

Review

# Catalytic Hydropyrolysis of Lignin for the Preparation of Cyclic Hydrocarbon-Based Biofuels

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**Abstract:** The demand for biomass utilization is increasing because of the depletion of fossil resources that are non-renewable in nature. Lignin is the second most renewable organic carbon source, but currently it has limited scope for application in the chemical and fuel industries. Lignin is a side product of the paper and pulp, sugar, and 2G bioethanol industries. Many research groups are working on the value-addition of lignin. Among the lignin depolymerization methods, catalytic hydropyrolysis is gaining attention and is playing a crucial role in developing biorefinery. The hydropyrolysis of lignin was conducted at a higher temperature in the presence of H<sub>2</sub>. The hydropyrolysis of lignin results in the selective formation of non-oxygenated cyclic hydrocarbons in a shorter reaction time. It is possible to use the cyclic hydrocarbons directly as a fuel or they can be blended with conventional gasoline. This review focuses on the prior art of pyrolysis and hydropyrolysis of lignin. Possible products of lignin hydropyrolysis and suitable synthetic routes to obtain non-oxygenated cyclic hydrocarbons are also discussed. The influence of various process parameters, such as type of reactor, metal catalyst, nature of catalytic supports, reaction temperature, and H<sub>2</sub> pressure are discussed with regard to the hydropyrolysis of lignin to achieve good selectivity of cyclic hydrocarbons.

**Keywords:** lignin; oxygenated aromatic compounds; hydropyrolysis; hydrodeoxygenation; metal catalysts; cyclic hydrocarbons



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## 1. Introduction

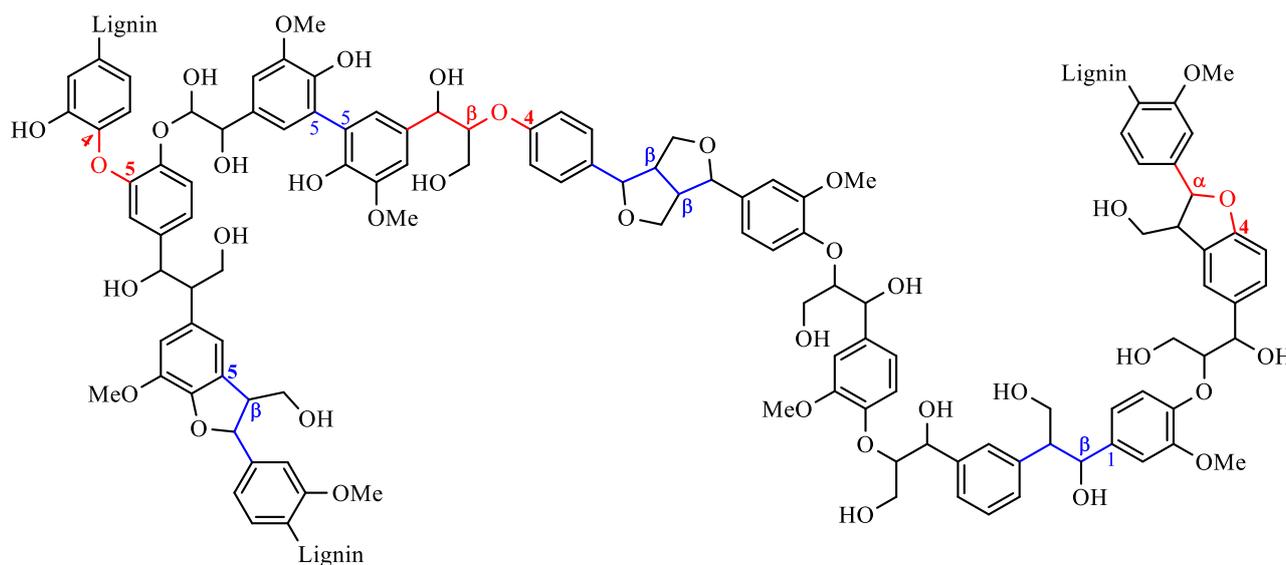
Greenhouse gas (GHG) emissions are increasing because of crude oil consumption, which is leading to global warming. Moreover, the case of global warming and our continuous dependence on fossil-based utility products are causing many environmental issues. Furthermore, fossil resources are limited and non-renewable. To avoid these limitations pertaining to crude-oil products, many renewable sources, such as solar, wind, tidal, and hydro, are being explored to generate electricity, yet only biomass is an alternative source for organic carbon-based fuel products (liquid, solid, gas), polymers, and chemical intermediates [1,2]. Various countries are initiating academia and industry collaboration to develop products from biomass. The biomass conversion is known to improve the economy of the country as well as the agri-sector, while also providing job opportunities, increasing the value of indigenous carbon, making countries self-reliant, and decreasing environmental pollution through complete utilization of agri-waste instead of incinerating it [3,4].

Biomass mainly consists of lignocellulosic materials, proteins, vegetable oils, and animal fats. Lignocellulosic biomass has gained interest in recent years due to favorable raw materials and the possibility of using it to make valuable products, such as fuels, chemicals, as well as energy through bio-refinery [5,6]. Generally, lignocellulosic biomass is 38–50% cellulose, 23–32% hemicellulose, and 15–25% lignin, and all together constitute about 80–90% of the total biomass. Lignin is a polymer that provides strength to the plant

body, with an irregular structure composed of three primary phenolic building blocks (coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol) connected through various linkages [7,8].

The core moiety of lignin is aromatic, i.e., benzene, which contains multiple functional groups including keto, aldo, methoxy, hydroxyl, carboxyl, phenyl, ester, and alkene, etc. [9]. Annually, 70 million tons of Kraft lignin is produced as a by-product in the pulp and paper industries, yet only a few companies are generating power from it and the utilization rate is low. However, the combustion of lignin to generate electricity and low-grade fuel is not very economically attractive [10,11]. Only *ca.* 2% of lignin obtained from pulp and paper industries is used to prepare specialty products. Lignin accounts for ~40% of the total energy density of lignocelluloses biomass, which is an attractive/alternative source in the preparation of transportation fuels [12]. Moreover, lignin is an alternative organic source for the preparation of epoxy resins, polymers, bisphenols, and phenolic resins, etc. [11,12].

Lignin consists of coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, usually denoting monolignols. The lignin bonds with C–C and C–O linkages including 46–60 wt.%  $\beta$ -O-4-Aryl ether, 6–8%  $\alpha$ -O-4-Aryl ether, 3.5–6.5% 4-O-5-Diaryl ether, 9–12%  $\beta$ -5-Phenylcoumaran, 4.5–11% 5-5-Biphenyl, 6–8%  $\beta$ -1-(1,2-Diaryl)propane, and 2–3%  $\beta$ -Resinol, etc. [13]. The general structure of the lignin is presented in Figure 1. Several lignin depolymerization methods have been reported and these are briefly discussed in the following sections.



**Figure 1.** Structure of the lignin.

Apart from the lignin depolymerization methods, pyrolysis is suitable for producing liquid fuels within a short reaction time [14]. Considering the techno-economics of lignin to liquid fuels conversion, the pyrolysis method is effective because it is an industry-related, large-scale process and does not require solvents. In fact, the solvent-based chemical process is costly, associated with solvent recovery operations, and leads to pollution, as compared to pyrolysis and gasification [15]. However, the pyrolysis of lignin is not a simple task since it produces a complex mixture, and it depends on the type of lignin and its construction composition [16].

Generally, biomass-derived pyrolysis oil has a high oxygen content (20–50 wt.%). The physicochemical properties and combustion performance of this oil differ from fossil-based crude oil. The lignin pyrolysis oil generally consists of phenols, methoxyphenols, methoxy-alkyl phenols, alkylbenzenes, and alkenyl aromatics, etc. The obtained biooil from simple pyrolysis (under inert atmosphere) is a low-grade fuel because it has high viscosity, low heating value, less stability, poor volatility, high water content, contains ash, and it is

corrosive. Therefore, the biooil is useful for combustion in industrial boilers, turbines, and engines. As such, pyrolysis biooil is not a standard transportation fuel to use in motor vehicles [17–20]. The biooil (derived from hydrolysis) has lower oxygen content and usually consists of non-oxygenated aromatic/alicyclic compounds, making them more suitable to use as a fuel. The hydrolysis and pyrolysis of lignin is discussed in the following sections.

## 2. Lignin Depolymerization Methods

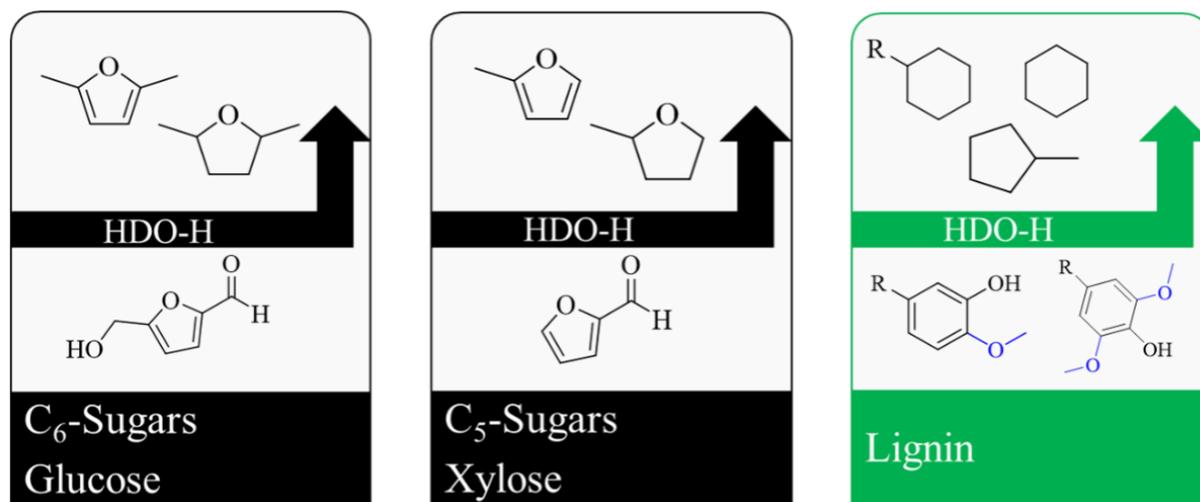
Methods such as hydrolysis, solvolysis, oxidative cleavage, pyrolysis, hydrolysis, and gasification are extensively reported for the depolymerization of lignin. Solid (polyaromatics), liquid (biooil, cyclic hydrocarbons), and gas (hydrogen, methane, carbon monoxide, and carbon dioxide) are generally formed during the depolymerization of lignin. The amount of biooil and its products selectivity depends on the depolymerization methods and its reaction conditions [21–23].

