



## Review

# Metal-Based Heterogeneous Catalysts for the Synthesis of Valuable Chemical Blends via Hydrodeoxygenation of Lignin-Derived Fractions

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**Abstract:** Currently, many research projects are focused on the conversion of renewable raw materials into chemicals and fuels. Lignocellulosic biomass is a raw material used for the production of bio-oils and black liquors. These biomass-derived fractions offer promising paths for the production of valuable chemical products. Various catalytic methods have been investigated for upgrading the biomass-derived fractions. Researchers are interested in the hydrodeoxygenation process (HDO); in this process, the oxygen groups are eliminated by breaking the C–O bonds and water as a product. Incorporating heterogeneous catalysts (i.e., noble metals, transition metals, and metal sulfides) improves this process. Most HDO review articles describe catalytic results for model phenolic compounds. However, there is also a need to investigate the catalytic activity of real biomass-derived fractions. This paper explains research results regarding the upgrading of lignin-derived fractions (i.e., black liquors) by HDO. The paper has been organized according to the type of heterogeneous catalyst and shows compelling results based on different experimental conditions. The final sections present an analysis of the documented results and outline perspectives about integrating lignin into the biorefinery framework.

**Keywords:** hydrodeoxygenation; heterogeneous catalysts; upgrading; lignin; black liquor



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## 1. Introduction

The exploration of renewable resources to produce fuels and chemicals has gained significant attention in response to escalating oil and petrochemical costs. Lignin, a biopolymer derived from lignocellulosic biomass, emerges as a prominent candidate in this field. Lignin considered a byproduct of industrial processes (i.e., paper manufacturing), has often been used in applications such as lignosulfonates, adhesive formulations, and polymer formulations [1].

In recent years, lignin has gained increasing attention owing to its unique status as a renewable raw material with basic chemical aromatic structures. These chemical structures, which constitute fundamental building blocks, have the potential to serve as precursors for an array of aromatic chemical products, including phenols, alkyl phenols, BTX, cyclic alcohols, and cyclic hydrocarbons.

The interest in lignin is in line with the broader initiative to establish novel operational units within the biorefinery framework, marking a significant stride towards sustainable biomass utilization.

Several thermochemical and catalytic processes have been proposed to effectively depolymerize lignin and upgrade its derived fractions (i.e., black liquors), for example, hydrodeoxygenation (HDO). A paramount challenge lies in the meticulous optimization of the experimental conditions to maximize the yield of valuable liquid fractions.

Crucial factors influencing this optimization include temperature, hydrogen pressure, catalyst selection, and physicochemical attributes of the catalyst itself, such as the surface area, porosity, and acid–base properties. However, the intrinsic nature of lignin requires careful investigation. The chemical structural network of this biopolymer is significantly influenced by factors such as plant species and extraction process.

Understanding and accounting for these variables are imperative for tailoring processes that efficiently harness the potential of lignin and its derivatives.

Numerous studies have focused on the hydrodeoxygenation of lignin model compounds, providing valuable insights into the influence of catalyst properties and experimental conditions, such as temperature and hydrogen pressure ( $H_2$ ), on the reaction mechanism and catalytic performance. Those systematic studies have been presented in reviews, and that information has facilitated the development of catalysts with particular properties, for example, catalysts that exhibit enhanced resistance to aqueous medium, and medium with low pH values [2–4].

However, the hydrodeoxygenation of lignin or lignin-derived fractions is a complex process encompassing intricate reactions, such as direct demethoxylation, hydrogenation, hydrogenolysis, demethylation, and trans-alkylation [5]. A comprehensive understanding of the intricate interplay between the chemical structure of lignin and catalyst performance is imperative to selectively cleavage the bonds and obtain the desired monomeric products.

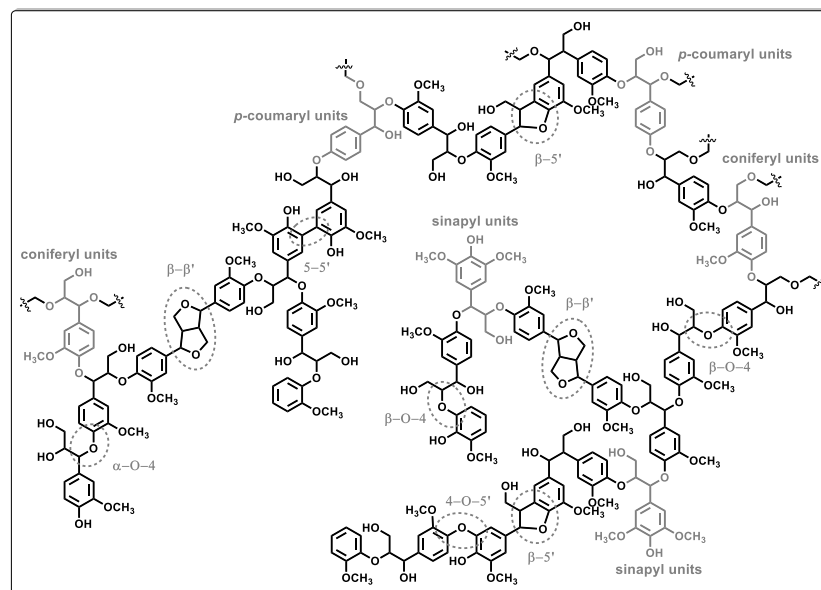
The type of information about the hydrodeoxygenation performance of lignin or lignin-derived fractions presented in papers is not standardized. The papers do not show uniform parameters for the evaluation or establishment of comparisons across diverse scientific investigations. Therefore, it is crucial to identify essential data such as the mass of lignin or lignin-derived fraction, the mass of the catalyst, the mass or volume of the solvent, the volume of the batch reactor, the hydrogen pressure (considering the temperature), and the mass or yield of products based on the mass of lignin. Those comprehensive data would allow the calculation of parameters such as O/C ratio, H/C ratio, and selectivity to monomers, which facilitate performance comparisons across various research studies.

This review focuses on studies about the hydrodeoxygenation of lignins or lignin-derived fractions, offering insights to support a broader understanding of heterogeneous catalyst performance in the hydrodeoxygenation of lignin-derived model compounds. Here are exposed different catalysts and the experimental conditions, the main results are highlighted focused on yield to liquid fractions and selectivity to particular monomers. The review presents conclusions focusing on the group of catalysts, and also presents future outlooks for this research field, to close the review some guidelines for improving the current catalytic systems are shown.

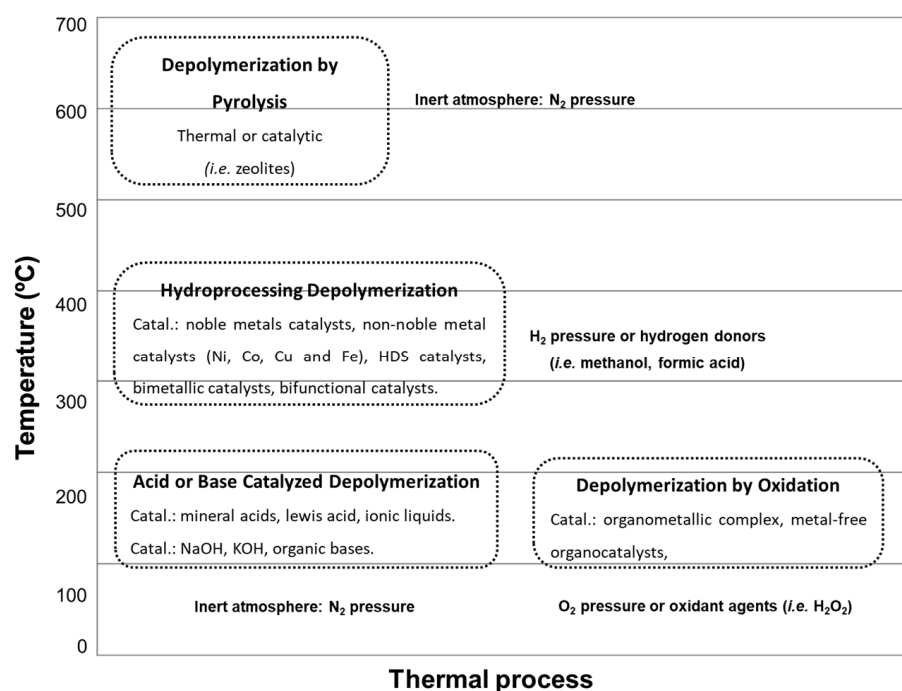
## 2. Hydrodeoxygenation for Upgrading of Lignin-Derived Fractions

Lignin is a biopolymer structured by cross-linked phenolic co-polymers and comprises three phenyl-propane monomeric units: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (see Figure 1). Lignin is a renewable feedstock,  $\approx 90\%$  of the current lignin production is utilized as fuel for incineration in industrial plants for energy recovery [6]. Approximately only a modest 10% of total lignin production is commercially transformed into industrial products, leaving the untapped potential for generating high-value chemical products [7,8].

Recent attention has been focused on lignin applications and the processes for lignin conversion into biofuel and chemical product synthesis [9,10]. Biological and thermochemical processes (pyrolysis, depolymerization, and hydrogenolysis, see Figure 2) are the main processes used to transform lignin into useful chemical products.



