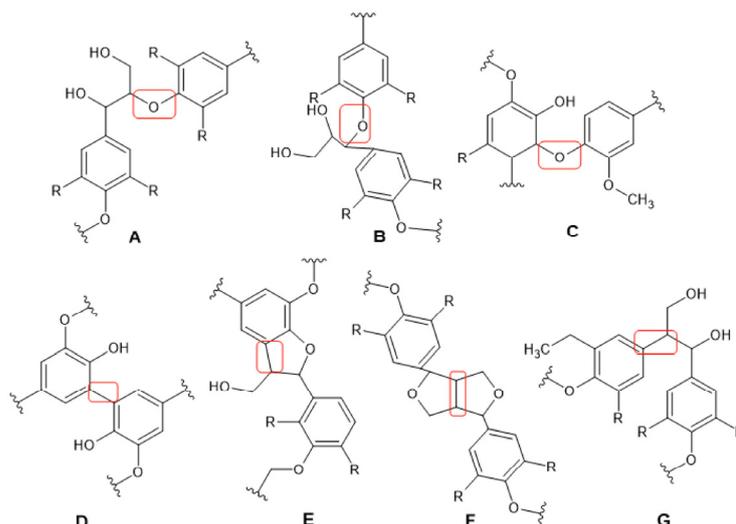


Figure 2. Chemical bonds found in lignin composed of both ether and carbon-carbon bonds (highlighted in red). (A) β -O-4, (B) α -O-4, (C) 4-O-5, (D) 5-5, (E) β -5, (F) β - β , (G) β -1. (Adapted from [17]).

Most of the lignins available in the industry are derived from the kraft pulping process that is responsible for the large majority of the paper pulp production in the world. The process involves the treatment of wood chips with a solution of hot water at 145–170 °C NaOH and Na₂S. Paper pulp is most often created from softwood coniferous trees, such as pines, firs, spruces, hemlocks, and larch. In turn, kraft lignin most often displays chemical properties that resemble those found in the lignin from these tree species [18]. It is important to note that during the pulping process, some of the original B-O-4 bonds found in lignin are disrupted, and new C-C bonds are formed, resulting in more recalcitrancy; this is known as “lignin condensation” [18].

Other pulping processes exist, such as organosolv pulping [19], which result in less condensed, higher-quality lignin but are not as widespread in the industry. Recently, the usage of ionic liquids in lignocellulosic waste pulping was researched [20], finding interesting results, but it currently remains at the laboratory scale.

It is critical to state that lignin elemental compositions are different from those seen in other feedstocks used in gasification, such as wood, cellulose, or coal. This is represented in Table 1.

Table 1. Elemental compositions of wood, cellulose, lignin, and coal.

Feedstock	C%	H%	O%	N%	S%	Ash%	Reference
Wood	50	6	42	1	-	4–10	[21]
Cellulose	44	6	49	-	-	-	
Lignin	42~66	4.6~6.18	23~41.4	0.07~2.9	0.06~5.27	0.4~27.2	[22]
Lignite coal	63.55	5.25	15.74	1.20	0.26	14.0	[23]
Anthracite Coal	89.07	3.53	1.49	0.69	0.20	5.01	[23]

While there are similarities between lignocellulosic feedstocks and coal in terms of elemental composition, the differences in their chemical structures are not well reflected by this information. In addition to these, lignin could contain large amounts of ash, depending on its origin [22].

1.2. Lignin Conversion Methods

Because of its peculiar structure and renewability, lignin has attracted attention for its potential in various applications, such as the synthesis of resins, adhesives, and fibers [24] in the case of material science and biologically active compounds, such as drug precursors, antioxidants, and nutraceuticals in the field of biology [25]. However, the scope of this review centers primarily on the gasification of lignin and its comparison to adjacent thermochemical conversion methods (pyrolysis and solvolysis). The thermochemical conversion methods for lignin could be classified by the temperature in which they happen and what their target product is; this is summarized in Table 2.

Table 2. Temperatures and main products from the most common thermochemical lignin depolymerization processes.

Method	Temperature	Products	Reference
Gasification	400–1000+ °C	Syngas	[26]
Pyrolysis	300–600 °C	Bio-oil, gaseous hydrocarbons, and char	[27]
Solvolysis	200–400 °C	Bio-oil and char	[28]

As observed, gasification requires higher temperatures compared to the other thermochemical methods, and it focuses primarily on the production of non-condensable gases, such as H₂, CO, CO₂, and CH₄ and heat, depending on the energetic balance of the process [29]. Gasification could be further divided into different types of processes depending on the gasification medium and the presence or absence of a catalyst.