- (i). Lignin depolymerization in the presence of water medium at a suitable temperature (100–350 °C) is hydrolysis. The hydrolysis of lignin may occur using acid or base catalysts. Several acidic homogenous ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ , heteropoly acids, ionic liquids, etc.) and heterogeneous (acidic metal oxide, zeolites, acidic resins/clays, sulfonated carbon materials, etc.) catalysts were extensively reported for acid-catalyzed hydrolysis/depolymerization of lignin. Biphasic medium, water, along with organic solvent or supercritical fluids were also reported for better conversion of lignin. Phenol, alkylphenols, methoxyphenols, alkenylphenols, alkyl/methoxy-phenols, and alkenyl/methoxy-phenols are primarily observed during the lignin hydrolysis [24].
- (ii). Lignin depolymerization in the presence of a solvent or a mixture of solvents at suitable temperatures is known as solvolysis. The process minimizes the formation of char and usually forms low-oxygen-containing aromatic hydrocarbons. Several organic solvents such as alcohols (methanol, ethanol, propanol, iso-propanol), oxanes (dioxane), ketones (acetone), alkanes (dodecane), etc., and a mixture thereof with water were frequently used for lignin solvolysis. The supported metal (Pt, Ru, Rh, Pd, Ni, Mo, Cu, and Co) catalysts displayed good yields of biooil (80–95%) [25].
- (iii). Thermal decomposition at high temperatures (300–1000 °C) under an inert atmosphere is called pyrolysis. Lignin pyrolysis ended up with gases (hydrogen, methane, carbon monoxide, and carbon dioxide), liquids (oxygenated cyclic hydrocarbons, especially hydroxy, methoxy, and alkyl-substituted benzenes), condensable vapors, and solid char. The thermal decomposition at high temperatures under  $\text{H}_2$  atmosphere is known as hydrolysis. Several supported metal catalysts were reported for the hydrolysis of lignin and, within this, hydrogenation and hydrodeoxygenation reaction plays an important role in obtaining high yield of non-oxygenated aromatic compounds. Syringol and guaiacol type molecules (from hardwood), guaiacol type phenols (from softwood), and a mixture of phenol, guaiacol, and syringol type compounds (from herbaceous) were predominantly observed during the pyrolysis. The non-catalytic pyrolysis-derived concoction is associated with poor stability and undergoes repolymerization to produce sticky material. Thus, the catalytic pyrolysis process improves the yield of biooil, and catalytic depolymerization produces the most stable products where there is less possibility for repolymerization [26].
- (iv). Oxidative cleavage of lignin in the presence of oxidants is known as oxidative lignin depolymerization. Several oxidants, such as  $\text{O}_2$ ,  $\text{KMnO}_4$ ,  $\text{H}_2\text{O}_2$ , and peroxy acids, etc., were reported for this type of reaction. The oxidative cleavage of lignin generally produces oxygenated-aromatic hydrocarbons (hydroxyl, carbonyl, and carboxyl-substituted benzenes). The oxygen radical species, obtained from oxidants during the reaction, perform multiple cleavages of the lignin and this leads to the formation of several oxygenated aromatic compounds [24,27].

- (v). Gasification is usually referred to a process of oxygen-deficient thermal decomposition of carbonaceous substances such as coal, petroleum, or lignocellulosic biomass with a major objective of producing valuable gaseous products such as hydrogen or syngas. Lignin gasification provides an array of hydrocarbons (gas, liquid, and solid) depending upon on the gasification temperature. The C/O ratio of lignin is high as compared to lignocellulose and other biomass sources, and thus formation of solid/tar, i.e., high-molecular-weight condensable organic hydrocarbons, usually take place [28].

### 3. Lignocellulose-Based Emerging Biofuels

Biomass-based fuels such as bioethanol from cellulose/hemicellulose-derived carbohydrates and biodiesel from vegetable oils are commercially available in the market. Moreover, bioethanol and biodiesel research is in progress to improve the product quality by considering price and purity. In addition, many research institutes/universities are working on emerging biofuels from lignocellulose biomass, with two important classes (Figure 2): 1. Furanic fuels, namely 2,5-dimethylfuran, 2,5-dimethyltetrahydrofuran, 2-methylfuran, and 2-methyltetrahydrofuran, which can be synthesized from corresponding C<sub>6</sub>/C<sub>5</sub>-carbohydrates through dehydration (to produce furanic compounds) followed by hydrodeoxygenation/-hydrogenation [29,30]; and 2. cycloalkane biofuels, namely cyclohexane, alkylated cyclohexanes, and alkylated cyclopentanes, etc., preferably in the range of C<sub>6</sub>-C<sub>12</sub> [31]. The cycloalkane-based biofuels are generated from lignin-derived phenolic compounds by hydrodeoxygenation/-hydrogenation and hydrodeoxygenation of lignin. The cycloalkanes can be used directly as fuel or blended with conventional petrol. Cycloalkanes blended with conventional gasoline are associated with several advantages, including improvements in the density and volumetric heating, minimization of NO<sub>x</sub> emissions, and decrease in particle pollution [32,33]. Jet fuels (JP-8, Jet A, JP-5) generally consist of 30–50 wt.% cycloalkanes in their fuel composition [34]. The cyclic hydrocarbons have high industrial applications with values of 800–1000 USD/ton as compared with aliphatic fuel components (500–600 USD/ton) [35].



**Figure 2.** Hydrodeoxygenation/-hydrogenation (HDO-H) of lignocellulose-based functional molecules to emerging biofuels.

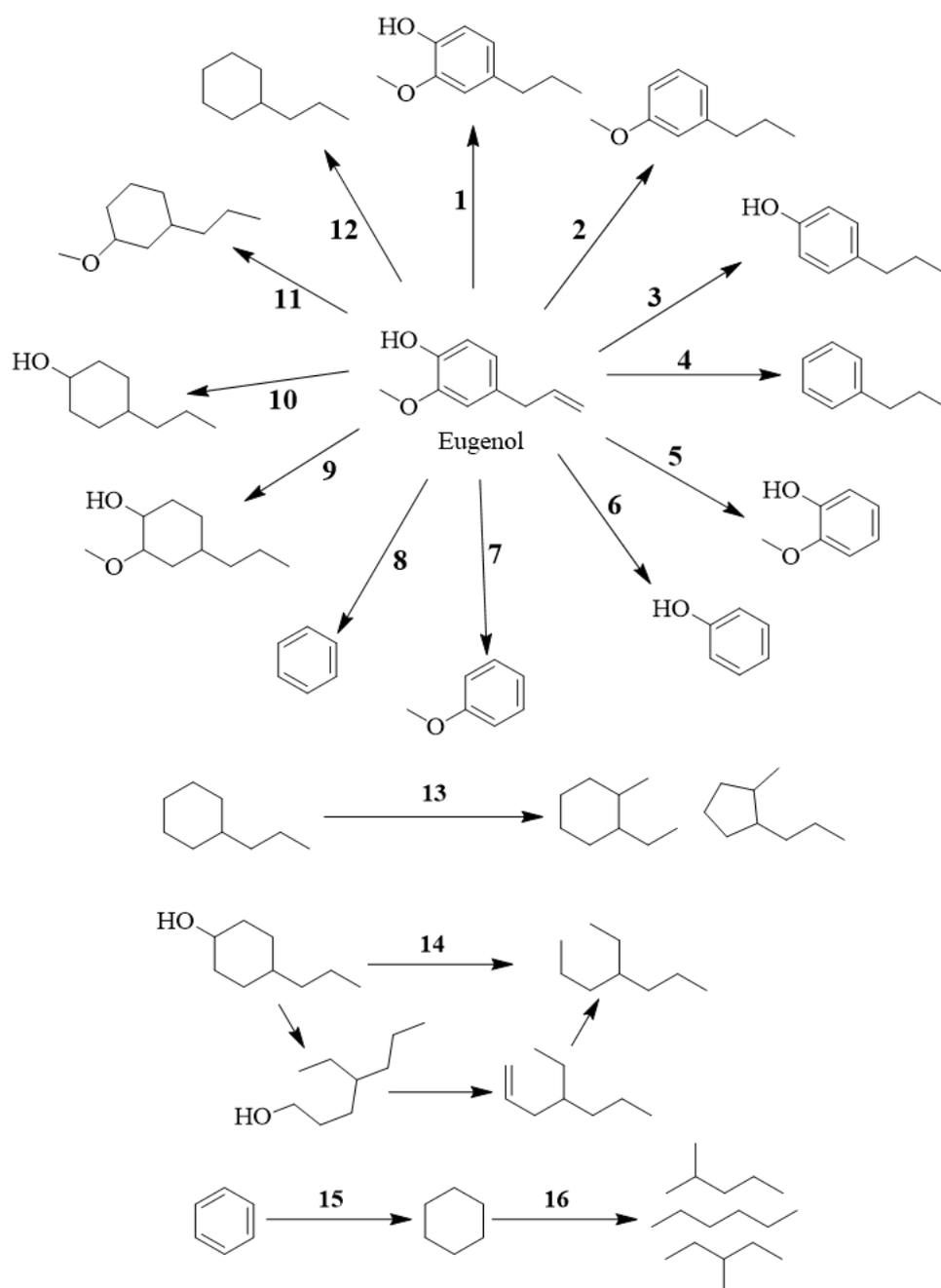
The lignin-derived vanillin is used in the flavoring, pharmaceutical, and food industries. The emerging sustainable aviation fuels consist of 20–30 wt.% aromatic compounds. The lower mononuclear aromatic compounds produce less soot compared with bi/tri nuclear aromatic compounds. The lignin-derived aromatic compounds consist of similar compositional properties to synthetic aromatic kerosene and are under study as per the guidelines of the ASTM International qualification process [36]. The ignition delay increases

with increasing alkyl chains in the aromatic ring [37]. The lignin-derived aromatic-rich biooil can replace the conventional furnace oil and can be burnt using suitably modified burners. In the food processing and textile industries, aromatic hydrocarbons can be used as a fuel for drying purposes. Biooil can be converted into higher quality transportation biofuel after up-gradation processes. The isolated aromatic hydrocarbons from lignin-derived concoctions can be used in fine chemical industries. Since biooil contains various chemical compounds, some of them are valuable. According to reports, bioadhesive and biopolymers can be synthesized from lignin-based aromatic hydrocarbons [36–38].