**Figure 1.** Illustration of the chemical structure of lignin, highlighting the fundamental phenylpropanoid units (p-coumaryl, coniferyl, and sinapyl) and predominant linkages.



**Figure 2.** Schematic overview of thermal processes and corresponding temperature ranges for the conversion of lignin into valuable chemical fractions.

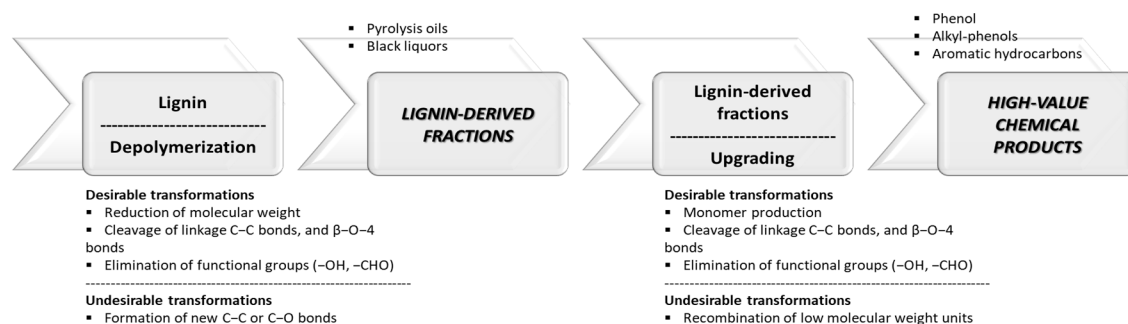
Pyrolysis, a rapid heating process under an inert gas atmosphere at temperatures between 500 and 600 °C, produces reaction mixtures in different phases: liquid, solid, and gaseous. The process can be carried out under thermal or combined thermal/catalytic conditions [11].

Depolymerization, generally carried out under pressure in an aqueous phase with a homogeneous alkaline catalyst at temperatures between 200 and 300 °C, produces a liquid organic phase containing oxygenated molecules (oligomers of medium molecular weight) and a solid fraction of residual lignin [12]. There is also further research on other methods of lignin polymerization to achieve organic fractions [13].

The organic fraction (i.e., solid lignin or black liquor) derived from either pyrolysis or depolymerization is a mixture of various phenolic compounds that do not have optimal industrial properties. Therefore, subsequent processes are essential to improve properties such as water content, pH, O/C ratio, and H/C ratio [14].

Currently, there are two extensively researched methods for upgrading lignin-derived fractions (lignin oils), zeolite cracking and hydrodeoxygenation. Zeolite cracking capitalizes on the high density of acid sites in zeolite materials, catalyzing cracking reactions (fractioning high molecular weight molecules into low molecular weight molecules) by eliminating oxygen, such as water, CO, and CO<sub>2</sub>. The second method, hydrodeoxygenation, is conducted under hydrogen pressure, temperatures between 300 and 400 °C, and a catalyst with metallic function, primarily removing oxygen functional groups as water molecules [15,16].

The transformation of lignin into industrial chemical products requires a combination of two stages: lignin depolymerization and hydrodeoxygenation of lignin-derived fractions (see Figure 3). This process requires moderate or high temperatures and moderate or high hydrogen pressure, the hydrogen can be supplied externally or produced in situ from the decomposition of chemical donors such as formic acid or isopropyl alcohol [17,18]. The presence of a hydrogenating catalyst is crucial, and the process can be executed in aqueous or organic solvents.



**Figure 3.** The sequence of stages proposed for the valorization of lignin into chemical products (first stage: depolymerization and second stage: upgrading). These two stages can be carried out in different reactors or the same reactor (one-pot).

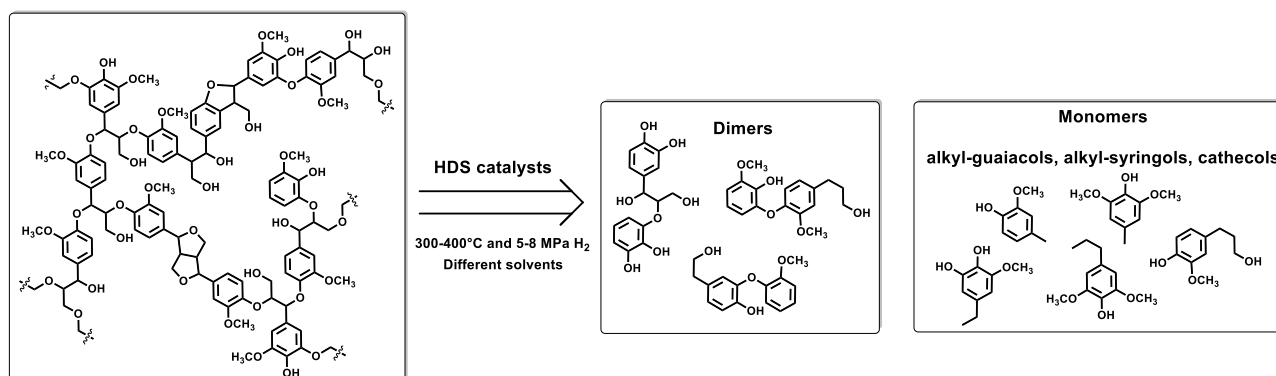
Under these experimental conditions, a complex process, including the breaking of C–O structural bonds in lignin, occurs. This process comprises mechanisms such as hydrogenolysis, demethylation, and demethoxylation reactions, which are often improved by the incorporation of bifunctional catalysts (metal–acid properties) [19]. The experimental setup allows for single (one-pot) or two-stage processes, yielding aromatic compounds with low oxygen content and aromatic hydrocarbons, including phenols, alkyl-phenols, and alkyl-benzenes [20,21].

The subsequent sections explore studies for different heterogeneous catalysts approaching lignin and lignin-derived oils to produce valuable liquid fractions for use as fuels or chemicals. Addressing the main challenge of developing robust heterogeneous catalysts capable of upgrading real biorefinery streams, it is paramount that aqueous streams contain a complex range of oxygenated compounds with different functional groups.

### 3. Hydrodesulfurization Catalysts (HDS)

Utilizing established hydrodesulfurization catalysts (HDS), such as NiMo and CoMo supported on alumina or zeolites, lignin can be transformed into fuels. These catalysts can hydrogenate the double carbon bonds and aromatic rings. By adjusting the thermodynamic conditions, it was possible to break the C–O bonds, thereby facilitating deoxygenation. A summary of the experimental results of HDS catalysts in the HDO of lignin (or lignin-derived fraction) is presented in Table 1. The resultant catalytic process yielded a spectrum of products, predominantly dimers and monomers, compared to alkyl-guaiacols, alkyl-

syringols, and alkyl-phenols (Figure 4). Additionally, discernible but comparatively lower yields of alkyl-cyclohexane, alkyl-benzene, alkyl-naphthalene, and alkyl-phenanthrene were obtained.



**Figure 4.** Overview of primary compounds produced by hydrodeoxygenation of lignin (or lignin-derived fractions) using hydrosulfurization catalysts. The characteristic representative experimental thermodynamic conditions are presented.

The NiMoS/Al<sub>2</sub>O<sub>3</sub> catalyst demonstrated notable efficacy in the hydrodeoxygenation of wheat straw soda lignin in a batch reactor. Under carefully defined experimental conditions, utilizing tetraline as the solvent, maintaining a 10 wt.% ratio of catalyst/lignin ratio, and operating at 350 °C under 8 MPa H<sub>2</sub>, exceptional outcomes were achieved. After 14 h, an impressive lignin conversion of approximately 85 wt.% was attained, resulting in a liquid fraction yield of 69 wt.% and an oligomer fraction yield of 25 wt.%. The liquid fraction comprises a diverse array of components, including alkyl-phenolics, guaiacols, catechols, aromatic hydrocarbons, naphthalenes, and alkanes. The identified compounds collectively account for approximately 40 wt.% of the liquid fraction. The strategic use of tetraline as a solvent, functioning as a hydrogen donor, proved advantageous in limiting recondensation reactions during lignin depolymerization. Furthermore, NMR analysis characterizing the oligomer fraction revealed the absence of β–O–4 linkages, underscoring the structural importance of C–O and C–C bonds within the lignin network [22].

Li N. et al. have presented findings on the generation of lignin-derived bio-oil through the hydrotreatment of alkali lignin. Their investigation involved the utilization of a MoS<sub>2</sub>-based catalyst and exploration of its combined effects with other metals, specifically MoS<sub>2</sub>/MxS<sub>2</sub> (where M = Ni, Co, or Ag). The most promising results were obtained by CoS<sub>2</sub>/MoS<sub>2</sub> catalyst and a catalyst/lignin ratio of 5 wt.%. Under moderate experimental conditions (310 °C, 2.5 MPa H<sub>2</sub>, and 1 h reaction time) in the presence of ethanol as a solvent, an impressive 91% lignin conversion and 86% bio-oil yield were achieved. The resulting bio-oil exhibited a distinctive composition characterized by the presence of phenols, esters, and acids, with variations attributed to the specific transition metal employed in the catalytic process [23].