Thermochemical conversion methods use various types of reactors both at the laboratory and industrial scale [30]. However, for solvolysis, batch reactors appear to be the most commonly used in most studies, with some examples of continuous reactors used for industrial or pilot-scale operations [28]. For both gasification and pyrolysis, there are three principal types of reactors used, fixed beds, fluidized beds, and entrained flow reactors [30], whose principal difference is how the feedstock interacts with the reaction medium used. In addition, these could be further divided into allothermal or autothermal processes, depending on whether the process could sustain its heat needs through exothermic reactions or is supplied heat externally [31].

As for which of these methods is the “best”, that was the subject of significant research focused on the techno-economic aspects of lignin conversion through hydrothermal [28] and oxidation [32] studies. To our knowledge, a techno-economic study that focuses exclusively on lignin gasification does not exist; however, from the perspective of purely the products obtained, the gasification of lignin allows for the production of synthetic fuels through the Fischer-Tropsch process by reacting the syngas at 150–300 °C in the presence of a transition metal catalyst [33], the production of methanol in a similar fashion [34], or the separation of H₂ from the produced syngas for other purposes. This allows the gasification process a degree of flexibility that the other thermochemical methods do not possess.

2. Extraction and Sorting of the Relevant Literature

A comprehensive literature search was carried out using Web of Science by using the search string containing lignin gasification, resulting in 1289 documents found as of August of 2022. Of these, 326 documents were sorted for consideration by looking at the title and abstract. Ultimately, 98 relevant papers were chosen for the review due to their relevance in regard to the central topic of “lignin gasification”.

These studies fell under the umbrella of lignin gasification. However, many of them were very distinct from each other in terms of the methodology, experimental equipment, and choice of experimental variables. It was decided to separate the studies into three groups for comparison purposes and also to better structure the review. The first group consisted of the gasification of dry powder lignin in the air or oxygen-containing reaction medium. The second group captured lignin gasification studies where water or steam was used to enhance the gasification process, and the third group of studies focused exclusively on the gasification of black liquor (BL) of different pulping processes. Within these groups, differences in the experimental methodologies and variables could be found, such as the presence or absence of a catalyst, temperatures, residence times, and reactor types, in addition to the metrics chosen for evaluating the performed experiments.

Where possible, the units across the studies were converted for ease of comparison in subsequent sections. However, not all studies reported the same metrics, which are needed for the comparison. The majority of the studies reported on the yields of H₂, CO, CO₂, and CH₄, along with overall gas yield in relation to the original amount of lignin involved in the experiment. Studies about BL gasification tended to report hot gas efficiency (HGE) and cold gas efficiency (CGE), which could be helpful for assessing the viability of the proposed processes from the energy perspective but were not further analyzed as this review focuses purely on the products obtained and their selectivity. It must be noted that the majority of the studies covered in this review relate to laboratory-scale gasification processes, with a few exceptions.

3. Lignin Gasification

Lignin gasification traditionally refers to a process of partial thermal oxidation that results primarily in the production of gaseous products consisting of H₂, CO, CO₂, and smaller proportions of short-chain gaseous hydrocarbons, char, or coke (solid products), ash and condensable aromatic-ring-containing organic compounds denominated as a bio-oil or tar, depending on the context. The oxidizing agent is usually air, oxygen, or water in the form of steam.

The aim of gasification is to transform a potentially very heterogeneous, low, or negative-value feedstock into a standardizable gas mixture that could be then used for power generation purposes or as feedstock in processes that require syngas for other products of other valuable molecules, such as methanol [34] and alkanes [33].

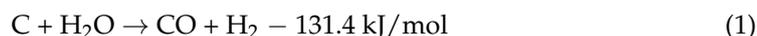
During the lignin gasification process, a large number of reactions and interactions happen simultaneously. However, they could be primarily grouped by the temperature window in which they happen:

- Drying (100–200 °C). It is the initial stage of the gasification process for solid lignin. The starting moisture content of lignin depends on the source and pretreatment.
- Primary pyrolysis reactions (200–400 °C). Pyrolysis reactions begin to occur in this temperature range and primarily sever the α - and β -ether bonds of the lignin structure. This was confirmed both in real lignin, and with model molecules [35]; however, C-C bonds remain stable in this temperature range. It is also during this temperature processing window where re-polymerization reactions could begin to occur, with volatile aromatic monomers produced, such as coniferyl aldehyde, isoeugenol, guaiaicol, 4-vinylguaiaicol, vanillic acid, and vanillin interacting with each other to form new C-C bonds.
- Combustion (400 °C~). Lignin oxidation reactions could happen at lower temperatures. However, the complete or partial combustion towards CO, CO₂, and H₂ begins to

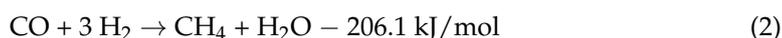
happen mostly after passing the ignition point of lignin [36]. H₂O could also be formed through the combustion of H₂ at this stage. The degree of combustion that happens depends entirely on the stoichiometric ratio of the oxidant to lignin, with low values resulting in a slower conversion and higher selectivity towards CO and H₂.