#### 4. Lignin Conversion in the Presence of H<sub>2</sub>

In an H<sub>2</sub> environment, the lignin and its related oxygenated aromatic compounds undergo many competitive reactions and form different products. The products vary depending on the reaction conditions and catalysts, for example, take eugenol (lignin model molecule), which can participate in different reactions and end-up with several products which are explained below (Figure 3):

- 1 Simple alkene chain double-bond hydrogenation to form *n*-propylguaiaicol; reaction conditions: Ni-based catalysts, 120–150 °C, 24–25 bar H<sub>2</sub> [39,40].
- 2 Alkene chain double hydrogenation, hydrodehydroxylation (hydrogenolysis of C–OH) to 1-methoxy-3-propylbenzene; reaction conditions: Ni-based catalysts, 120–150 °C, 24–25 bar H<sub>2</sub> [39,40].
- 3 Alkene chain double hydrogenation, hydrodemethoxylation (hydrogenolysis of C–OCH<sub>3</sub>) to 4-propylphenol; reaction conditions: Ni/SBA-15, 260 °C, 30 bar H<sub>2</sub> [41].
- 4 Alkene chain double hydrogenation, hydrodehydroxylation (hydrogenolysis of C–OH), hydrodemethoxylation (hydrogenolysis of C–OCH<sub>3</sub>) to propylbenzene; reaction conditions: Rh/Nb<sub>2</sub>O<sub>5</sub>, 260 °C, 5 bar H<sub>2</sub>; MoO<sub>x</sub>@NC, 450 °C, 1 bar H<sub>2</sub> [42,43].
- 5 Alkene chain double hydrogenation, hydrodealkylation (hydrogenolysis of C–C) to guaiaicol; reaction conditions: Pt/γ-Al<sub>2</sub>O<sub>3</sub>, 300 °C, H<sub>2</sub> [44].
- 6 Alkene chain double hydrogenation, hydrodealkylation (hydrogenolysis of C–C), hydrodemethoxylation (hydrogenolysis of C–OCH<sub>3</sub>) to phenol; reaction conditions: Pt/γ-Al<sub>2</sub>O<sub>3</sub>, 300 °C, H<sub>2</sub> [44].
- 7 Alkene chain double hydrogenation, hydrodealkylation (hydrogenolysis of C–C), hydrodehydroxylation (hydrogenolysis of C–OH) to anisole; reaction conditions: Pt/HY, 250 °C, 40 bar H<sub>2</sub> [45].
- 8 Alkene chain double hydrogenation, hydrodealkylation (hydrogenolysis of C–C), hydrodemethoxylation (hydrogenolysis of C–OCH<sub>3</sub>), hydrodehydroxylation (hydrogenolysis of C–OH) to benzene; reaction conditions: Ni/HZSM-5, 350 °C, 20 bar H<sub>2</sub> [46].
- 9 Alkene chain double hydrogenation, aromatic ring hydrogenation to 2-methoxy-4-propylcyclohexanol; reaction conditions: Pd/C, 250 °C, 30 bar H<sub>2</sub> [47].
- 10 Alkene chain double hydrogenation, aromatic ring hydrogenation, hydrodemethoxylation (hydrogenolysis of C–OCH<sub>3</sub>) to 4-propylcyclohexanol; reaction conditions: Co/TiO<sub>2</sub>, 200 °C, 10 bar H<sub>2</sub>; Ru-based catalysts, 160–200 °C, 10 mL/H<sub>2</sub> or 30 bar H<sub>2</sub> [48–50].
- 11 Alkene chain double hydrogenation, aromatic ring hydrogenation, hydrodehydroxylation (hydrogenolysis of C–OH) to 1-methoxy-3-propylcyclohexane; reaction conditions: Ni/MCM-4+HZSM-5, 200 °C, 50 bar H<sub>2</sub> [51].
- 12 Alkene chain double hydrogenation, aromatic ring hydrogenation, hydrodemethoxylation (hydrogenolysis of C–OCH<sub>3</sub>), hydrodehydroxylation (hydrogenolysis of C–OH) to propylcyclohexane; reaction conditions: Ru/CNT, 220 °C, 50 bar H<sub>2</sub> [52].



**Figure 3.** Reactions and related products from eugenol under  $H_2$  environment. Side reactions of formed hydrocarbons during hydrodeoxygenation-hydrogenation of lignin-derived aromatic compounds.

The formed cyclohexane-based hydrocarbons from lignin-derived aromatic compounds further undergo different side reactions such as isomerization, hydrogenolysis, and hydrocracking, etc. and form corresponding products that are mentioned in Figure 3.

- 1 Intra-molecular alkyl-transformation of propylcyclohexane produces methyl/ethyl/propyl-substituted cyclohexane/cyclopentane [53,54].
- 2 Propylcyclohexanol forms open-chain alkanes through C–C hydrogenolysis, dehydration followed by double-bond hydrogenation [55,56].
- 3 Non-oxygenated aromatic hydrocarbons form cycloalkanes by simple ring hydrogenation [57].
- 4 Ring opening of cycloalkanes by hydrocracking into open-chain alkanes [53].

## 5. Hydropyrolysis of Lignin into Cyclic Hydrocarbons

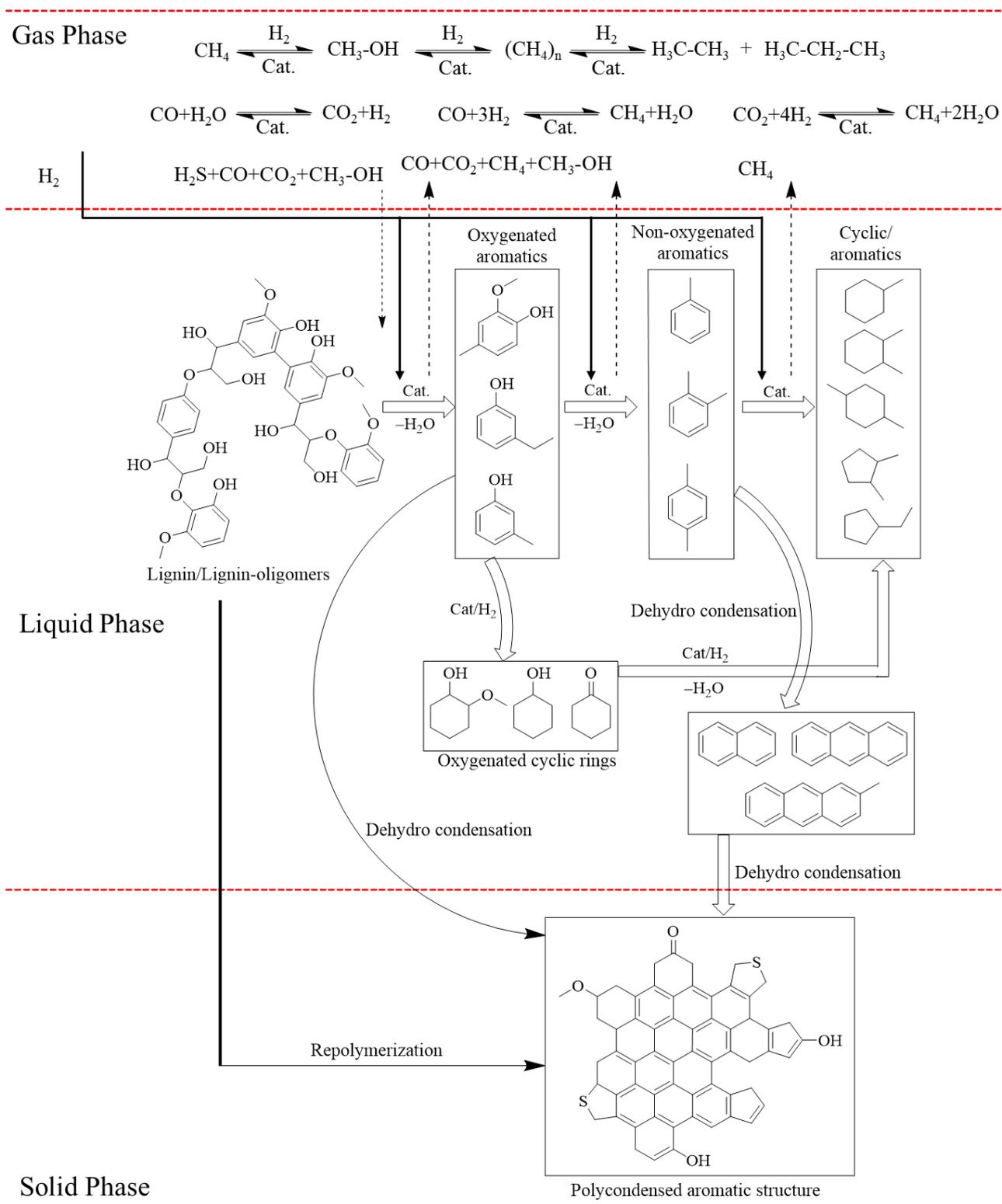
Various pre-treatments (before pyrolysis) improve the yield of biooil, which are discussed below [58].

- 1 Chemical treatment: a. dilute acid (HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>) treatment minimizes the ash content and removes the elements (Na, K, S, P, Si, Cl, Mg, Fe, Al, etc.); b. base treatment isolates the lignin from lignocellulose biomass and improves the quality of the oil. Moreover, chemical pre-treatment weakens the linkages in the lignocellulose biomass, which easily breaks down during pyrolysis and hydrodeoxygenation processes.
- 2 The physical treatment such as size reduction using milling or grinding of biomass usually provides a high yield of biooil. Also, heat and mass transfer are high in this case which leads to good cleavage capacity.
- 3 The pretreatment of biomass with the hydrothermal process using a Soxhlet extractor to remove the colorants, pectin, dust particles, and elements, etc., the treated biomass provide with good-quality and low-viscosity biooil.
- 4 Biological pretreatment is also one of the gateways to produce highly selective biooil; for example, the white-rot-fungus-treated biomass forms selectively aromatic hydrocarbons and suppresses the coke yield. In fact, the white-rot fungus has the capability to disconnect the refractory cell walls of lignocellulose.

The lignin hydropyrolysis experiments are generally carried out in Hastelloy or SS-made high-pressure and high-temperature static or continuous reactors. The reactor vessel is loaded with lignin and a catalyst. After that, the reactor is purged with inert gas (to remove the air) 2–3 times before pressurizing/feeding with a fixed amount of H<sub>2</sub>. Further, the hydropyrolysis is carried out at desirable temperatures and time duration. After completion of the reaction, the reactor is cooled to room temperature and then the excess H<sub>2</sub> is released. The gaseous product yield and its composition are determined by gas chromatography (GC) equipped with a TCD detector. The solid residue (unreacted lignin and catalyst) is separated from the biooil by centrifugation. Further, the catalyst is separated from the mixture of unreacted lignin and catalyst by calcinations; and the recovered catalyst is useful for the next reaction cycle. The obtained liquid products such as lignin oil (organic products) and H<sub>2</sub>O are separated by phase separation methods. The product concoction of biooil is identified via GC-MS, equipped with an FID detector. The degree of lignin depolymerization and the presence of low-molecular weight monomers/oligomers in the product mixture are analyzed by gel permeation chromatography (GPC). The elemental composition of the hydropyrolysis oil and unreacted lignin is calculated using CHNS analysis. The NMR analysis of liquid products provides information about chemical composition such as the presence of aromatic, aliphatic, and alicyclic moieties.