Continuing this line, Wu et al. investigated the ethanolysis of enzymatic lignin using MoS<sub>2</sub> as a catalyst. Their focus extended to the critical influence of appropriate ratios of Mo<sup>+x</sup> species on the catalytic processes involved, particularly demethoxylation and alkylation reactions [24].

In recent studies, the effectiveness of NiMoS-supported carbon and carbon-ZrO<sub>2</sub> catalysts in the hydrodeoxygenation of softwood lignin has garnered attention. The introduction of ZrO<sub>2</sub> into the catalyst formulation contributed to the formation of acid sites, thereby enhancing hydrogenolysis reactions. However, an excess of ZrO<sub>2</sub> reduces the organic liquid-phase yield, favoring oligomer formation. These findings underscore the intricate balance required in formulating catalysts for optimal performance [25].



Exploration of zeolites as solid supports for NiMo catalysts has provided valuable insights. NiMo impregnated over USY with varying Si/Al ratios displayed enhanced yields, underscoring the pivotal role of the total acidity in influencing the liquid phase yield. The catalyst with lower total acidity exhibited moderate selectivity towards monocyclic and alkyl-benzene compounds, while the highly acidic counterpart demonstrated improved selectivity [26].

Using a template technique, a mesoporous NiMoS catalyst was synthesized using SBA-16 and MCM-41 (100% silica) as templates. NiMoS-SBA exhibited commendable activity (mass ratio of catalyst/lignin: 1/10) under conditions of 400 °C, 8.0 MPa H<sub>2</sub>, and 5 h reaction period. Research on Kraft lignin and enzymatic lignin has demonstrated significant differences in oil-phase yields, reaching 65 wt.% and approximately 84 wt.%, respectively. The structural characteristics inherent to each lignin played a crucial role in determining the distribution of hydrodeoxygenation product yields. Under various reaction conditions, the maximum total monomer yield was 47 wt.% for Kraft lignin and reached 76 wt.% for enzymatic lignin. In the oil phase, alkyl-phenols dominated as the primary chemical groups in both Kraft and enzymatic lignin [27].

Lignin can be converted into high-quality gasoline using a two-stage process. In the initial stage, lignin underwent depolymerization facilitated by a homogeneous alkaline catalyst (NaOH) in the presence of ethanol within a supercritical medium maintained at 320 °C and 12.0 MPa. The second stage involves hydrogenation, which ultimately yields naphthenic and paraffinic hydrocarbons. Catalysts such as sulfide, NiMo, or CoMo supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are employed for the second stage of this transformative process [28].

Moreover, products derived from depolymerization can be further converted into alkyl aryl ethers. This transformation was achieved in a hydrocracking reactor equipped with a solid superacid catalyst (Pt/SO<sub>4</sub>/ZrO<sub>2</sub> or Pt/WO<sub>4</sub>/ZrO<sub>2</sub>) operating within a temperature range of 340–375 °C. Notably, the in situ conversion of phenols to ethers occurs when zirconia-based catalysts (WO<sub>4</sub>/ZrO<sub>2</sub> or SO<sub>4</sub>/ZrO<sub>2</sub>) are combined with methanol in the temperature range of 225–275 °C. These resulting products hold potential applications as valuable fuel additives [29].

Kubička D. et al. presented a study on the hydrodeoxygenation of lignin utilizing commercial NiMoP/Al<sub>2</sub>O<sub>3</sub> catalysts under specific conditions, 320–380 °C and 4–7 MPa H<sub>2</sub> pressure. Their investigation explored critical parameters, such as temperature and hydrogen pressure, and revealed that elevating these values could effectively minimize the production of condensation products. Furthermore, the activation method employed for the catalyst, specifically sulfidation, significantly influenced its performance. The catalyst exhibited heightened activity when the sulfidation stage was conducted before the catalytic process, emphasizing the importance of the activation sequence in optimizing performance [30].

Cheah Y. W. et al. reported on the catalytic activity of transition metals as promoters in the MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for the hydrodeoxygenation of Kraft lignin. Among the tested transition metals, NiMo exhibited superior deoxygenation activity compared to those of ZnMo and FeMo. NiMo displayed high selectivity toward deoxygenated aromatic and cyclic monomers, above 75%. In contrast, the other two catalysts, ZnMo and FeMo, demonstrated high selectivity toward naphthalene and anthracene derivatives, reaching approximately 65% and 80%, respectively [31].

Sulfide catalysts, specifically NiW and NiMo, were evaluated for hydrodeoxygenation of kraft lignin in batch reactors. This study underscores the pivotal role played by the catalyst support in achieving favorable lignin conversion and high phenolic monomer yields. Notably, catalysts with basic or neutral properties, exemplified by sulfide NiW/C and NiMo/MgO-La<sub>2</sub>O<sub>3</sub>, outperformed their acidic counterparts, illustrating the significance of tailored catalyst support preferences in optimizing performance [32,33].

**Table 1.** Compilation of lignin hydrodeoxygenation results across various studies investigating hydrodesulfurization (HDS) catalysts.

Hydrodesulfurization Catalyst	Type of Lignin or Lignin-Derived Fraction	Experimental Data	Main Results	Ref.
NiMoS/Al <sub>2</sub> O <sub>3</sub>	Wheat straw soda lignin	Catalyst/lignin: 10 wt%, 350 °C, 8 MPa H <sub>2</sub> , 14 h reaction time. Tetraline as solvent and H <sub>2</sub> donor.	Lignin conversion ≈ 85 wt.% Yields = 69 wt.% liquid fraction, and 25 wt.% oligomers Composition liquid fraction: 40 wt.% referred to alkyl-phenolics, guaiacols, catechols, aromatic hydrocarbons, naphthalenes, and alkanes.	[22]
CoS <sub>2</sub> /MoS <sub>2</sub>	Alkali lignin Product: Lignin-derived bio-oil	Catalyst/lignin: 5 wt.%, 310 °C, 2.5 MPa H <sub>2</sub> , 1 h reaction time. Ethanol as a solvent	Lignin conversion = 91% Yield = 86% as bio-oil. Phenols, esters, and acids were identified as the main products in bio-oil.	[23]
NiMoS-SBA	Kraft lignin vs. Enzymatic hydrolysis lignin	Catalyst/lignin: 1/10 mass ratio, 400 °C, 8.0 MPa H <sub>2</sub> , 5 h reaction time.	Yield oil-phase = 65 wt.% (Kraft lignin) and ≈84 wt.% and (Enzymatic lignin) Yield total monomers = 47 wt.% (Kraft lignin) and 76 wt.% (Enzymatic lignin)	[27]
NiMoP/Al <sub>2</sub> O <sub>3</sub>	Enzymatic hydrolysis lignin	Catalyst/lignin: 1/4–1/1 mass ratio, 320–380 °C, 4–7 MPa H <sub>2</sub> , Semi-continuous tubular reactor.	Yield organic phase = 15 wt.% Naphthenes (≈45 wt.%), aromatic (25 wt.%), and oxygenates (≈12 wt.%) as the main products in the organic phase	[30]
MoS <sub>2</sub> /γ-Al <sub>2</sub> O <sub>3</sub> Promoters: Ni, Fe, Zn	Kraft lignin	Catalyst/lignin: 1/3 mass ratio, 340 °C, 4 MPa H <sub>2</sub> , 5 h reaction time. Hexadecane as solvent	NiMoS <sub>2</sub> /γ-Al <sub>2</sub> O <sub>3</sub> , selectivity to deoxygenated aromatic monomers (12%), and deoxygenated ciclo-alkane monomers (62%).	[31]
NiW/AC activated carbon	Kraft lignin	Catalyst/lignin: 1/4 mass ratio, 320 °C, 3.5 MPa H <sub>2</sub> , 8 h reaction time. Methanol as solvent	Yield methanol soluble products (MSPs) = 82% Monomeric product yield (MSPs) = 28.5 wt.% (based on lignin intake)	[32]
NiMo/MgO-La <sub>2</sub> O <sub>3</sub>	Kraft lignin	Catalyst/lignin: 1/20 mass ratio, 350 °C, 10 MPa H <sub>2</sub> , 4 h reaction time. Solvent free	Lignin conversion = 87% Yield dichloromethane soluble products (DSPs) = 48% Monomeric product yield (DSPs) = 26.4 wt.% (based on lignin intake)	[33]

#### 4. Noble Metal Catalysts

Catalysts based on noble metals such as Pt, Pd, and Ru have been used for the hydrodeoxygenation of lignin. Notably, favorable yields of the organic phase were achieved when processing lignin extracted from *Pinus radiata*, employing 5 wt.% Pd/C, with operating conditions of 195 °C, 3.45 MPa H<sub>2</sub> pressure, and utilizing a dioxane/water mixture (1:1) as the solvent. It is worth noting that the type of method for lignin extraction exerted a discernible influence on both the yield of the organic phase and the selectivity of various monomers [34].

One study focused on carbon-supported Pt-, Pd-, and Ru-based catalysts revealed the effectiveness of these catalysts in lignin hydrodeoxygenation (corn stalk lignin) using an

ethanol/water mixture (65 vol.%) as the solvent under conditions of 250 °C and 2.0 MPa H<sub>2</sub> pressure. These catalysts consistently achieved yields  $\geq 70\%$  in the organic phase, with ethyl-4-guaiacol and ethyl-4-phenol as the primary products. Under the specified reaction conditions, no significant disparities were observed in the yields of the organic phase. Suggesting that the metal component did not exert a pronounced influence on overall performance. However, the selectivity of the primary products is influenced by the ruthenium catalyst [35].