- Secondary pyrolysis reactions (400 °C~). Demethoxylation reactions targeting the aromatic ring begin to occur at approximately 450 °C [35], resulting in the formation of catechols with the methoxy group hydrogenating into CH₄ or further oxidizing into CO/CO₂. The intramolecular H abstraction from the methyl groups could also lead to the formation of phenols. These reactions compete with combustion reactions.
- Coking and PAH formation (550 °C~). Lignin-derived monomers could begin to convert to coke and polyaromatic hydrocarbons (PAHs) at this temperature range, with PAHs forming from ~600 °C and their production intensifying as the temperature approaches ~700 °C [37].
- Reduction (800–1000 °C). In the presence of sub-stoichiometric concentrations of the oxidizing agent, reduction reactions involving single-carbon molecules could begin to take place. Some of these reactions are endothermic and often involve H₂O as a product or reactant; they are shown as follows:

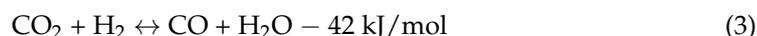
Water-gas reaction:



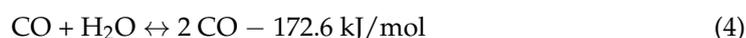
Methanation of carbon monoxide:



Shift reaction:



Bounded reaction:



Methane reaction:



Boudouard reaction:



Reactions (1)–(6) could be largely considered secondary, as their reactants are provided by the primary reactions that take place as the process temperature rises.

All these reactions take place through the gasification process and compete with each other as the temperature rises, and the selectivity depends upon the heating rate, residence time, and ratio of the oxidant to lignin present [38]. Water as a reaction medium in the presence or absence of oxygen changes the way these reactions take place, both due to the role of water as a reactant at high temperatures and also because of the enhanced heat transfer that happens when used as the gasification medium. The reactor design in the continuous processes may also play a role in controlling the reactions that happen by allowing for longer residence times if desired [39].

In this work, we intentionally excluded gasification studies that used CO₂ as the gasification agent, both entirely or partially, due to the limited number of studies and the fact that the effect of CO₂ in those cases is not very clear. The subsequent sections of this review deal with the gasification of isolated lignin powder in oxidative and super-critical water media and, finally, the direct gasification of black liquor.

3.1. Lignin Gasification in Oxidative Media

A summary table of the oxidative lignin gasification studies is shown below in Table 3. Lignin gasification in oxidative media usually involves the use of air or controlled O₂/N₂ mixtures at different oxidant and lignin ratios. The ratio of oxygen to lignin has two important effects in the process; first, it controls the speed of the conversion of the lignin, with a higher oxygen-to-lignin ratio resulting in a faster conversion towards the gaseous products. However, the higher the oxygen-to-lignin ratio, the more the gasification process begins to border on combustion; this also means that the process becomes more exothermic as the oxygen-to-lignin ratio rises but also increases the selectivity to CO₂ [38]. The second effect of the oxygen-to-lignin ratio is that it controls the ratios of CO-to-CO₂-to-H₂ produced, where lower values of oxygen-to-lignin ratio slow the conversion of lignin but also increase the selectivity towards CO and H₂, due to the limited availability of oxygen in the reactor at a specified point in time. The yield of the solid and liquid products is also affected by the oxygen-to-lignin ratio; naturally, the higher it is, the more likely the coke and char products are to decompose into CO, CO₂, and H₂. At certain oxygen-to-lignin ratios, the process also could become self-sustaining due to the overall exothermic nature of the process, and reports of energy efficiencies from 51 to 78% based on the initial lignin heating value are found in the literature [38].

It must be noted that lignin tends to produce less gas and more tar than the other components of lignocellulosic biomass, such as cellulose and hemicellulose [40]. In addition to this, pressure as an experimental variable seems to have little effect on the yield of non-condensable gases but seems to incentivize the formation of liquid products [41]. The number of oxidative lignin gasification studies that involve the use of a catalyst is limited, with natural minerals (dolomite, olivine, and lime) [42] and Na₂CO₃ being used [43]. Dolomite was shown to enhance the yield of H₂ and minimize the tar yield [44].