The thermal decomposition at high temperatures under an H<sub>2</sub> atmosphere is known as hydropyrolysis. The major product in the hydropyrolysis of lignin is biooil, which predominantly consists of non-oxygenated aromatic hydrocarbons and cycloalkanes. Several reactions are involved during the hydropyrolysis, such as hydrogenation, hydrodeoxygenation (hydrogenolysis), dehydration, isomerization, repolymerization, condensation, and dehydrocondensation, etc., and the resulting products are biooil (mixture of cyclic hydrocarbons), gases (CO, CO<sub>2</sub>, CH<sub>4</sub>, etc.), and solids (polyaromatics). The gas fraction consists of various gasses as mentioned above. The CO and CO<sub>2</sub> are formed via hydropyrolytic decomposition of the oxygenated molecular structure of lignin. The CH<sub>4</sub> is obtained from the thermal cleavage of O–CH<sub>3</sub> bonds [59]. The liquid fraction consists of diverse structural components, and it depends on the catalyst and reaction conditions. The light liquid portion is associated with monomeric cyclic hydrocarbons and the heavy liquid portion consists of bi- and tri-nuclear aromatic compounds such as naphthalene and anthracene, etc. Initially, under H<sub>2</sub>, the lignin is converted into phenolic and methoxylated phenolic compounds, which undergo further hydrodeoxygenation and form aromatic compounds which finally transform into cycloalkanes via the intermediates of any of these compounds: cyclohexanol, cyclohexanone, methoxy-cyclohexanol, and cyclohexene. The solid by-product is formed

by dehydro-condensation of mono-nuclear oxygenated/non-oxygenated aromatics and polynuclear aromatics [60,61]. The schematic representation of hydrolysis is mentioned in Figure 4.



Xie et al. reported catalytic pyrolysis of lignin using microwave irradiation using Co/ZSM-5 in an inert atmosphere. The catalyst improved the yield of biooil which consists of oxygenated aromatic compounds including furans, phenols, and methoxyphenols, etc. [18]. The acidity and water content of hydrolysis oil are lesser as compared to oil obtained through inert atmospheric pyrolysis. The inert atmospheric pyrolysis oil consists of more oxygenates such as alcohols and carboxylic acids, which could be a reason for the high acidity (pH = 2.8 to 4.5). Moreover, the hydrophilicity nature of oxygenates usually attracts the water, thus the oxygenated aromatics have a high moisture content [62]. The pyrolysis-derived oxygenated aromatic concoction has limited application scope in the industry [63]. Hydrolysis results in a high carbon ratio in the compounds by the removal of oxygen as H<sub>2</sub>O. The hydro-cleavage avoids the formation of free radicals and prevents polycondensation reactions [64]. The advantages of the hydrolysis of lignin are the selective hydro-cleavage of C–O–C and C–C linkages, and that it prevents repolymerization of monomeric compounds to polyaromatics. The biooil (obtained from hydrolysis) quantity and quality depend on many factors such as reaction temperature, H<sub>2</sub> pressure, reactor design (batch, grid type, microwave, pyroprobe, fluid bed, fluidized two-stage, etc.), reaction time, catalyst-to-lignin ratio, and the catalyst [65,66].

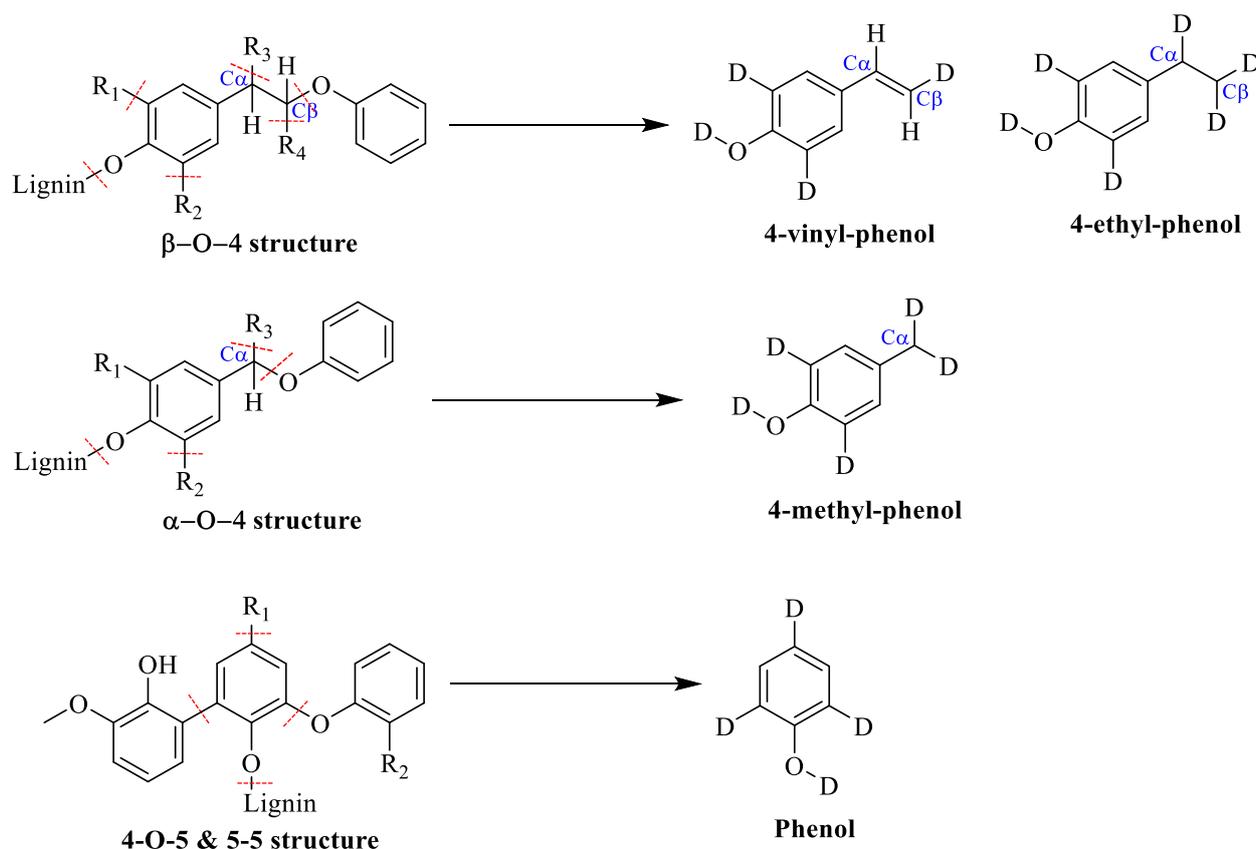
Resende et al. reported the effect of H<sub>2</sub> pressure and reaction temperature on the pyrolysis of biomass (rice husk) using an HZSM-5-based hierarchical catalyst. From this study, the authors revealed that: 1. pyrolysis under H<sub>2</sub> relatively increases the hydrocarbons and C<sub>1</sub>–C<sub>3</sub> gas yield, which suggests that the H<sub>2</sub> promotes hydrogenolysis and decarboxylation reactions; 2. increasing the H<sub>2</sub> pressure from 1 bar to 35 bar increases the yield of hydrocarbons up to 10% (39% to 49%) and decreases the coke yield which indicates that, H<sub>2</sub> pressure plays a key role in the hydrolysis reaction, and at high pressure, the hydro-cleavage ability is greater; 3. the reaction temperature is also a key factor for hydrolysis, with increased temperature from 300 °C to 400 °C increasing the hydrocarbon yield up to 11% (from 38 to 49), in fact, the moderate pyrolysis temperature (400–600 °C) show a better yield of cyclic/alicyclic hydrocarbons and further increment shows decomposition of these cyclic molecules which leads to the formation of chain hydrocarbons [67].

### 5.1. Non-Catalytic Hydrolysis of Lignin

In biorefinery, the pyrolysis process is used to maximize the yield of biooil from biomass. The non-catalytic biomass pyrolysis normally results in unstable hydrocarbons in poor yields [68]. Biswas et al. studied the non-catalytic pyrolysis of various biomass sources at 450 °C under the N<sub>2</sub>. The corn cob showed high yield (47%) of biooil which consists of various oxygenated aromatic compounds such as phenols, furfural, cresols, hydroxyphenols, methoxyphenols, and methoxybenzenes, etc. [69].

Wang's research group studied the non-catalytic hydrolysis of lignocellulose biomass (pinewood sawdust) using a single and two-stage reactor. High biooil yield, lower char yield, and inhibition of repolymerization were observed while using a two-stage reactor as compared to a single-stage reactor. The non-catalytic process resulted in a low biooil yield (15%), and it consists of benzene, toluene, xylenes, phenol, anthracene, naphthalene, indene, and alkyl-naphthalenes, etc. Around 15% biooil, 34% gases (CO<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>), 36% water, and 19% char were reported for the hydrolysis of pinewood sawdust at 700 °C and 50 bar H<sub>2</sub> [64].

Bai's research team studied the non-catalytic hydrolysis of lignin using sodium formate as a hydrogen source. This experiment increased the yield of smaller aromatic compounds such as phenols and alkylated phenols and decreased the yield of alkenyl-, aldo-, and keto-substituted aromatic compounds. The hydrolysis was tested with deuterated sodium formate instead of sodium formate to understand the cleavage of the bonds in the lignin (Scheme 1). The product distribution using deuterated sodium formate concluded that various bonds in the lignin, such as β-O-4, α-O-4, 4-O-5, and 5-5 were, hydro-cleaved to form corresponding products [70].



**Scheme 1.** Hydroropyolysis of lignin using sodium formate as a hydrogen source.

Wang's research group studied non-catalytic hydroropyolysis of lignin (extracted from Chinese fir) at high temperatures/pressures and compared the results with inert atmospheric (He) pyrolysis. At 20 bar  $H_2$  pressure with increased reaction temperature from 400 °C to 600 °C, the biooil yield increased (from 16% to 26%). Similarly, at a constant temperature (500 °C) with increasing  $H_2$  pressure from 10 to 20 bar, the authors observed an increased yield of biooil (from 11% to 22%). In comparison with inert atmospheric pyrolysis, hydroropyolysis showed a better yield of biooil. The gas ( $CO$ ,  $CO_2$ ,  $CH_4$ , ethylene, propane, propene, butene, etc.) amounts in hydroropyolysis were more comparable with inert atmospheric pyrolysis which indicates that the C–O and C–C bond cleavages (in the lignin) are greater in the hydroropyolysis process. Non-methoxylated aromatic products (18% out of 26% total yield) such as phenol, methylphenol, ethylphenol, propylphenol, 1,2-dihydroxybenzene, and 2-allyl-4-methylphenol, etc., were observed in the hydroropyolysis of lignin [71]. The Pienihäkkinen research group introduced hydroropyolysis of hydrolyzed lignin (by-product of the lignocellulosic to ethanol process) using ethanol as a hydrogen source without any catalyst at high temperature (500–600 °C). The ethanol-assisted pyrolysis yielded 42% biooil [72].