The noble metal plays a crucial role in determining the distribution of the hydrodeoxygenation products derived from lignin. In a comparative study conducted by Van den Bosch et al., Pd/C and Ru/C catalysts were assessed for their catalytic activity. These findings indicate that Ru/C can reduce the OH content in lignin-derived products, particularly phenolic monomers. Pd/C, on the other hand, displayed lower C–O hydrogenolysis activity, preserving  $\gamma$ –OH in the side chain and resulting in the primary products 4-n-propyl guaiacol and 4-n-propyl syringol. The distinctive activity of Ru/C in removing  $\gamma$ –OH from the side chain led to the predominant formation of 4-n-propyl guaiacol and 4-n-propyl syringol as the major product [36]. Studies by other researchers have validated this observation, with Ru-based catalysts being employed for the hydrodeoxygenation of both lignin and phenolic monomers and dimers, providing further support for the role of Ru in influencing the specific pathways of lignin transformation [37,38].

Xu W. et al. reported the utilization of a high-loading metal catalyst (20 wt.% Pt/C) in the hydrodeoxygenation of switchgrass lignin. This catalyst exhibited notable efficacy, yielding primary products, such as *p*-cresol, phenol, guaiacol, 4-methyl guaiacol, 4-propyl guaiacol, 4-ethyl guaiacol, and vanillyl alcohol. The authors quantified significant alterations in lignin characteristics. For example, a 75% reduction in average molecular weight, a 50% reduction in O/C ratio, and a 10% increase in H/C ratio, all of that is suggestive of substantial structural transformations related to the fractioning of oligomers to monomers [39].

Bouxin F. et al. delved into the hydrodeoxygenation process applied to various lignins dissolved in a methanol/water mixture (1:1) and 1 wt.% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, experimental conditions of 300 °C and 2.0 MPa H<sub>2</sub> pressure. The authors established a correlation between the performance of HDO reaction with (1) the lignin extraction method and the content of  $\beta$ -O-4 bonds, and (2) the type of solvent utilized. These works help to understand the intricate relationship between lignin extraction methods, the chemical characteristics of lignins, and the way those relationships influence the monomer yields and the chemical composition of the produced HDO fractions [40,41].

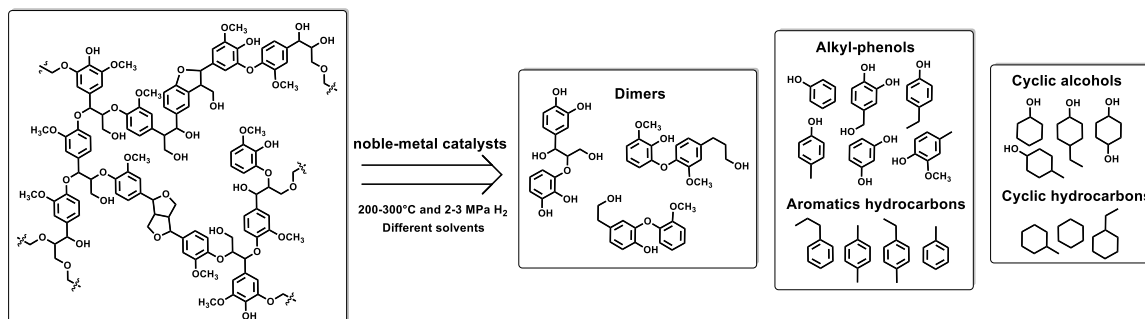
Hita I. et al. investigated the efficacy of commercially available catalysts featuring noble metals supported on carbon or alumina. Their findings underscored the significant influence of both catalyst support and noble metals on the yield and composition of the oil fraction. Notably, catalysts supported on alumina outperformed their carbon-supported counterparts. The presence of numerous weak acid sites, particularly on alumina, potentially synergizes with the metal particles, facilitating the cleavage of the C–O bonds. The resulting oil fraction is rich in aromatic, hydrocarbon, and alkyl phenolic compounds. The Rh/Al<sub>2</sub>O<sub>3</sub> catalyst achieved the highest yield with a monomer yield of 30 wt.%. It is noteworthy that the catalyst experienced a phase transformation during the hydration process, transitioning from  $\gamma$ - and  $\alpha$ -phases to the formation of the boehmite phase [42].

The above works have demonstrated that the choice of solvent, specifically alcohols such as methanol or isopropanol, or a mixture of alcohol/water, proved to be more effective than using water alone. Alcohols play a crucial role in preventing the recombination of the fragments generated during the process. The studies further revealed that the choice of metal in the catalyst (Pt, Ir, or Rh) significantly influenced both the monomer yield and selectivity of the final products.

Shao Y. et al. achieved the one-pot hydrodeoxygenation of lignin using a porous Ru/Nb<sub>2</sub>O<sub>5</sub> catalyst. This catalytic system facilitated the efficient reduction in oxygen content in a specific type of organosolv lignin under conditions of 250 °C, 0.7 MPa H<sub>2</sub>, and



20 h. Notably, the 2%Ru/Nb<sub>2</sub>O<sub>5</sub> catalyst demonstrated superior performance, exhibiting a 10–15% increase in the yield of the organic phase compared to the 2%Ru/ZrO<sub>2</sub> and 2%Ru/Al<sub>2</sub>O<sub>3</sub> catalysts. The organic phase produced using 2%Ru/Nb<sub>2</sub>O<sub>5</sub> consisted of ≈90% hydrocarbons, including arenes, cycloalkanes, and aliphatic alkanes [43]. (Figure 5)



**Figure 5.** Summary of the primary compound groups produced by hydrodeoxygenation of lignin (or lignin-derived fractions) using noble-metal-supported catalysts. The typical experimental thermodynamic conditions are presented.

The researchers employed Density Functional Theory (DFT) calculations to elucidate the enhanced cleavage of C–O bonds in Nb<sub>2</sub>O<sub>5</sub> compared to other metallic oxides, specifically focusing on the adsorbed phenol molecules. The energy data for phenol adsorption and C–O bond cleavage provided insights into the hydrogenation of phenyl rings. This approach contributes to a fundamental understanding of the mechanisms underlying the catalytic process [43,44].

These findings align with the outcomes presented by Jiang W. et al. who explored the hydrodeoxygenation activity of Ru supported on solid acid support (H-ZSM-5) when applied to lignin substrates. Under specific reaction conditions (mass ratio catalyst/lignin: 1/1, 3.0 MPa H<sub>2</sub>, 300 °C, 6 h), the 5% Ru/H-ZSM-5 catalyst demonstrated notable hydrocarbon yields of approximately 51% and 97%, predominantly composed of aromatics and six-member aliphatic compounds [45].

Ruthenium deposition on composite solid support (carbon/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) was investigated for the hydrodeoxygenation of lignin-derived bio-oil through pyrolysis. The Si/Al ratio in the support facilitates the creation of Brønsted acid sites, which are crucial for promoting the saturation of aromatic rings. Following a 48 h process at 120 °C and 3.0 MPa H<sub>2</sub>, a substantial yield of alkyl cyclohexanols was achieved as a result of the efficient hydrogenation of total phenolic compounds present in the bio-oil [46].

A ruthenium-based catalyst supported on zirconium oxide was employed for the depolymerization of lignin through HYD/HDO under mild reaction conditions (i.e., 250 °C and 2.2 MPa H<sub>2</sub>). The catalyst featuring a predominantly monoclinic phase of ZrO<sub>2</sub> demonstrated enhanced performance and improved yields in the organic phase. Phenolic monomers are the predominant compounds in the organic phase. This process exhibited versatility, applying lignin dissolved in either water or water/ethanol mixtures, and achieving organic phase yields of approximately 50%. The obtained results were comparable to those exhibited by a commercial catalyst with double the Ru loading (5 wt.% Ru/C). Major products identified in the organic phase included guaiacol, vanillin, and acetovanillone [47,48].

Ru/NbOPO<sub>4</sub> was introduced as a combination of NbOx species and phosphates, with robust Brønsted acid sites. This catalyst facilitates the efficient cleavage of both C–O and C–C linkages within lignin. The one-pot conversion of different types of lignin using this multifunctional catalyst resulted in excellent yields of monocyclic hydrocarbons (1.5 times the yields reached by the reference method: nitrobenzene oxidation method). This one-pot process, operating under moderate reaction conditions, presents a promising option to produce fractions of monocyclic hydrocarbons (C6–C9) from lignin [49].

The inclusion of Lewis acid sites enhances the hydrodeoxygenation of lignin. A catalyst incorporating Ru and ZnO supported on SBA-15 exhibited notable activity in generating phenolic monomers from hydrolysis lignin, yielding 42.5 mol%, which is nearly double the yield achieved by the Ru/SBA-15 catalyst (yield 22.5 mol%). The authors explored the synergistic effect between Ru and ZnO by conducting an experiment catalyzed by a physical mixture of Ru/SBA-15 and ZnO/SBA-15, yielding results similar to the Ru/SBA-15 catalyst. The characterization of Ru/SBA-15 versus Ru-ZnO/SBA-15 revealed a higher concentration of Lewis acid sites for the latter catalyst. TPR experiments further indicated strong interactions between Ru and ZnO. Additionally, the oxophilic properties of ZnO contributed to stabilizing reaction intermediates, and the electron transfer from Ru to ZnO facilitated the activation of H<sub>2</sub> molecules [50].