Table 3. Comparison of the found oxidative lignin gasification studies.

Ref.	Conditions	Reactor Type	Catalyst	Results	Notes
[43]	1000 °C, 0.24 kg lignin/h	Entrained flow gasifier	Dolomite/Na ₂ CO ₃	8% vol yield of H ₂ and 13.5% vol yield of CO, at 46% C conversion for the Na ₂ CO ₃ catalyst	<ul style="list-style-type: none"> • Na₂CO₃ resulted in increased CO formation but a slightly reduced H₂ yield • No comment on the autothermicity
[42]	740–860 °C, 0.3 kg lignin/h	Fluidized bed	Lime, olivine, and dolomite	35% H ₂ yield <i>v/v</i> , 1.25 NI/g of gas yield	<ul style="list-style-type: none"> • A higher temperature increased the gas and H₂ yields • Equivalent ratio information was available • Used steam • Barely autothermal
[38]	550–850 °C, 20–30 kg lignin/h	Updraft gasifier	None	Max H ₂ yield of 49 g/kg lignin along with 330 g/kg of CO, another notable run was 35 g/kg lignin H ₂ with 842 g/kg lignin of CO, both of them were under O ₂ and steam	<ul style="list-style-type: none"> • Used oxygen and steam • Lower equivalence ratios of O₂ and H₂O resulted in a massive increase in CO, which may be good • Autothermal
[40]	1000 °C 0.25 ER for O ₂ , 0.24 kg lignin/h	Entrained flow gasifier	None/ashes	H ₂ yield of 9 vol%	<ul style="list-style-type: none"> • Lignin had a lower gasification efficiency compared to pure hemicellulose/cellulose and also a higher tar yield than others • No comment on the autothermicity

Table 3. Cont.

Ref.	Conditions	Reactor Type	Catalyst	Results	Notes
[44]	500–900 °C, batch operation of 12 g lignin/run	Fixed bed reactor	None	Maximum gas yield of 57% at 900 °C	<ul style="list-style-type: none"> Used air as the oxidant Did not report the yields of specific chemicals in the gas phase Allothermal
[41]	835.8 °C at bed temperature, lignin feeding rate not available	Circulating fluidized bed reactor	None	17.62 vol% yield of H ₂ at 5 bar pressure with 21.16 vol% CO	<ul style="list-style-type: none"> Gasifying agents included CO₂, O₂, and H₂O Pressure did not affect the selectivity towards any gas product Autothermal

3.2. Lignin Gasification in Water or Steam

Water as a reaction medium was used in a large number of studies for biomass gasification due to its interesting properties as a solvent when passing its critical point at 373 °C and 220 bars [45], achieving densities between a gas and liquid, resulting in enhanced heat transfer, and a residence time that was only dependent on the flow rate of the process [46]. In the case of lignin gasification, super-critical water was tested both catalyzed and uncatalyzed with interesting results. Below in Table 4, a summary of the lignin gasification studies in water or steam media is shown. Higher lignin content in the feedstocks for the super-critical water gasification (SCWG) was associated with lower conversion rates, owing to the formation of reactive aromatic molecules that could readily re-polymerize and condense. Naturally, in the case of pure lignin as a feedstock, char formation became more prevalent and was addressed in different ways that deviated from what would be required for low-lignin feedstocks by either using higher temperatures than normal (900–1400 °C), employing alkali salts to minimize lignin repolymerization, or using heterogeneous transition metal catalysts. The SCWG of organosolv lignin at 900 °C at a 10 to 20 s residence time achieved a carbon conversion of 59.9% and 0.89 mol of H₂ and 0.1 mol of CO per mol of C [47]; in this study, they also applied SCWG to wood, bark, and delignified bark, finding that while the yield of H₂ obtained across feedstocks was similar, the yield of CO for organosolv lignin was four times lower than that produced from wood. A year later, another study using lignin as feedstock for SCWG at 900–1400 °C confirmed that temperatures above 900 °C increased the concentration of CO in the produced gas roughly three-fold while still maintaining a similar H₂ yield to that obtained at 900 °C [48]. Studies involving the use of a catalyst involved lower temperatures (400–650 °C), where the use of alkali salts improved the gasification performance by preventing the formation of solid residues and enhancing the yield of hydrogen production via the water-gas shift reaction (WGSR) [49]. In the case of heterogeneous catalysts, the presence of acid sites seemed to correlate positively with an increased carbon conversion and H₂ yield [50], particularly in [51], it was shown that the demand for acid sites for lignin was different from cellulose in regard to maximizing the yield of H₂. Some of the problems commonly found in SCWG are excessive char formation and salt precipitation, both of which could cause fouling and clogging [52].