### 5.2. Catalytic Hydroropyolysis of Lignin

Catalytic pyrolysis improved the yield of biooil, the selectivity of specific products also increased and mostly resulted in mononuclear aromatic compounds. Moreover, the obtained biooil (hydrocarbons) from catalytic pyrolysis is more stable than the non-catalytic pyrolytic product concoction [70]. Three types of catalysts are primarily reported for the hydroropyolysis/hydrodeoxygenation of lignin to generate non-oxygenated aromatic compounds under the  $H_2$  environment, such as (i) supported metal catalysts; (ii) metal oxides; and (iii) metal sulfides/carbides/nitride/phosphide. The hydroropyolysis activity of the catalyst depends on the metal as well as the nature of the support (textile properties

and functional groups) [73]. The hydrolysis process biooil is generally better quality (less oxygen content) than biooil formed via inert atmospheric pyrolysis [74].

#### 5.2.1. Acid-catalyzed Hydrolysis of Lignin

Many solid acid catalysts were reported for the pyrolysis of lignin and lignocellulose biomass; however, only a few reports disclosed acid-catalyzed hydrolysis. Zeolitic catalysts were screened for pyrolysis and hydrolysis of lignin and important findings are described below and mentioned in the Table 1.

The Choi research group reported pyrolysis of poplar wood-derived lignin in an inert (He) atmosphere at 600 °C for 20 s using an HZSM-5 catalyst with Si/Al ratios (30–280). Various aromatic hydrocarbons, such as benzene, xylene, toluene, naphthalene, creosol, hydroxyl-substituted phenols, phenol, and methoxy/alkyl-substituted phenols, etc., were obtained as products during this reaction (Table 1, entry 1). The authors concluded that acidity of the catalyst is proportional to the aromatic hydrocarbon productivity; among the different screened Si/Al ratio (30–280) HZSM-5 catalysts, the HZSM-5 (Si/Al-30) showed high catalytic activity, high acidic sites, and the acidity of HZSM-5 (Si/Al-30) could be the reason behind it. The fatty acid impurity in the lignin was improved in the yield of aromatic hydrocarbons and this was confirmed by pyrolysis of *n*-hexadecanoic acid and octadecanoic acid and ended with a good yield of BTX (benzene, toluene, xylenes). Generally, the fatty acids under high temperatures form alkenes and are further converted into aromatic hydrocarbons via oligomerization and cyclization, followed by aromatization in the presence of an acid catalyst. The pyrolysis process was also investigated for several lignin-based aromatics (creosol, alkylcatechols, alkylsyringols, and vanillin) and those predominately yielded xylenes as the major product [12].

The Park research group demonstrated catalytic pyrolysis of Kraft lignin using a fixed bed two-stage reactor under an N<sub>2</sub> atmosphere at 500–600 °C. In the first reactor, lignin was converted into various phenolic compounds (methoxy phenols, catechols, and alkylphenols) with the help of a pre-mixed (in lignin) natural zeolite. In the second reactor, the pyrolyzates formed in the first reactor were converted into smaller aromatic hydrocarbons such as benzene, xylene, toluene, and alkylphenols using an HZSM-5 catalyst. The authors found that the two-stage catalytic pyrolysis (natural zeolite-HZSM-5) strategy produced less coke and a higher quality biooil as compared with independent (natural zeolite or HZSM-5) catalytic pyrolysis. A 30–35% yield of biooil was reported in the work using this dual catalytic/reactor setup (Table 1, entry 2) [68].

Ataíde et al. reported two acid catalysts, ZSM-5 and Nb<sub>2</sub>O<sub>5</sub>, for pyrolysis of Kraft lignin at 550 °C in the presence of H<sub>2</sub>. The ZSM-5 catalysts mainly consist of Brønsted acidic sites which initiated hydrodeoxygenation and aromatization to form a high quantity of aromatic hydrocarbons, especially xylenes and toluene. The Nb<sub>2</sub>O<sub>5</sub> has high acidity (Brønsted and Lewis) and participates in the hydrodeoxygenation and hydrogenation, followed by ring opening of cyclic compounds; thus, the catalytic system formed high selectivity for aliphatic hydrocarbons such as hexadecane, pentadecane, and tridecane, etc. [75,76].

Jing Bai's research group reported the effect of acid pretreatment of biomass (peanut shells) on biooil production. Towards pyrolysis, the HCl-pretreated peanut yielded 44% biooil and the acetic acid-treated one resulted in a 43% yield using a ZSM-5 catalyst. The products observed in this case are acids, ketones, anhydrosugars, esters, aldehydes, phenols, alcohols, and aromatics. The acid treatment of biomass weakens the bonds, which leads to easier cleavage of lignocellulose composition and reduced yield of char. Moreover, this work investigated the effect of pyrolysis temperature on the composition of biooil. When the temperature is increased from 450 °C to 600 °C, the researchers observed a high yield of aromatic hydrocarbons (50% from total yield) (Table 1, entry 3). Many reactions are involved in the transformation of aliphatic compounds (pyrolysis intermediates) to aromatics at high temperatures, for example, diels-alder, alkyl group transfer, alkylation, deoxygenation, condensation, and aromatization, etc. [20].

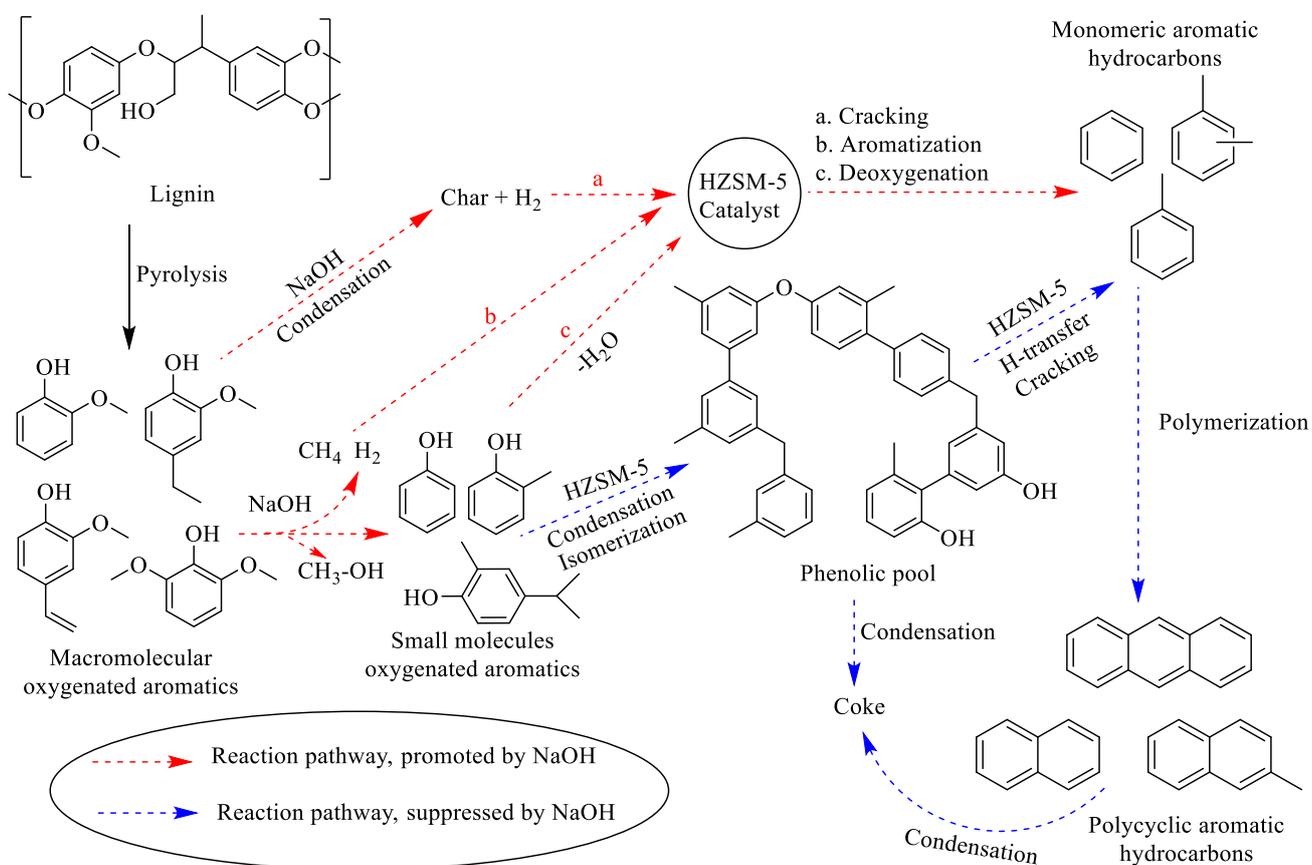
**Table 1.** Acid-catalyzed pyrolysis and hydropyrolysis of lignin.

S. No	Source	Catalyst	Reaction Conditions	Yield of Biooil(%)	Ref.
1	Poplar wood-derived lignin	HZSM-5 (Si/Al-30)	Pyrolysis at 600 °C, 20 s, He, catalyst to lignin ratio (2:1)	35.7 mg/g of aromatic hydrocarbon	[12]
2	Kraft lignin	1. Natural zeolite 2. HZSM-5	Pyrolysis in two stage-reactor 1. 500 °C, N <sub>2</sub> , catalyst to lignin ratio (1:1) 2. 600 °C, N <sub>2</sub>	30–35% of biooil with mixture of oxygenated and non-oxygenated aromatic compounds	[68]
3	Acid-treated lignin (derived from peanut shells)	HZSM-5	Pyrolysis at 600 °C, N <sub>2</sub> , catalyst to lignin (1:2)	43–45% of biooil (50% sel. of aromatic hydrocarbons)	[20]
4	Kraft lignin	HZSM-5	Pyrolysis at 600 °C, 10 min, N <sub>2</sub> , catalyst to lignin (1:1)	Yield of biooil is not reported but selectivity towards the methoxy/alkyl aromatics hydrocarbons (50% sel.)	[10]
5	Kraft lignin	HZSM-5	Hydropyrolysis at 450 °C, 10 bar H <sub>2</sub> for 60 min.	47% yield of biooil (50 wt.% of aromatic hydrocarbons)	[11]
6	Kraft lignin	HY and FeReOx/ZrO <sub>2</sub>	Hydropyrolysis (using HY) followed by hydrodeoxygenation (using FeReOx/ZrO <sub>2</sub> )	75% selectivity towards phenolic compounds	[77]

Huang et al. studied the effect of zeolite pore size and acidity on biooil yield (from lignin) at 600 °C under an N<sub>2</sub> atmosphere. They employed different zeolites (H-β, HY, and HZSM-5) by varying pore size and acidity to convert the Kraft lignin. Zeolites with an average pore size between 6.5 Å to 8.4 Å and moderate to strong acidity contribute to a high yield of biooil (Table 1, entry 4). Generally, the weak acidic sites initiate the breaking of alkyl chains and rearrangement of ether bonds, and the moderate to strong acidic sites promote deoxygenation through a dehydration reaction [10]. The addition of a base to the acid-catalyzed pyrolysis improved the selectivity of aromatic hydrocarbons by promoting the following reactions: a. hydro-cracking of char (formed during lignin disconnection); b. aromatization of CH<sub>4</sub> (formed during lignin hydrogenolysis (C–C and O–CH<sub>3</sub>)) in presence of H<sub>2</sub> [78]; and c. deoxygenation of lignin-derived oxygenated-aromatics by dehydration reaction [79]. The base enhances the in-situ H<sub>2</sub> supply and promotes the above-mentioned reactions, which reveals a high amount of non-oxygenated compounds. The reaction network of lignin pyrolysis, the effect of acid and base catalyst role, and related reaction products are mentioned in Scheme 2 [80].