Niobium oxide (Nb<sub>2</sub>O<sub>5</sub>) is another metallic oxide investigated as a solid support. A catalyst leveraging the Ni-Re combination supported on Nb<sub>2</sub>O<sub>5</sub> demonstrated efficiency in catalytically converting Kraft lignin into aromatic monomers. Under the conditions of 330 °C, 3 h, and ethanol in a supercritical state, the 5%Ni-5%Re/Nb<sub>2</sub>O<sub>5</sub> catalyst achieved outstanding oil yields of 35 wt.% of lignin monomers, particularly aromatic alcohols. The synergistic combination of acid and oxophilic sites in the catalyst facilitated a selective cleavage of C–O bonds in lignin oligomers [51].

Understanding the operational mechanisms of catalysts is imperative for devising characterization experiments and uncovering the synergistic effects among metallic species. In the case of Ir-ReO<sub>x</sub>/SiO<sub>2</sub>, the performance of the catalyst in the hydrodeoxygenation of various lignin types was significantly influenced by Ir and ReO<sub>x</sub>. ReO<sub>x</sub> species primarily contribute to the cleavage of C–O bonds, while Ir species play a crucial role in the hydrodeoxygenation and saturation of benzene rings [52].

Abu-Omar M. et al. highlighted the synergistic effects of a catalyst combining Zn<sup>2+</sup> ions and Pd<sup>0</sup> supported on carbon to facilitate the cleavage of β–O–4 bonds in lignin. This catalytic system was tested for the hydrodeoxygenation of lignin, achieving a total organic phase yield of 41%, with propyl-guaiacol and propyl syringol as the primary products. The proposed mechanism suggests that Zn<sup>2+</sup> ions play a pivotal role in activating and eliminating hydroxyl groups at the C<sub>γ</sub> position of the β–O–4 ether bond. This process involves the formation of a six-membered ring with the coordination of a Zn<sup>2+</sup> ion and oxygen atoms in the C<sub>α</sub> and C<sub>γ</sub> positions [53,54].

Table 2 compiles the catalytic performance of different noble-metal-based catalysts in the HDO process of lignin or lignin-derived fractions.

**Table 2.** Compilation of lignin hydrodeoxygenation results across various studies investigating noble metal-based catalysts.

Noble-Metal-Based Catalyst	Type of Lignin or Lignin-Derived Fraction	Experimental Data	Main Results	Ref.
5 wt.% Pd/C	Enzymatic hydrolysis lignin	Catalyst/lignin: 0.18/0.67 (mass ratio), 195 °C, 3.45 MPa H <sub>2</sub> , 24 h reaction time. Dioxane/water (1:1 vol.) as solvent	Yield = 89 wt.% oil fraction (based on lignin input). Composition oil fraction: 21 wt.%, dihydro-coniferyl alcohol and 4-n-propyl guaiacol as the main products	[34]
5 wt.% Ru/C	Enzymatic hydrolysis lignin	Catalyst/lignin: 1/5 mass ratio, 250 °C and 2.0 MPa H <sub>2</sub> , 3 h reaction time Ethanol/water (65 vol.%) as solvent	Yield ≈ 72 wt.% to liquid products (EtOAc soluble phase) (based on initial lignin). Composition liquid fraction: ethyl-4-guaiacol and ethyl-4-phenol as the primary products.	[35]

Table 2. Cont.

Noble-Metal-Based Catalyst	Type of Lignin or Lignin-Derived Fraction	Experimental Data	Main Results	Ref.
Pd/C vs. Ru/C (5 wt.%)	Extracted birch sawdust (19.5 wt% Klason lignin)	Catalyst/lignin: 1/10 mass ratio, 250 °C and 3.0 MPa H <sub>2</sub> , 3 h reaction time Methanol/water (65 vol.%) as solvent	Yield = 49 (C%) Pd and 48 (C%) Ru to monomers (based on the weight of lignin oil). Selectivity to main products: Pd (propanol-4-guaiacol + propanol-4-syringol) vs. Ru (n-propyl-4-guaiacol + n-propyl-4-syringol)	[36,37]
20 wt.% Pt/C	Organosolv lignin (switchgrass)	Catalyst/lignin: 1/10 mass ratio, 350 °C and formic acid (H <sub>2</sub> donor), 4 h reaction time Ethanol as solvent	Yield = 21 wt.% total of identified products Composition liquid fraction: ethyl-4-phenol and propyl-4-guaiacol as the main products.	[39]
5 wt.% M/Al <sub>2</sub> O <sub>3</sub> M = Ru, Pd, Pt, and Rh	Kraft lignin	Catalyst/lignin: 1/20 mass ratio, 450 °C, 10 MPa H <sub>2</sub> , 4 h reaction time Methanol/water (1:1 vol.) as solvent	Yields to organic phase = 30.4 wt.% (Ru), 40.3 wt.% (Pt), 37.5 wt.% (Pd), and 41.5 wt.% (Rh). Composition of organic phase: lignin oil and soluble fractions in dichloromethane or acetone.	[42]
2 wt.% Ru/Nb <sub>2</sub> O <sub>5</sub>	Birch lignin	Catalyst/lignin: 2/1 mass ratio, 250 °C, 0.7 MPa H <sub>2</sub> , 20 h reaction time Water as solvent	Yield to organic phase = 35.5 wt.% Composition: arenes (59.5 wt.%), cycloalkanes (24.2 wt.%), dicyclic arenes + dicyclic cycloalkanes (6.3 wt.%), aliphatic alkanes (1.7 wt.%).	[43]
2.8 wt.% Ru-Nanocarbon/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	Alkali lignin bio-oil	Catalyst/lignin bio-oil: 50 mg/0.5 mL mass ratio, 120 °C, 3 MPa H <sub>2</sub> , 48 h reaction time t-butyl-alcohol as solvent	The catalyst was able to hydrogenate the aromatic rings of the lignin-derived compounds included in the bio-oil. From aromatic to cycloalkanes.	[46]
Ru-10ZnO/SBA-15	Enzymatic hydrolysis lignin	Catalyst/lignin: 1/1 mass ratio, 220–240 °C, 2 MPa H <sub>2</sub> , 4 h reaction time Methanol as solvent	Yield to organic phase ≈ 42.5 mol% (220 °C) and 51.3 mol% (240 °C)	[50]
Ir-ReO <sub>x</sub> /SiO <sub>2</sub> (1 wt% Ir and 5 wt% Re)	Different types of lignins	Catalyst/lignin: 1/1 mass ratio, 260 °C, 4 MPa H <sub>2</sub> , 10 h reaction time n-hexane as solvent	Yield to lignin oil = 15.3 C mol% (organosolv), 14.2 C mol% (enzymatic hydrolysis), 16.6 C mol% (alkaline) Yield to monomers = 29 C mol% (organosolv), 14.6 C mol% (enzymatic hydrolysis), 9.3 C mol% (alkaline)	[52]

#### Combination of Different Catalysts and Stages (One-Pot Experiments)

A proposed two-stage process, including hydrogenolysis followed by hydrodeoxygenation, has demonstrated efficacy for the transformation of lignin into hydrocarbons and methanol. The initial stage was conducted in an acidic medium (either aqueous or organic solvent, such as dioxane), Pt/C, or Rh/C catalysts under specific conditions of 200 °C and 4 MPa H<sub>2</sub> pressure. Optimal results were achieved using a mixture of aqueous H<sub>3</sub>PO<sub>4</sub> and dioxane (1:1) combined with a Pt/C catalyst, yielding monomers and dimers at 46% and 12%, respectively. Subsequently, these monomers were efficiently converted to alkanes and

methanol using a Pd/C catalyst, resulting in quantitative yields. The final hydrocarbon yields reached 90% for the C8-C9 fraction and 82% for C14-C18 compounds [55].

Liguori L. et al. delved into the depolymerization of lignin through a dual-catalyst approach. In this method, a solid acid polymeric resin (Nafion SAC-13) was employed for depolymerization, whereas a palladium-based catalyst (Pd/C) facilitated hydrodeoxygenation. In situ generation of hydrogen was achieved using formic acid as a hydrogen donor. This synergistic combination of catalysts demonstrated peak monomer yields ranging from 13 to 18%, for guaiacol, catechol, and resorcinol at 300 °C for 4 h. Notably, the monomer yield exhibited dependence on the specific type of lignin employed [56].

A catalytic system integrating hydrogenation activity (noble metals supported on metallic oxides) and dehydration activity using zeolites has been documented for lignin hydrodeoxygenation at 250 °C and 4–5 MPa H<sub>2</sub>. The combination of 5%Ru/Al<sub>2</sub>O<sub>3</sub> and H-Y zeolite exhibited an optimal lignin conversion of approximately 60%, and aromatic hydrocarbons emerged as the predominant products. The authors suggested that the choice of solid support plays a crucial role in determining product selectivity. Specifically, catalysts with metal/C configurations demonstrated superior selectivity for cyclic hydrocarbons, whereas metal/Al<sub>2</sub>O<sub>3</sub> configurations yielded the best results for aromatic hydrocarbons [57].