From the perspective of the process design, a high ratio of water-to-lignin resulted in a lower likelihood of char formation by reducing the effective concentration of re-polymerizable species at any point during the experiments, though if the concentration of lignin was too low, it could result in an unreasonably big reactor for a specific gas output. The degree of endothermicity of the overall process was also strongly dependent on the ratio of lignin-to-water, with high lignin concentrations allowing for breaking even in terms of the energy spent [53], though no specific reports for energy efficiency were found for lignin gasification in super-critical water conditions.

Table 4. Comparative table of the studies about lignin gasification in water or steam media.

Ref.	Conditions	Reactor Type	Catalyst	Results	Notes
[47]	900 °C, 10–20 s residence time, lignin feeding rate not available	Entrained flow reactor	None	0.89 mol H ₂ per mol of C and 0.1 mol of CO per mol of °C at 900 C	<ul style="list-style-type: none"> Study showed that lignin may not be good for CO production High yield of PAHs produced from lignin compared to other tested feedstocks No comment on the autothermicity
[48]	900–1500 °C, 1 to 8 min residence time, 1.08 kg lignin/h	Fixed bed reactor	None	49.37 vol% H ₂ yield and 35.07 vol% CO yield at 1500 °C also 54.11 vol% H ₂ yield and 11.07 vol% CO yield at 900 C	<ul style="list-style-type: none"> Unusual concentration units Potential H₂ yield was introduced as a metric, interesting Biomass with more lignin may be suitable for H₂ production No comment on the autothermicity
[50]	650 °C, 26 MPa, 0.65 g lignin/run	Batch reactor	NiMgAl	12.9% highest gas yield, max 39.06 % mol selectivity towards H ₂	<ul style="list-style-type: none"> Proof that high strong acid sites could enhance H₂ production, probably through dehydration No yield of CO reported No comment on the autothermicity
[51]	650 °C, 50 min residence time, 0.65 g lignin/run	Batch reactor	K ₂ CO ₃ , NiCe/Al ₂ O ₃	2.86 mmol H ₂ /g lignin with K ₂ CO ₃ , 18.0 mmol/g lignin overall gas yield, and 2.15 mmol H ₂ /g lignin with NiCe/alumina with an overall 12.9 mmol gas/g lignin yield	<ul style="list-style-type: none"> Higher catalyst loading results in more H₂ K₂CO₃ may be better than any available heterogeneous catalyst Further proof that strong acid sites correlate with performance The variables affecting H₂ production were in the order of: temperature > catalyst loading > catalyst type > biomass type No comment on the autothermicity
[54]	300–600 °C, 90–410 bar, 1.2 g lignin/run	Batch reactor	None/K ₂ CO ₃	18.99 mol H ₂ /kg C in feedstock without catalyst, 23.47 mol H ₂ /kg C in feedstock with K ₂ CO ₃ , both at 600 C	<ul style="list-style-type: none"> K₂CO₃ enhanced the yield of the overall gas at all temperatures, seemingly by reducing the solid formation No CO formation No comment on the autothermicity
[55]	550 °C in the pyrolysis stage, 750 °C in the second stage, batch operation with 2 g lignin/run	Two-stage fixed bed reactor	None (sand) or 10% Ni/Al ₂ O ₃	25.5 mmol/g feedstock of H ₂ , 6.44 mmol/g feedstock of CO with catalyst at conditions in the left	<ul style="list-style-type: none"> Vol% of gases was also available Lignin produced the most char of all the feedstocks used No comment on the autothermicity
[56]	400 °C, 1 h reaction time, batch operation with 0.1 g lignin/run	Batch reactor	Ru/C	73.5% overall gas yield, 7% H ₂ , no CO reported	<ul style="list-style-type: none"> Ru/C seemed to enhance the conversion to gas and yield of H₂ at a lower temperature than the other processes No comment on the autothermicity

Table 4. Cont.