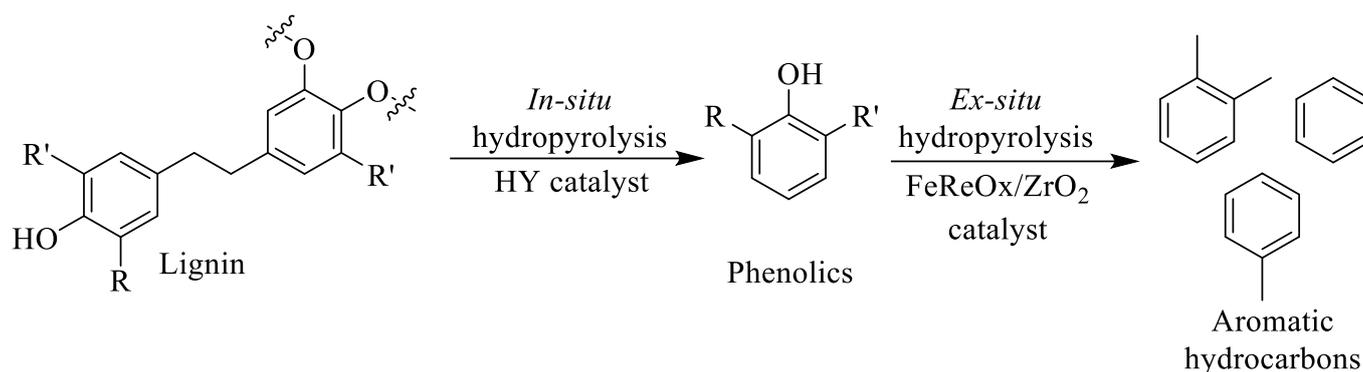
The Xu research group introduced hydropyrolysis of lignin using a pre-mixed ZSM-5 catalyst under a H<sub>2</sub> environment (10 bar H<sub>2</sub>) at 450 °C for 60 min. The authors observed changes in the yield of biooil by varying the method of pyrolysis, a 47% yield of biooil was reported using H<sub>2</sub> (hydropyrolysis) which is 5–7% more than the inert atmospheric pyrolysis under similar conditions (Table 1, entry 5). Moreover, the hydropyrolysis product mixture consists of high quantity of aromatic hydrocarbons (~50% of the total amount of biooil) preferably BTXs. The hydropyrolysis decreased the O/C ratio of oxygen-containing aromatic compounds, and the concoction of hydropyrolyzed oil (of lignin) showed a high heating value (38 MJ/Kg). The reusability of catalysts is important in catalytic pyrolysis reactions because the use of a high number of catalysts is generally required. If the catalyst is recycled/reusable, this ultimately decreases the final price of the biooil. This work investigated the reusability of the ZSM-5 catalyst, after the reaction, the catalyst was calcined at 700 °C and dried for 5 h (at 80 °C) to remove the biochar and unreacted lignin.

Interestingly, the pretreated ZSM-5 (calcined at 700 °C) catalyst showed similar catalytic activity for the second reaction cycle with a slight decrease in the yield of biooil [11].



**Scheme 2.** Reaction network of lignin pyrolysis using HZSM-5 catalyst and effect of NaOH.

The Park research group revealed in-situ catalytic hydropyrolysis of lignin followed by ex-situ catalytic hydrodeoxygenation (Scheme 3). This two-step strategy offered good selectivity for aromatic hydrocarbons. The in-situ hydropyrolysis of lignin using the HY zeolite catalyst showed high selectivity (75%) of phenols which were observed less selectivity (30%) in the case of non-catalytic hydropyrolysis (Table 1, entry 6). The char formation while using the HY catalyst is lesser because the acidic sites of the catalyst improved the decomposition of linkages in the lignin, which leads to high liquid product yield. The authors tested catalysts such as Fe/HBeta, FeReOx/MCM-41, Fe/ZrO<sub>2</sub> and FeReOx/ZrO<sub>2</sub> for hydrodeoxygenation-hydrogenation of pyrolyzates produced in the first step. Among the used catalysts, the FeReOx/ZrO<sub>2</sub> showed high selectivity towards aromatic hydrocarbons which could be due to the following reasons: 1. The oxophilicity of Iron metal in FeReOx/ZrO<sub>2</sub> catalyst consists of strong interaction with aromatic oxygenates which enhances the hydrodeoxygenation reaction; 2. The FeReOx/ZrO<sub>2</sub> catalyst has appropriate and balanced acidic sites (mild and strong) which lead to effective hydrodeoxygenation and dehydration to attain aromatic compounds; and 3. the phenolic monomers were trapped less in the case of ZrO<sub>2</sub> pores which could be the reason for the reduced coke formation as compared with other catalytic supports [77].



**Scheme 3.** In-situ and ex-situ catalytic hydropyrolysis to produce non-oxygenated aromatic hydrocarbons.

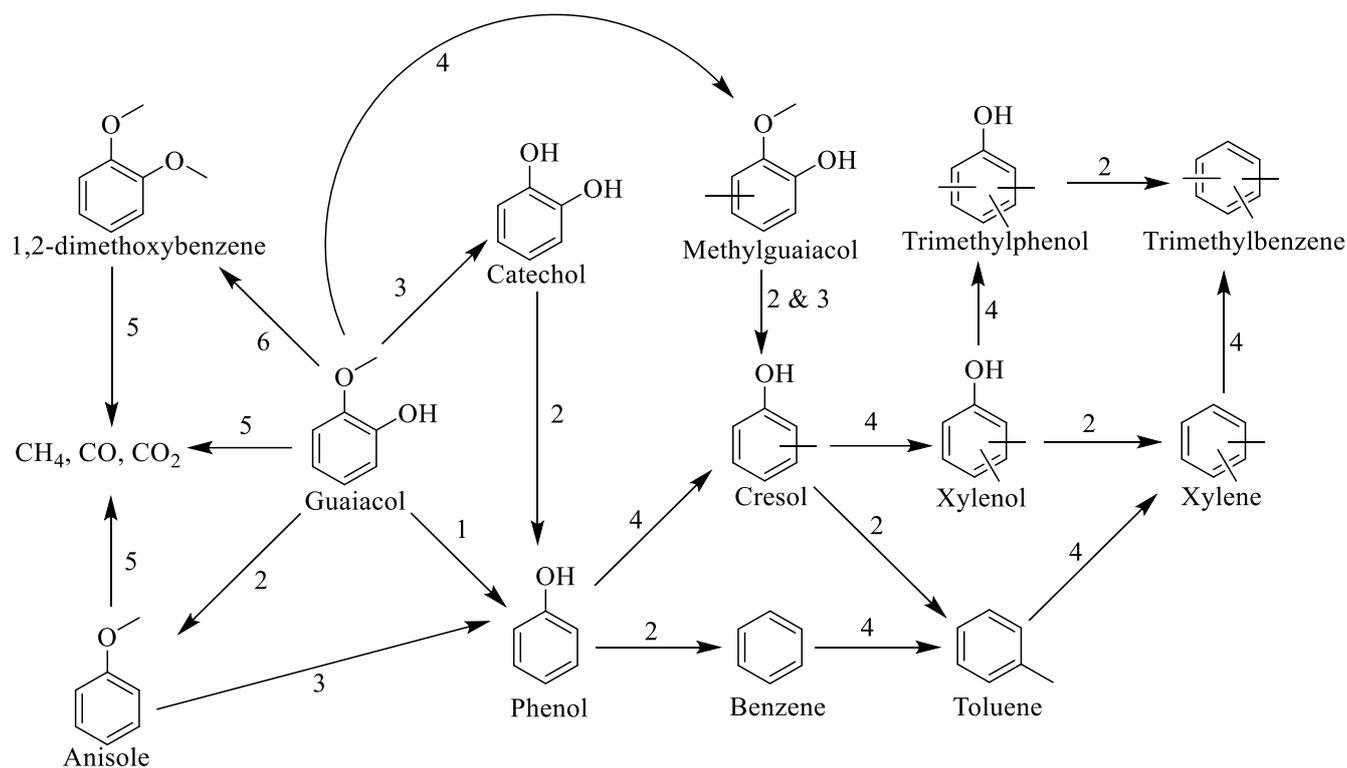
### 5.2.2. Supported Metal Catalyzed Hydropyrolysis of Lignin

Several metals (Pd, Ru, Fe, W, Ni, Mo, and Pt) and catalytic supports, for example, zeolites, activated carbon, and metal oxides, were frequently used for the hydropyrolysis. The supported metal catalytic system for the hydropyrolysis of various lignins is discussed below.

Meier et al. investigated different metal-supported catalysts for the hydropyrolysis of organocell and Kraft lignin in a batch and a semi-continuous reactor in the presence of  $H_2$ . For the blank experiment (without catalyst), they reported only a 15% yield of biooil, and the presence of catalysts Pd/C and Ni-Mo/aluminosilica resulted in 81% and 66% yields of biooil (Table 2, entry 1). The catalyst helps to dissociate various bonds in the lignin and promotes the production of smaller aromatic hydrocarbons. In this work, the effect of  $H_2$  pressure was also studied, a high yield (63%) of biooil was observed at 120 bar, and at 30 bar  $H_2$  the biooil yield was greatly reduced, only 18%. The Pd/C-catalyzed biooil mainly consists of substituted (methyl, ethyl, and propyl) cyclohexanones and Ni-Mo/aluminosilica-catalyzed hydropyrolysis oil contains monophenols such as catechols, phenols, and guaiacols [81,82].

Resende's research group studied the hydropyrolysis of lignin into aromatic/cycloalkanes-based hydrocarbons using HZSM-5 and Pd/HZSM-5 as catalysts at 650 °C and 17 bar  $H_2$ . Formation of 45% and 26% of aromatic hydrocarbons were reported using Pd/HZSM-5 and HZSM-5 under the above-mentioned reaction conditions and the catalyst-to-lignin ratio was 20:1 (Table 2, entry 2). Temperature plays an important role in the product distribution during the hydropyrolysis of lignin. The authors observed that at lower pyrolysis temperatures, i.e., 300 °C, the formation of cycloalkanes including cyclopentanes, alkylcyclopentanes, cyclohexane, and alkylcyclohexanes were observed, and at high temperatures (>400 °C) they did not observe cycloalkanes [83].