In the study conducted by Laskar D. et al., a hybrid catalyst system comprising Ru/Al<sub>2</sub>O<sub>3</sub> and zeolite H-Y was employed for the hydrodeoxygenation of lignin in the aqueous phase (0.33 wt.%) under operating conditions of 280 °C and 4.0 MPa H<sub>2</sub>. The zeolite acid sites exhibited a synergistic effect with the metallic sites, facilitating the selective cleavage of the C–O–C bonds in the lignin oligomers, resulting in the production of dimers and trimers. Additionally, these acid sites promoted alkylation reactions, contributing to the formation of bi-cycloalkanes [58]. This integrated system demonstrated promising outcomes, achieving a lignin conversion of approximately 60%, a product yield of 20%, and a notable selectivity of approximately 90% toward cycloalkanes and aliphatic hydrocarbons [59].

Based on previous results, researchers developed a bifunctional catalyst, Ru/HY, to investigate its efficacy in the hydrodeoxygenation (HDO) of softwood lignin. This catalyst was designed to possess two distinct types of active sites integrated into the same support; the synergistic effects enhance the catalytic activity. The superior performance of the bifunctional catalyst (Ru/H-Y) was evident, with the hydrocarbon yield surpassing that of the physical mixture of catalysts (Ru/Al<sub>2</sub>O<sub>3</sub> + H-Y) by 10 wt.%. The observed enhancement in catalytic activity could be attributed to the concept of the “intimacy criterion,” emphasizing the significance of proximity between active sites [60].

The structural features of each lignin source play a crucial role in achieving the optimal depolymerization yields. Lignins characterized by a higher content of ether linkages, particularly β–O–4 and α–O–4 bonds, exhibited greater susceptibility to breakdown than lignins dominated by aliphatic C–C bonds. Notably, lignins with methyl groups and shorter side chains tended to reduce the number of labile sites within the lignin structure, influencing the overall depolymerization process positively [61].

In an innovative approach, Ouyang X. et al. proposed a multistage process aimed at producing aromatic hydrocarbons and phenols from pine wood lignin. The first stage involved reductive depolymerization facilitated by Pt/C under controlled conditions (230 °C, 3.0 MPa H<sub>2</sub> pressure, and methanol/water as the solvent). This initial stage yielded promising results, achieving a 15 wt.% monomer yield, with notable compounds including 2-methoxy-4-propyl phenol, guaiacol, methylguaiacol, and ethylguaiacol. The second stage was carried out on a demethoxylation/dealkylation process using a physical mixture of the MoP/SiO<sub>2</sub> + H-ZSM-5 catalyst (mass ratio: 1/1). Operating at 350 °C, 9.0 MPa, with an H<sub>2</sub> flow rate of 30 mL·min<sup>−1</sup>, this stage resulted in a calculated yield of 9.6 mol% to phenol, demonstrating the potential of this multistage approach for lignin valorization [62].

## 5. Nickel-Based Catalysts

Nickel (Ni) is a key transition metal in the hydrodeoxygenation (HDO) process, and the nickel Raney<sup>®</sup> catalyst is a prominent choice for lignin hydrodeoxygenation. This catalyst has demonstrated effectiveness in the conversion of lignin model compounds, bio-oils derived from lignin, and isolated lignins, as evidenced by numerous studies [63,64]. The solvent in the reaction medium is a critical factor influencing HDO yield. The polarity and basicity of the solvent play pivotal roles in breaking lignin ether bonds, including  $\beta$ -O-C and  $\alpha$ -O-C linkages. Notably, investigations into the hydrodeoxygenation of lignin model dimers have revealed optimal conversions in the presence of aprotic non-polar solvents, such as n-heptane and decaline [65]. Table 3 presents the experimental results of different Ni-based catalysts in the HDO of lignin or lignin-derived fractions.

The catalyst composition, specifically the Ni/Al ratio and the type of promoter metal plays a crucial role in shaping the product distribution during the hydrodeoxygenation of organosolv lignin in methanol, conducted at elevated temperatures (360 °C) and high hydrogen pressures (7 MPa H<sub>2</sub>). The distinct impact of the Ni-Raney<sup>®</sup> catalyst, sourced from various commercial suppliers, on the fractions (light oil, heavy oil, and tar) can be effectively visualized and understood through a Van Krevelen plot [66]. Notably, this type of catalyst has demonstrated significant activity in lignin hydrodeoxygenation even under milder experimental conditions (280 °C, 0.5 MPa H<sub>2</sub>, 1 h). The resulting yield of 7.4% for the main compounds, predominantly comprising phenolic monomers, holds substantial promise for potential applications as valuable chemical industrial products [67].

Forchheim, D. et al. conducted a comprehensive exploration of a two-stage process designed for the transformation of lignin into phenolic derivatives. In the initial stage, hydrothermal treatment involving water at elevated temperatures (>400 °C) and brief reaction durations was employed. The second stage involved hydrodeoxygenation using a nickel Raney<sup>®</sup> catalyst in a fixed-bed reactor operating at 250 °C. Throughout this process, the authors achieved notable selectivity, with catechol emerging as the predominant product in the first stage, whereas phenol was predominant after the second stage. Intensifying temperatures enhanced the overall yields for both stages [68].

Nickel supported on carbon exhibited remarkable efficacy in the conversion of lignosulfonates at 200 °C and 5.0 MPa H<sub>2</sub>, employing various solvents. Optimal outcomes were observed when glycerol or ethylene glycol was used as the solvent, resulting in the highest yields of compounds, such as ethyl-4-guaiacol and propyl-4-guaiacol ( $\approx$ 80%). It is noteworthy that the catalyst's performance was assessed in the presence of alternative solvents such as water or cyclohexane, but no discernible conversions were observed [69].

Hydrodeoxygenation of corncob lignin from biorefinery was conducted using 20 wt.% Ni/C as a catalyst in various solvents (240 °C, 3 MPa H<sub>2</sub>, and 4 h). The highest monomer yield of approximately 12% was obtained when alcohols were employed as the solvent. Analysis by ICP-OES of the catalyst post-reaction revealed less than 0.5% Ni leaching into the reaction medium, indicating the robust stability of Ni/AC for lignin hydrogenolysis [70].

Hydrodeoxygenation with hydrogen donors, such as short-chain alcohols or organic acids, was investigated using a catalyst 10 wt.% Ni supported on carbon. This study focused on organosolv lignin derived from birch sawdust with solvents and hydrogen donors, including methanol, ethanol, and ethylene glycol. The results revealed a 50% conversion rate and a remarkable 90% selectivity towards monomers, particularly propyl-guaiacol and propyl syringol. The proposed mechanism suggests that, in the first stage, lignin undergoes fragmentation through alcoholysis. Subsequently, in the second stage, these fragments are converted into monomers on the Ni/C catalyst [71].

Labidi J. et al. explored the hydrodeoxygenation (HDO) of lignin using microwave radiation under specific conditions (140 °C, 30 min). This study investigated organosolv lignin derived from olive tree pruning residues, as catalysts for various metals (Ni, Ru, Pd, and Pt) supported on mesoporous alumina (Al-SBA-15), and either decaline or formic acid as solvents/hydrogen donors. These findings suggest that Ni-based catalysts can serve as alternatives to noble metal catalysts with 10 wt.% Ni/Al-SBA-15 catalyst demonstrating



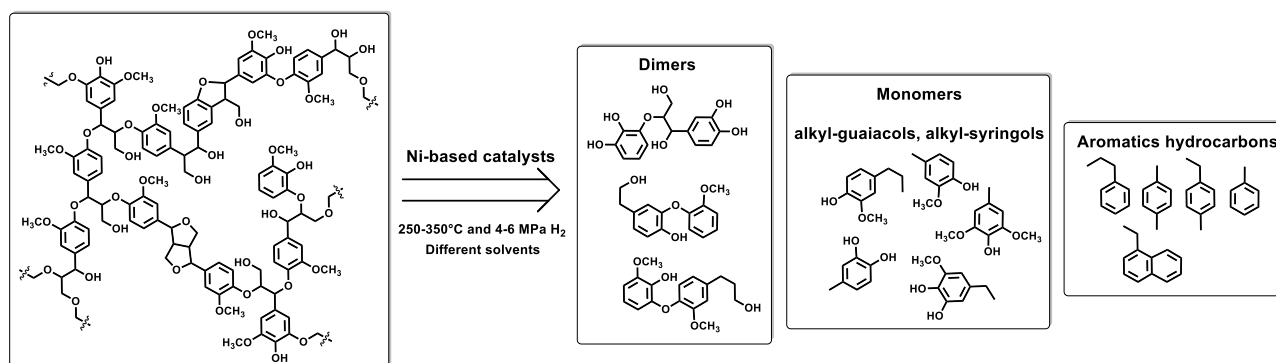
the highest organic phase yields, reaching 17% or 30%. The solvent significantly influenced the selectivity of monomers in the organic phase. For example, tetralin resulted in syringol-type monomers, while formic acid produced a notably higher yield of syringol-type monomers compared to guaiacol-type monomers, emphasizing the solvent's impact on product distribution [72].