Ref.	Conditions	Reactor Type	Catalyst	Results	Notes
[57]	399–651 °C 50 min reaction time, 0.65 g lignin/run	Batch reactor	None	1.59 mmol/g lignin at 651 °C 26 MPa, with an overall gas yield of 16.1	<ul style="list-style-type: none"> • Pressure had a low impact on the outcomes • The importance of the H₂O-to-lignin ratio increased after 600 °C • Allotthermal, based on the calculations

3.3. Black Liquor Gasification

The “black liquor” or pulping liquor gasification studies were carried out at 375–700 °C at varying residence times ranging from a few seconds [58] to almost 1 h [59]. Because the solvent used in most of the pulping processes was water, there were similarities between these studies and those that used water as the reaction medium, as seen in the previous section. However, the key difference between the two is that pulping liquor contains wood extractives, cellulose, and hemicellulose residues, as well as the chemicals used in the pulping process in addition to partially depolymerized lignin. During the lignin precipitation process necessary for the usage of lignin in oxidative and water as reaction media studies, a certain degree of repolymerization could happen [60]. Because of this, the idea of directly gasifying the pulping liquor could be attractive, as it could lead to lower solid residue formation and, by extension, higher possible gas yields. While a fair comparison across different studies is not easy, it seems that in regard to the maximum possible yield of H₂, the gasification of black liquor is comparable to lignin gasification in a water medium. One important difference is that various studies [61–63] reported diminished or no presence of CO and CO₂ in the resulting gas, with an increased presence of CH₄ in some instances, depending on the residence time [63] and temperature [62].

The black liquor (BL) gasification studies did not usually involve any additional catalyst except for the alkali species already found in the pulping liquor. However, the exception to this was the usage of reactors composed of Inconel 625 alloy, which were proven to display catalytic activity and improve the yield of H₂ [64]. It is important to note that various studies used batch reactors for the gasification of BL; while this is fine for studying the reactions, practical problems associated with the use of continuous flow-through reactors were reported, with concentrations as low as 5% of total dry solids in the feed, causing clogging of the reactor [62]. This is important when assessing the energy balance of a study, as very concentrated BL may allow for the overall process to be exothermic if carried out in a batch reactor but could be unfeasible in a continuous reactor. Energy efficiency as high as 102.4% was reported in terms of the gas produced compared to the initial feedstock [65].

Overall, the gasification of BL showed promise for the production of H₂, but not so much for syngas as it was difficult to tune the CO concentration in the products. Below in Table 5, a comparative summary table for the BL gasification studies discussed is shown.

Table 5. Comparative table of the black liquor gasification studies found.

Ref.	Conditions	Reactor Type	Catalyst	Results	Notes
[64]	500–700 °C, BL flowrate specified as higher than [66]	Tubular-flow through reactor	Ni/None (Inconel 625)	50.32% vol H ₂ yield without a catalyst at 700 °C; 60.18% vol H ₂ yield with a catalyst at 600 °C	<ul style="list-style-type: none"> • Mol% results were also available • CO₂, CO, CH₄, and other gases' yields were available • The pressure did not affect the results • Energy efficiency was also present • No comment on the autothermicity

Table 5. Cont.

Ref.	Conditions	Reactor Type	Catalyst	Results	Notes
[58]	375–650 °C 5–120 s reaction time, approximately 1.87 g lignin/run	Quartz capillary	None	75.86% gas yield, 23.78 % of hydrogen in the feedstock as H ₂ gas, 12.78% of C as CO as gas (optimal conditions)	<ul style="list-style-type: none"> The concentrations of other gases were also present Energy efficiency was also present No comment on the autothermicity
[61]	400–600 °C 30 min reaction time, 26–103 g lignin/run	Batch reactor	None	5.03% gas yield at 600 °C 25% H ₂ yield, no CO yield	<ul style="list-style-type: none"> No presence of CO No comment on the autothermicity
[59]	600–750 °C, 10–50 min reaction time, amount of BL not specified	Batch reactor	Inconel 625, no catalyst	Max H ₂ yield of 75%, negligible CO yield, no mention of the actual conversion	<ul style="list-style-type: none"> The gasification efficiency was available No comment on the autothermicity
[62]	500–700 °C, 36.18 g BL/h	Flow through reactor	SS 316 reactor, no catalyst	Max H ₂ yield of 49%, CO concentration dropped to nearly 0% at 700 °C from 27% to 500 °C	<ul style="list-style-type: none"> CO disappeared as the temperature rose, resulting in more H₂ and CH₄ The hot gas efficiency was available Yield in mol/kg was also available No comment on the autothermicity
[63]	550 °C, 10–60 mL BL/min	Flow through reactor	No catalyst	Max H ₂ yield of 66.11% and CO yield of 5.86% at 550 °C with a 10 mL/min flow rate	<ul style="list-style-type: none"> CO₂ was not present due to sodium bicarbonate formation The CH₄ concentration rose with lower residence times No comment on the autothermicity
[66]	400–600 °C, 10 min reaction time, amount of BL not specified	Batch quartz reactor		57.8 mol/kg max H ₂ yield for Soda BL at 600 °C and 0.5 mmol/kg at this value too	<ul style="list-style-type: none"> No comment on the autothermicity
[65]	400–600 °C 25 MPa, 4.94 to 13.71 s residence time, 52 mL BL/h	Flow through reactor	None	11.26 mol/kg of H ₂ at 600 °C no CO at this temperature.	<ul style="list-style-type: none"> CO₂ rose with temperature, but H₂ did not change much after 500 °C The gas efficiency was available No comment on the autothermicity