The Uemura research team reported Pd-Fe/Al-MCM-41 and Pd-Co/Al-MCM-41 catalysts for hydropyrolysis of lignin-derived biooil using a two-stage catalytic pyrolysis reactor at 400 °C, 1 bar  $H_2$  with 90 mL/min  $H_2$  flow rate. Authors observed that benzene as the main product of hydropyrolysis of methoxyphenols which is formed via two different paths such as: 1. through catechol and phenol intermediate while using Pd-Co/Al-MCM-41 catalyst; and 2. via an intermediary of phenol only, using the Pd-Fe catalyst. The bimetallic catalytic system (Pd-Co and Pd-Fe) catalyzed the hydrogenolysis of oxygenated aromatic compounds effectively to minimize the oxygen functionality. The reported bimetallic catalytic hydropyrolysis reduces the heavy oil content as compared with non-catalytic hydropyrolysis which is because of these catalysts, also initiates the cracking reaction to produce smaller molecules from large molecules (lignin-derived). In this work, the oxygen-free aromatic products such as benzene and mono/di-methyl benzenes were observed as major products from lignin-derived methoxyphenols, the synthetic protocol involves many reactions, including: 1. hydrodemethoxylation, 2. hydrodehydroxylation, 3. hydrodemethylation, 4. alkylation (methylation), 5. hydrocracking, and 6. etherification. The reaction network is mentioned in Scheme 4 [60].



**Scheme 4.** Reaction network of guaiacol hydrodeoxygenation over Pd-Fe and Pd-Co catalysts: 1. hydrodemethoxylation, 2. hydrodehydroxylation, 3. hydrodemethylation, 4. alkylation (methylation), 5. hydrocracking, and 6. etherification.

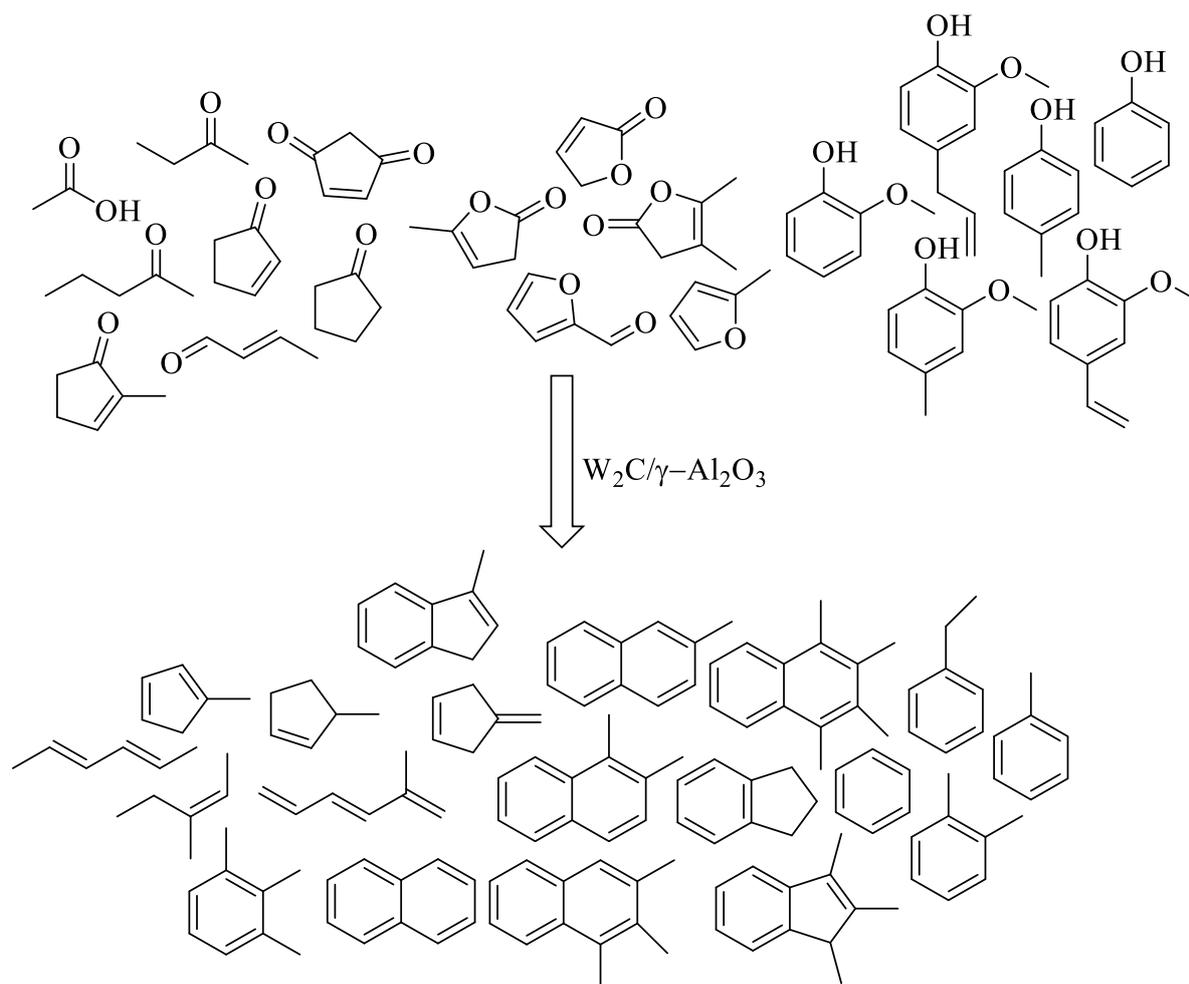
The Heeres research group investigated the hydroxyolysis of lignin and screened several catalysts for this conversion. The important findings of the different works, reported by Heeres research team are discussed below.

- I. Disclosed hydroxyolysis of pyrolytic lignin using Ru/C at 400 °C, 4 h, 100 bar H<sub>2</sub>, which resulted in high liquid product yield, i.e., 75%, of which monomeric compounds comprise 50% (Table 2, entry 3). Several products, including 18–20% phenolic compounds (phenol, cresols, methoxyphenols, alkylphenols), 14–15% aromatic hydrocarbons (benzene alkylbenzenes, xylenes, naphthalene, and methyl-naphthalene), and 6–7% cycloalkanes (cyclohexane, alkylcyclohexanes, alkylcyclopentanes), were identified as the major products in this work [35].
- II. Screened various catalysts (Ru/C, Ru/Al<sub>2</sub>O<sub>3</sub>, Ru/TiO<sub>2</sub>, Pd/C, Pd/Al<sub>2</sub>O<sub>3</sub>, Cu/ZrO<sub>2</sub>) for the hydrotreatment of Alcell lignin at 400 °C and 100 bar H<sub>2</sub>. From the studied catalysts, the Ru/TiO<sub>2</sub> showed a high yield of biooil (78%), comprising alkylphenolics (9 wt.%), aromatic hydrocarbons (2.5 wt.%), and hydroxyphenols (3.5 wt.%) (Table 2, entry 4) [84].
- III. Reported hydroxyolysis of Kraft lignin with NiMo and CoMo metallic catalysts on different supports: acidic (Al<sub>2</sub>O<sub>3</sub> and ZSM-5), neutral (activated carbon), and basic (MgO-La<sub>2</sub>O<sub>3</sub>). The hydroxyolysis was carried out at 350 °C, 100 bar H<sub>2</sub> for 4 h. The basic sulfide NiMo/MgO-La<sub>2</sub>O<sub>3</sub> catalyst showed high catalytic activity to obtain greater monomeric cyclic hydrocarbon yield (26 wt.%), consisting majorly of alkyl-phenolic compounds (Table 2, entry 5). The neutral activated carbon supported metal catalysts showed moderate conversion of lignin, and acidic supports (Al<sub>2</sub>O<sub>3</sub> and ZSM-5) were found to be less active in the conversion because in the presence of acidic support re-condensation between reaction intermediates is initiated, which results in the solid residue [15].

- IV. Low-priced catalysts, i.e., Limonite ( $(\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O})$ ), were investigated for the conversion of Kraft lignin at  $450\text{ }^\circ\text{C}$ , 100 bar  $\text{H}_2$  for 4 h. The catalyst resulted in  $\sim 34\%$  of low-molecular-weight aromatic hydrocarbons (phenol, alkylphenols and alkylbenzenes, alkylnaphthalenes, and alkyl anthracene) and a trace amount of cycloalkanes. The recycled Limonite catalyst (after the first run) was pre-treated at  $450\text{ }^\circ\text{C}$  and used for the second cycle, which showed a good yield of aromatic hydrocarbons with 25% yield. The authors concluded that Limonite is a cheap and potential catalyst for making bio-based phenolics and aromatics from lignin through the hydrodeoxygenation reaction [85].
- V. Investigated catalytic (Ru/C, CoMo/alumina, phosphided NiMo/C) hydrodeoxygenation of Kraft lignin in two-step hydrolysis, and as they observed a high yield of monomeric phenolic compounds (alkylphenols) as compared with single pyrolysis [86].
- VI. Reported several metal (Ni, Mo, W, NiMo, NiW) phosphide catalysts supported on activated carbon for the hydrolysis of Kraft lignin at  $400\text{--}500\text{ }^\circ\text{C}$ , 100 bar  $\text{H}_2$  for 4 h. The 10NiMoP/AC catalyst showed a 71% yield of biooil (with 100% mass balance) as compared with other catalysts. Moreover, the catalyst yielded (45.7 wt.%) high monomeric aromatic hydrocarbons such as alkylphenols and alkyl aromatics. The authors did not observe corresponding peaks of methoxy groups and C–O–C linkages of biooil (obtained via hydrotreating of the Kraft lignin using the NiMoP/AC catalyst), suggesting that common ether linkages were broken, leading to the formation of monomeric aromatic hydrocarbons [61].
- VII. Phosphided NiMo on different supports were reported for hydrolysis of lignin at  $400\text{ }^\circ\text{C}$ , 100 bar  $\text{H}_2$  for 2 h. The catalytic supports used in this work are activated carbon,  $\text{SiO}_2\text{-Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{MgO-Al}_2\text{O}_3$ , and  $\text{TiO}_2$ . Among them, the NiMoP supported on  $\text{SiO}_2$  produced a high yield (68%) of biooil, 52% monomeric compounds including 31% alkylphenols, 8% aliphatic compounds, and 5.7% aromatic compounds, etc. The  $\text{SiO}_2$  support consists of medium acidity which produced a higher yield than the basic ( $\text{MgO-Al}_2\text{O}_3$ ) and high-acid supports ( $\text{SiO}_2\text{-Al}_2\text{O}_3$ ). However, a reason behind the high activity of NiMoP/ $\text{SiO}_2$  is not reported [2].