Anderson E. et al. investigated a co-catalytic system employing a metal-based catalyst (Ni/C) in conjunction with a homogeneous acid catalyst (0.1M H<sub>3</sub>PO<sub>4</sub>) for the hydrodeoxygenation of lignin extracted from corn stover, utilizing methanol as the solvent. The incorporation of H<sub>3</sub>PO<sub>4</sub> was found to enhance the monomer yield, increasing it from 28 to 38% at a reaction temperature of 200 °C. The resulting product distribution was primarily characterized by monomers as methyl coumarates and methyl ferrulates. Interestingly, the introduction of the homogeneous acid catalyst did not alter the distribution of oxygenated monomeric products but did lead to an increase in hydrocarbon products [73].

A catalyst consisting of nickel supported on amorphous silica-alumina has been investigated for the hydrodeoxygenation (HDO) of various lignin varieties. The catalyst activity is notably influenced by the specific surface area of the supports and the particle size of the nickel. The large external surface area role is crucial in ensuring the effective dispersion of metallic particles and facilitating the easy diffusion of lignin macromolecules. Remarkably, these experimental systems have demonstrated excellent performance metrics, including lignin conversion rates of  $\geq 80\%$ , oil fraction yields  $\approx 50\%$ , and hydrocarbon selectivity  $\geq 90\%$  [74–76].

The presence of Brønsted acid sites has been identified as a contributing factor to achieving higher lignin conversion and hydrocarbon yields. These acid sites play a catalytic role in the dehydration of alcohols, which act as intermediates in the overall process. Interestingly, the Ni particles exhibited greater stability on zeolite supports. Nickel supported on H-BEA reached superior liquid fraction yields compared to Ni supported on SiO<sub>2</sub>, particularly when n-hexadecane was utilized as a solvent [77].

Recently, Kong L. et al. conducted a study in alignment with the work of Kasakov S. et al., wherein they compared various solid supports characterized by different Brønsted acid properties, including H-Beta, HZSM-5, MAS-7, MCM-41, and SAPO-11. The researchers developed a series of Ni-based catalysts, which were then evaluated for the hydrodeoxygenation of Kraft lignin using isopropanol as a hydrogen donor at 330 °C for 3 h. Among the catalysts, Ni-Cu supported on H-Beta exhibited the most favorable performance, achieving approximately 50% monomer yield and displaying high selectivity toward hydrocarbons (approximately 95%). The other catalysts exhibited improved selectivity for cyclic alcohols and ketones. These outcomes were attributed to the total acidity of each support and the strength of the acid sites. In the main gaseous products, higher quantities of CH<sub>4</sub> and CO were observed over Ni-Cu/MAS-7 and Ni-Cu/MCM-41, possibly resulting from the efficient cracking of methyl and carbonyl groups [78] (Figure 6).



**Figure 6.** Schematic representation of the main compound groups obtained from hydrodeoxygenation of lignin (or lignin-derived fractions) with nickel-based supported catalysts. The representative experimental thermodynamic conditions are presented.

Furthermore, morphological characteristics proved to be crucial in the lignin hydrodeoxygenation process. The size and shape of the pores played a pivotal role in inducing better liquid fraction yields. Additionally, the ratio between micro and mesoporosity significantly influences the overall yield. Three catalysts based on Ni and supported on hierarchical mesoporous silica-alumina mixed oxide were tested (Ni/ASA-1, Ni/ASA-2, and Ni/ASA-3). Among these, Ni/ASA-1 demonstrated an impressive yield of  $\approx 43\%$  in the liquid fraction, with a composition rich in cyclic hydrocarbons ( $\approx 97\%$ ). Notably, it exhibited the best selectivity for the C6-C9 fraction ( $\approx 83\%$ ). The authors noted that the catalyst showed robust activity under a range of catalyst/lignin mass ratios: 12.5%, 25%, and 50%. Impressively, even after four catalytic cycles, the catalyst maintained excellent performance, showing only a 3% decline in liquid phase yield while preserving remarkable hydrocarbon selectivity [79].

A novel and efficient catalyst for the hydrodeoxygenation of organosolv lignin is nickel supported on zirconium phosphate (Ni/Zr-P). The zirconium phosphate (ZrP) in this catalyst provides adjustable Lewis and Brønsted acid sites, which have been confirmed to be effective in cleaving C–O bonds. Furthermore, the interactions between  $\text{Ni}^{\delta+}$  and Zr species promoted the generation of new active sites, enhancing hydrogen adsorption. The catalyst 15%Ni/ZrP-2.0, utilizing isopropanol as the solvent (270 °C, 2.0 MPa  $\text{H}_2$ , and 4 h), exhibited optimal performance, achieving 87% lignin conversion. The yield of phenolic monomers was 15% and 48% for phenolic dimers + trimers. Importantly, the total phenolic monomer yield is correlated with the type of biomass from which the lignin was isolated [80].

Moreover, the Ni/Zr-P catalyst demonstrated activity through direct hydrogenation of the aromatic ring pathway. Also, this catalyst was tested for the upgrading of lignin-derived bio-oil, displaying good activity with a 25.8% hydrocarbon yield after 12 h. The optimal results were obtained under the reaction conditions of 250 °C, 3.0 MPa, a mass ratio of bio-oil/catalyst: 1/1, and dodecane as the solvent [81]. Furthermore, this type of catalyst (Ni-W/ZrP) has been employed for lignin depolymerization and hydrodeoxygenation, leading to the production of bio-oils enriched in phenolic monomers. Notably, this catalyst efficiently utilized hydrogen generated in situ from formic acid, with isopropanol serving as the solvent. This characteristic is advantageous for an initial stage in the industrial process of lignin utilization [82].

**Table 3.** Compilation of lignin hydrodeoxygenation results across various studies investigating Ni-based catalysts.

Ni-Based Catalyst	Type of Lignin or Lignin-Derived Fraction	Experimental Data	Main Results	Ref.
Nickel Raney <sup>®</sup>	Organosolv lignin (Eucalyptus wood)	Catalyst/lignin: 1/30 mass ratio, 280 °C, 0.5 MPa $\text{H}_2$ , 1 h reaction time. 1-butanol as solvent.	Yield = 7.4 wt.% monomers (based on the initial mass of lignin) Composition liquid fraction: diphenyl-methane-4-ethyl, 2,4-dimethyl-3-(methoxycarbonyl)-5-ethyl furan, trimethoxy-benzene	[67]
Serie of Ni-based catalysts (10 wt% Ni loading)	Lignosulfonate	Catalyst/lignosulfonate: 1/10 mass ratio, 200 °C, 5 MPa $\text{H}_2$ . Ethylene glycol as solvent.	Lignosulfonate conversion > 60%. Selectivity of 75–95% for alkane-substituted guaiacols, dimers.	[69]

Table 3. Cont.

Ni-Based Catalyst	Type of Lignin or Lignin-Derived Fraction	Experimental Data	Main Results	Ref.
5 wt.% Ni/activated carbon	Corncob lignin	Catalyst/lignin: 1/5 mass ratio, 240 °C, 3 MPa H <sub>2</sub> , 4 h reaction time. Methanol as solvent.	Yield = 12.1 wt.% monomers (based on the initial mass of lignin) Composition of liquid fraction: propyl/propenyl guaiacol and syrinol, mono-phenols of ethyl/vinyl phenol and guaiacol, and methyl coumarate/ferulate and derivatives.	[70]
10 wt.% Ni/carbon	Organosolv lignin	Catalyst/lignin: 1/5 mass ratio, 200 °C, 5 MPa H <sub>2</sub> , 6 h reaction time. Methanol as solvent.	Lignin conversion = 42%. Selectivity to main monomers = 97 wt.% Main monomers: propyl-4-guaiacol, and propyl-4-syringol	[71]
10 wt.% Ni/Al-SBA	Organosolv lignin (Olive tree pruning)	Catalyst/lignin: 1/1 mass ratio, 140 °C, 0.5 h reaction time. Tetraline as solvent and H <sub>2</sub> donor.	Yield ≈ 17 wt.% oil fraction (based on the initial mass of lignin)	[72]
5 wt.% Ni/Al-SBA-15	Organosolv lignin	Catalyst/lignin: 1/2.5 mass ratio, 300 °C, 7 MPa H <sub>2</sub> , 8 h reaction time. Methylcyclohexane as solvent.	Lignin conversion = 84%. Selectivity to monomers = 99% (cycloalkanes)	[76]
Ni-Cu/H-Beta (Ni-Cu: 20–20 wt.% loading)	Kraft lignin	Catalyst/lignin: 1/2.5 mass ratio, 330 °C, 7 MPa H <sub>2</sub> , 3 h reaction time. Isopropanol as solvent.	Lignin conversion = 98 wt.% Yield to monomers ≈ 51 wt.% Monomers: aromatics, cyclic ketones/alcohols, cycloalkanes, alkanes.	[78]
28 wt.% Ni/ASA (amorphous silica-alumina)	Kraft lignin	Catalyst/lignin: 1/8 mass ratio, 300 °C, 6 MPa H <sub>2</sub> , 160 min reaction time. Dodecane as solvent.	Yield to liquid fraction = 42.8 wt.% Selectivity: 96.7% base don cyclo-alkanes + bicyclo-alkanes.	[79]
15 wt.% Ni/ZrP-2.0	Organosolv bagasse lignin	Catalyst/lignin: 1/5 mass ratio, 270 °C, 2 MPa H <sub>2</sub> , 4 h reaction time. Isopropanol as solvent.	Lignin conversion = 89 wt.% (based on lignin input). Yield to phenolic monomers ≈ 15 wt.% Yield to biochar = 8.1 wt.% (based on lignin input).	[80]

## 6. Summary and Conclusions

Systematic research on various types of catalysts is imperative to elucidate the de-activation mechanisms and ascertain the long-term catalytic performance, particularly when focusing on lignin as a raw material in biorefinery production. This necessitates the incorporation of systematic changes in the reaction conditions to fine-tune the catalyst properties, with a specific emphasis on controlling the selectivity of products. Developing robust catalysts that exhibit enhanced resistance to water, low pH (acidic compounds), and efficient control of coke formation represents a significant challenge. Diverse catalyst categories have been explored in this field.