4. Economic, Energetic, and Technological Perspectives of Lignin Gasification

This section aims to clarify the pros and cons of lignin gasification from economic, energetic, and technological readiness perspectives. It is important to note that this refers only to lignin derived from pulping processes, bio-ethanol productions, and other processes that produce lignin-rich waste as side-streams and not necessarily to the entirety of potentially available lignin in nature. The reasoning behind this is that while the usage of lignin-containing biomass in nature, such as agricultural waste, is attractive, it also represents a significant logistical challenge to efficiently collect, transport, and store this feedstock over time due to the sparse concentration of biomass per square kilometer, the low energy density and the inconsistent availability [67]. Compared to this, lignin available from existing pulping processes or bioethanol plants could be seen as an easy-to-secure, readily available feedstock that could be integrated with other processes. The estimates for the total lignin output exist, with figures of approximately 100 million tons per year, comprised mostly of lignosulphonate (~88%), kraft lignin (~9%), and a growing though a still small fraction of organosolv lignin from bioethanol productions (~2%) [68].

4.1. Economic and Energetic Perspective

From the economic perspective of lignin, assessing the value of lignin as a resource is difficult. Other kinds of biomass, such as agricultural waste, are thought to have negative or zero economic value until they are valorized, but in the case of lignin, this is harder to assess, as it is currently combusted in the recovery boilers of pulping plants to regenerate the chemicals used in pulping and provide heat to power the cooking process, in addition to the regulations that specify the disposal methods available, high-temperature incineration among them. Similarly, in the case of cellulosic ethanol plants, lignin is burned to generate steam, heat, and electricity [69].

Because of the previously mentioned current applications of lignin, the minimum economic value that it holds is the equivalent that it produces in energy, be it directly as heat or in the form of electricity if combusted. This is a perspective shared by other authors [70]. This means that the hypothetical value of lignin is tied to its geographical location in this context, as the cost of heat and electricity change depending on the country and location within a particular country.

Lignin gasification could provide heat, syngas, and small amounts of gaseous hydrocarbons depending on the choice of gasification method, reactor design, process conditions, and catalyst choice, if any, as discussed in the previous sections. In view of this, three different possible approaches are identified with regard to the previously discussed gasification methods:

- Syngas production via the SCWG of lignin; the focus of the process is purely the production of H₂-rich syngas that would then be used as feedstock for other processes, ideally at high lignin concentrations to minimize the degree of endothermicity of the process.
- Syngas and heat co-production via oxidative lignin gasification; this process is focused on the production of syngas in addition to heat by integrating the gasification process with heat exchangers to valorize the residual heat of the products.
- The gasification of black liquor; this process only applies to pulping processes and prioritizes the production of H₂ gas over other co-products. This process is possibly the easiest to integrate with existing pulping facilities, as it overcomes the need to precipitate the lignin from black liquor and could be more seamlessly integrated into the rest of the process.

Of these, oxidative lignin gasification is possibly the most straightforward alternative to implement, as it is inherently exothermic and is a more mature technology compared to the other two, showing parallels with coal gasification [71].

Additionally, H₂ gas is foreseen to gain great importance over the next few decades as part of the energy mix of many countries that aim to achieve carbon neutrality [72,73], representing an opportunity for lignin. Whether the production cost of H₂ from lignin gasification would be competitive with current natural gas-derived hydrogen or green hydrogen produced from renewable energy remains to be seen and would ultimately depend on the energy policies and pricing mechanisms implemented in the near future.

From a purely energy-centric point of view, many authors criticized the feasibility of using biomass in general as a source of energy [74], touted to be CO₂-neutral and renewable, but also suffering from limitations that restrict its potential in supplanting the role currently fulfilled by crude oil and natural gas. Because of this, authors point to the fact that the usage of lignocellulosic biomass as building materials may be a more sustainable and less CO₂-intense [75] application. From this perspective, lignin derived from pulping streams occupies a specially interesting spot due to its unique structure composed of aromatic units and the fact that it is potentially available in large quantities as side-streams of already economically feasible processes. With this in mind, in the following section, a brief forecast of lignin valorization technology in the upcoming future is provided.

4.2. Comparison to Other Lignin Conversion Methods and Recommendations

Currently, lignin has limited but relatively well-established applications, primarily for heat and power generation to regenerate pulping chemicals in the case of pulp production or to provide heat for processes within cellulosic ethanol biorefineries. Other notable current applications, albeit at a lower scale, include the usage of lignin as a binder for coal and mineral dust briquettes, as well as a binder for wood-related materials [76] and its application in cement mixtures, where it improves the concrete performance [77]. It is worth noting that these last two current applications are comparatively very small to lignin's usage in heat and power generation.

Having stated this, emergent methods for lignin valorization stray away from energy generation-related focuses and move more towards higher complexity technologies that intend to take advantage of the fact that lignin is already a highly functionalized polymer. This means that rather than breaking down lignin's complex structure into simpler C1 molecules or H₂, the aim is to transform it into materials that benefit from the existing functional groups already found in lignin. Some of the most notable examples include carbon materials [78], phenolic compounds, and resins [79], with applications in automotive and spacecraft industries, medicine, and biomedical materials.

Whether these emerging technologies would partially or entirely supplant lignin's current role as a source of energy and syngas would ultimately depend on the concurrent developments of other technologies, price fluctuations, and forecasts of crude oil and policy that may enhance lignin's competitiveness over other raw materials. Figure 3 demonstrates an interpretation of how the current and emergent lignin applications would change over time as technologies mature and move towards potentially more economically attractive applications.

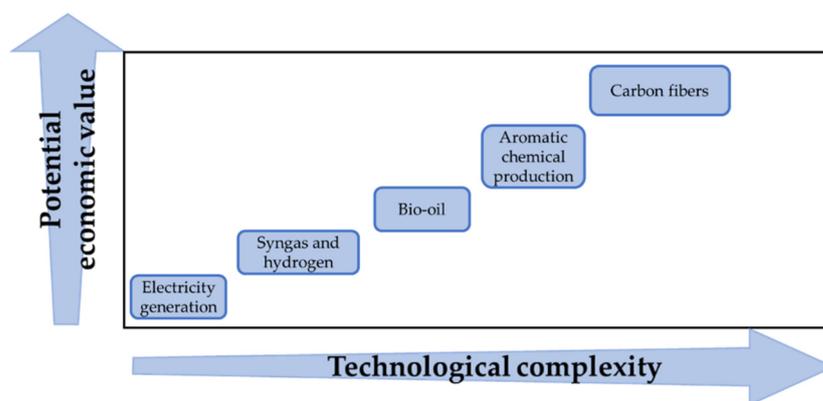


Figure 3. Applications of lignin as feedstock in terms of economic value vs. technological complexity.

Because of the aforementioned emerging technologies, the outlook for lignin gasification as a stand-alone technology in the long-term is uncertain. However, currently and in the near future, the increased interest in H₂ production and the demand for biomass-derived syngas to synthesize sustainable hydrocarbons may allow it to retain or gain importance, at least in the short term.

In light of the expected increase in H₂ demand and the likelihood that lignin-derived H₂ would have to compete in terms of cost with other renewable sources of H₂ as well as other applications of lignin, the cost of feedstock beyond the minimum energy value in terms of heat or electricity may increase. Lignin gasification research should focus not only on optimizing the yields of H₂ or syngas but also on the recovery of heat in exothermic processes to minimize costs; this could potentially be achieved through innovative catalyst designs that are both active and resistant to deactivation, but simultaneously cheap to deploy in large quantities.

5. Conclusions

In this review, we analyzed the existing lignin gasification processes by dividing them into oxidative, water-related, and black liquor gasification categories. While progress and a better understanding of the gasification process were achieved over the past decades, inherent limitations associated with both the nature of lignin as a feedstock as well as the reactions involved in the process mean that higher yields of H₂ and syngas may not be possible without deploying more intricate catalysts. The majority of the studies covered focused solely on the process conditions and reactor designs, with only a limited number of studies involving catalysts being available. This may be due to the poor return on investment associated with the use of complex, potentially expensive heterogeneous catalysts to obtain what may be perceived as low-value gaseous products and heat.

Whether lignin gasification would gain importance as a lignin valorization technology in the future would largely depend on the concurrent development of other technologies. However, there seems to be a clear trend towards the usage of lignin in applications of higher technological complexity that may provide higher economic benefits, ultimately taking priority over lignin gasification in the future.

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