1. Hydrodesulfurization catalysts, such as NiMoS and CoMoS, originally tailored for oil refinery stream upgrading, have been repurposed for lignin-derived fraction upgrading. Despite yielding positive outcomes in the liquid fraction, characterized by dominant dimers and alkyl phenolic compounds, these catalysts require an external sulfur source and are constrained by the demanding experimental conditions.
2. Noble metal catalysts, notably Pd, Ru, and Pt supported on solid oxide surfaces, originally designed for hydrogenation or dehydrogenation, have been investigated

for lignin depolymerization. The intricate balance between the Lewis and Brønsted acid sites plays a pivotal role in the selective cleavage of C–O bonds. While showing higher hydrogenation and hydrogenolysis activity under moderate conditions, challenges persist in controlling intrinsic catalytic activity, leading to increased hydrogen consumption and the preferential formation of cyclic hydrocarbons over aromatics.

3. Nickel-based catalysts, serving as cost-effective alternatives to noble metals, exhibit hydrogenation activity conducive to lignin-derived fraction upgrading. Operating under elevated experimental conditions compared with noble metals, these catalysts yield a liquid fraction predominantly composed of dimers, alkyl phenolic compounds, and aromatic hydrocarbons (BTX). The synergy between the solid support and the intrinsic activity of nickel, coupled with the influence of the support acid properties on mechanistic reactions, underscores the significance of these catalysts in lignin HDO.

## 7. Future Outlooks

Currently, lignin valorization is at an intermediate stage and faces obstacles that need to be resolved before large-scale implementation. The complicated composition of the products resulting from lignin upgrading processes (i.e., hydrodeoxygenation and pyrolysis) makes it difficult to clarify the conversion mechanisms, separation, and purification of the products. In addition, a special mastery of the thermodynamic aspects and a good knowledge of the kinetic aspects are indispensable [78]. The use of energy-intensive reactions further complicates the application of these technologies. Overcoming these challenges is crucial for lignin utilization to become a practical and sustainable large-scale operation.

Based on recent advances in lignin utilization research, several critical aspects need to be considered.

1. Lignin utilization in a biorefinery requires a one-pot strategy, and researchers have explored the synergistic effects of combining two different types of catalysts. Examples include a) the combination of noble-metal-supported catalysts (i.e., Pd/C) with solid acid catalysts (i.e., zeolites) and b) the combination of noble-metal-supported catalysts (i.e., Ru/ZrO<sub>2</sub>)
2. With homogeneous alkaline catalysts (i.e., NaOH), however, the mechanisms underlying these processes are still unclear and lower conversion and selectivity have been observed.
3. As an alternative, a tandem process has been researched, which generally comprises two stages. In the first stage, the depolymerization of lignin is facilitated by an alkaline homogeneous catalyst (i.e., NaOH), resulting in a liquid fraction containing a complex mixture of lignin-derived oligomers. Subsequently, the resulting liquid fraction is hydrodeoxygenated in the second stage with a bifunctional catalyst. Although both strategies offer advantages and disadvantages, a common challenge is the accurate control of hydrogen consumption and recombination of the fragmented components.
4. During the hydrodeoxygenation process, the reaction still relies on harsh conditions and noble metal catalysts. A key goal is to first develop milder experimental conditions and then replace the expensive precious metals with more economical and environmentally friendly metal-based catalysts. Research into waste-based catalysts is a promising way to tackle this problem. Understanding the reactivity of isolated lignin is crucial. Natural lignins contain free radicals that are activated by degradation reactions and self-condensation. In contrast, isolated lignin (especially industrial lignin waste) exhibits lower activity and unpredictable quality as the aromatic structures are partially and non-selectively broken down during industrial processing. Therefore, improving the quality and reactivity of industrial lignin by-products has emerged as a key focus for subsequent valorization and reaction.

## 8. Further Improvements of Metal Oxide Catalysts

As this review shows, single and mixed oxides play a key role in the future upgrading of lignin as they are easy to synthesize, cheap catalysts with large surface area, and high

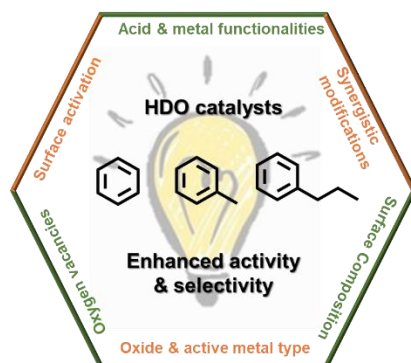
activity in the conversion of lignin derivatives [83]. Even though so much research has been carried out in this field, there is still much room for improvement to make these oxides more active and selective. The directions in which research should move could focus on adapting the surface of these oxides to improve activity and selectivity and further enhance the lignin derivatives, increase their market value, and avoid many purification steps. The questions we should ask ourselves to improve this area of catalysis could be:

1. Do oxygen vacancies play an important role? Much research has been carried out to find out how oxygen vacancies can affect catalytic behavior, especially in HDO reactions [84]. Based on the current state of research on vacancies in lignin-derived oxygenates, it is clarified that vacancies in the HDO reaction can act as acidic sites, promote substrate adsorption, and regulate product distribution, while vacancies in catalysts can increase stability and reducibility, improve metal dispersion and increase redox capacity [85]. The role of oxygen vacancies is to act as acid sites and regulate product distribution in the reaction. However, it should be noted that the improvement of deoxidation performance by oxygen vacancies is not always given. After the concentration has reached the extreme value, the improvement effect is rather flat. In addition, oxygen vacancies can also improve the stability and reducibility of the catalyst. However, according to the current state of research, vacancies can be further improved in the catalytic conversion of lignin and some improvements to the state of the art should be implemented:
  - (a) There are few methods for the preparation of vacancies, and there is a lack of safe and simple methods. Developing more convenient, safe, and energy-saving preparation methods is crucial. As this concept is in the field of photocatalysis, a multidisciplinary team could develop a more suitable method for oxide surface engagement and characterization.
  - (b) There is a lack of knowledge about how a vacancy is generated. A deeper understanding of the mechanism should provide intelligent methods to generate this vacancy. Moreover, it is still not clear what role they play in upgrading the lignin fraction. Even though the improvements in the use of low-oxygen oxides are known, the reaction mechanisms are not clear.
  - (c) A few real lignin raw materials are also used as research objects, but the majority of tests are focused on oxygen-deficient molecules as lignin model compounds. In order to represent real lignin objectively, model compounds cannot be used anymore, or as alternative a mixture of compounds shall be as close as possible to real lignin, should be used. It is imperative to understand the interactions between the various components of real lignin to develop a method for converting it into a high-value chemical.
2. Is the active surface area so important in driving the reaction? Conventionally is believed that a higher surface area leads to a higher catalytic performance, [86], and this is true for some types of reactions, but for HDO the composition of this surface is more important than its active surface area, based on the BET area. The oxide can serve as a support for other materials containing the active sites (i.e., metal nanoparticles), but can also catalyze reactions alone or in combination with active sites from other phases (i.e., at the interfaces between metal nanoparticles and metal oxides). According to some authors, [87] controlling the layering of this surface will lead to higher catalytic activity. However, the mechanisms of interaction with the substrate and the formation of active sites in the layers are still unclear and further research should be conducted in this direction.
3. Is the interaction of the metal-support interface a key parameter or is the acidity of the support? It is generally recognized that the HDO of lignin derivatives requires a bifunctional catalyst in which hydrogenation at a metal site is followed by sequential dehydrogenation/deoxygenation at the support. However, the role of the support and the metal-support interface is controversial. For example, some authors suggest that the deoxygenation reaction occurs at the acid sites, [88] while others claim that the



defect sites of the support are responsible for the deoxygenation activity [89]. More research needs to be carried out to find out the critical aspect of the surface of the metal oxide, as these types of catalysts can be easily modified to become more acidic or have more defects. If we knew that aspects have the biggest impact, we could develop a better catalyst that increases activity and selectivity.

Figure 7 shows a scheme of the conclusions extracted from this part of the review.



**Figure 7.** Scheme of conclusions to increase the activity and selectivity of metal oxide catalysts in the HDO of lignin fractions.

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