Vinu et al. studied the fast pyrolysis of lignin under a  $\text{H}_2$  environment using  $\text{W}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$  at  $500\text{ }^\circ\text{C}$ . The  $\text{W}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$  catalyst showed good activity while using pinewood-derived lignin and resulted in 17% BTX, 18% alkyl benzenes, 15–17% naphthalene and alkylnaphthalenes, 7–8% alkylcyclopentanes & alkylcyclopentenes, 5% linear alkanes, 1–2% furanic compounds, and only trace amounts ( $<1\%$ ) of phenols and other oxygenates (Table 2, entry 9). The catalyst showed good catalytic activity for the hydrodeoxygenation of lignin-derived oxygenated aromatic compounds which yielded aromatic and alicyclic hydrocarbons with 90% selectivity (Figure 5) [87].

Wang's research group reported a bimetallic Ni<sub>x</sub>Mo/ZrO<sub>2</sub> catalyst for the hydrolysis of lignin (milled wood extracted from Chinese fir). The catalyst consisted of 26% condensable hydrocarbons (18–19% aromatics and 6% cycloalkanes) at  $400\text{ }^\circ\text{C}$  and atmospheric  $\text{H}_2$  pressure (Table 2, entry 10). The synergistic effect of Mo and Ni enhances the formation of non-oxygenated aromatic hydrocarbons. The Mo metal initiates the cleavage of methoxy moieties in the methoxyphenolics, and the Ni metal promotes the cleavage of hydroxyl moieties in the phenolic compounds and also initiates the hydrogenation of the benzene ring (Scheme 5). The combined properties of the bimetallic catalyst provided a good yield of monomeric non-oxygen-containing aromatic/alicyclic hydrocarbons [88].

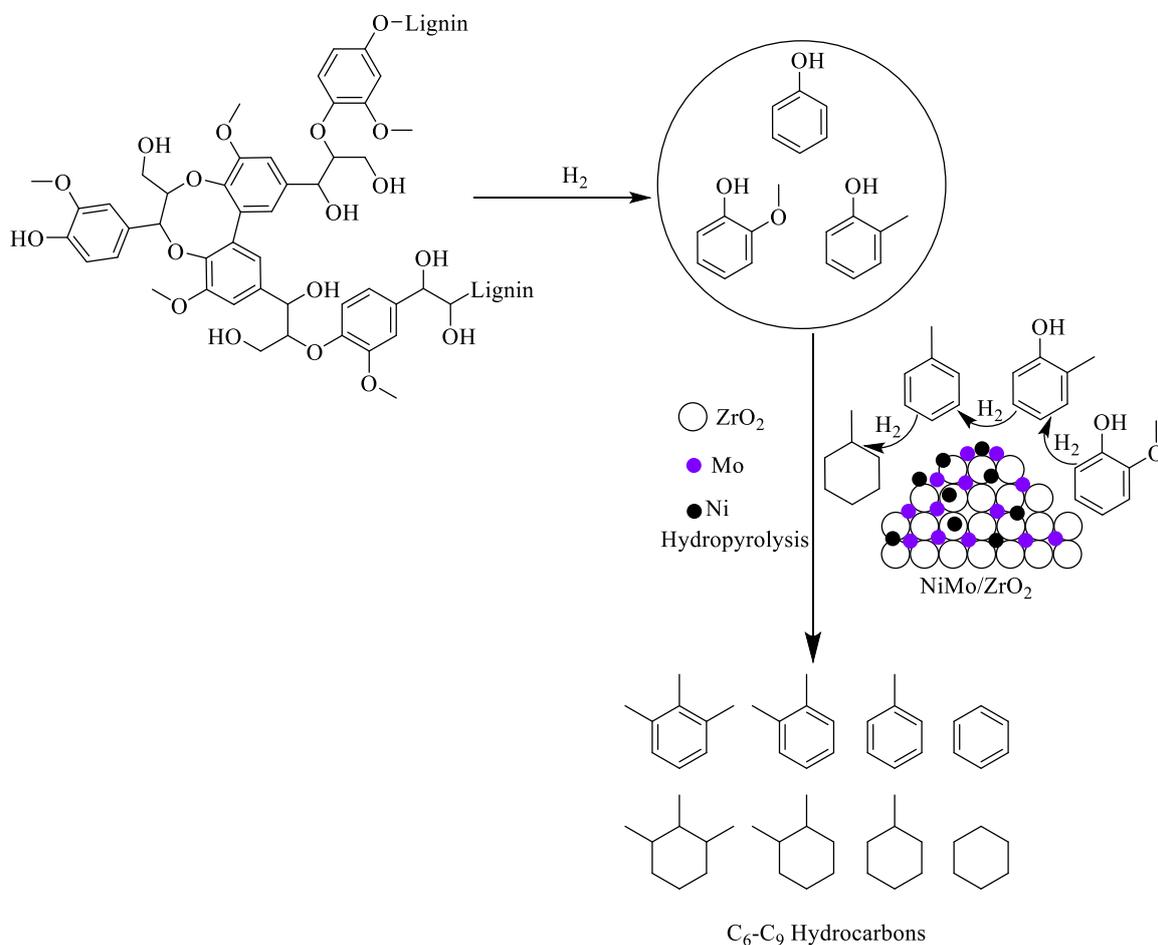


**Figure 5.** Hydroropyrolysis/hydrodeoxygenation of lignin-derived oxygenates using  $W_2C/g-Al_2O_3$ .

Sanna's research group studied the hydroropyrolysis of lignin using Fe, Ce, and Pd metal catalysts supported on  $ZrO_2$  at 600 °C and 1 bar  $H_2$ . The Fe/ $ZrO_2$  catalyst revealed better selectivity (65–67%) for non-oxygenated aromatic compounds (benzene, toluene, and xylene) as compared with other metal catalysts (Table 2, entry 11). The appropriate acidic/reduction sites in Fe/ $ZrO_2$  provide complete hydrodeoxygenation to remove methoxy and hydroxyl groups in the lignin which yields high selectivity of non-oxygenated cyclic hydrocarbons. Moreover, the oxophilicity character of Fe adsorbs the oxygenated aromatics, and the reactant molecules are therefore close to the active sites of the catalyst. The high reduction potential of Fe(0), good dispersion of Fe nanoparticles on the  $ZrO_2$ , mesoporosity and Lewis acid sites of the  $ZrO_2$  support are additional advantages of Fe/ $ZrO_2$  towards achieving high catalytic activity to remove oxygenates [89].

The Johansson research group investigated different pyrolysis methods for the conversion of lignin, such as non-catalyzed thermal pyrolysis, HZSM-5 catalyzed pyrolysis (under nitrogen atmosphere), and Pt/ $TiO_2$  catalyzed hydroropyrolysis (under hydrogen atmosphere) at 400 °C in a fixed-bed reactor. The non-catalyzed thermal pyrolysis provided a high yield of biooil; however, it consisted of many oxygenated aromatic compounds, ketones, carboxylic acids, alcohols, and methoxy groups, which were confirmed by NMR analysis. The HZSM-5 pyrolysis and Pt/ $TiO_2$  hydroropyrolysis resulted in a moderate yield of biooil (35–37%) (Table 2, entry 12). The oxygen content and carbon residue of the biooil obtained from thermal pyrolysis, HZSM-5 pyrolysis, and Pt/ $TiO_2$  hydroropyrolysis were 35, 26, and 12% *w/w* and 31, 23, and 6% *w/w*, respectively, indicating an efficient upgrading via Pt/ $TiO_2$  hydroropyrolysis. The authors concluded that the obtained biooil

from Pt/TiO<sub>2</sub>-catalyzed hydropyrolysis has good quality with low oxygen content and can possibly replace fossil-fuel-based gasoline [90].



**Scheme 5.** Catalytic hydropyrolysis of lignin over NiMo/ZrO<sub>2</sub>.

The Creaser research group screened Y zeolite, NiMo-supported Y zeolite, and physically mixed NiMo + Y zeolite catalysts for hydropyrolysis of Kraft lignin at 400 °C, 35 bar  $H_2$  for 5 h under batch reaction conditions. The non-catalytic hydropyrolysis showed 18% biooil yield and 47% solid residue, while using Y zeolite alone the biooil slightly increased to 21%, and solid residue decreased to 37%. The acidity of Y zeolite initiates dehydration, isomerization, and hydrocracking reactions, which leads to a good yield of biooil. Further screening of the NiMo-supported Y zeolite (NiMo/Y) showed a high yield of biooil (31%) and decreased amount of solid residue (27%) (Table 2, entry 13 and 14). The bifunctional (metallic sites and acidic sites) properties of the NiMo/Y catalyst are beneficial for high catalytic activity for hydropyrolysis. The metallic nature of the NiMo/Y catalyst could be the reason for the high hydrodeoxygenation activity as compared with Y zeolite. The authors claimed 61% selectivity of cyclic hydrocarbons (cycloalkanes and alkylbenzenes) using NiMo/Y, which was greater than that in the case of Y zeolite (30% selectivity) and non-catalytic (10% selectivity) pyrolysis [91].

Shi et al. investigated a two-stage reactor for the conversion of pine sawdust. In the first reactor, they simply conducted non-catalytic pyrolysis of lignin. The pyrolysis vapors of the first reactor enter the second reactor where the hydropyrolysis occurs. The authors disclosed NiMo/HZSM-5 catalyst for the hydropyrolysis step which showed a good yield (24 wt.% with respect to dried biomass) of biooil at 320 °C and 50 bar  $H_2$  (Table 2, entry 15). The hydropyrolysis oil consists of many monomeric compounds such as aromatic hydrocarbons, cyclohexanes, decalins, and cyclopentanes, etc. The three important sites (metallic,

acidic, and oxophilic) in the NiMo/HZSM-5 catalyst are the reason for the good catalytic activity for hydrolysis: 1. the acidic sites of the support promote pyrolysis oil yield by dehydration, isomerization, and hydrogenolysis reactions; 2. the oxophilic character of Mo<sup>+4</sup> interacts with oxygenated aromatic compounds, which are nearby Ni(0) sites; and 3. the metallic Ni(0) sites promote hydrodeoxygenation and hydrogenation [92].

**Table 2.** Supported metal-catalyzed hydrolysis of lignin.

S. No	Source	Catalyst	Reaction Conditions	Yield of Biooil (%)	Ref.
1	Kraft and Organosolv lignin	Pd/C and Ni-Mo/aluminosilica	Hydrolysis at 350–450 °C, 120 bar H <sub>2</sub>	81% (using Pd/C) and 66% (using Ni-Mo/aluminosilica) yield of biooil	[81,82]
2	Lignin derived from hybrid poplar	Pd/HZSM-5	Hydrolysis at 650 °C and 17 bar H <sub>2</sub> , catalyst-to-lignin ratio of 20:1	45% yield of aromatic hydrocarbons	[83]
3	Pyrolytic lignin	Ru/C	Hydrolysis at 400 °C, 100 bar H <sub>2</sub> for 4 h	75% yield of biooil (50 wt.% of monomeric compounds)	[35]
4	Alcelllignin	Ru/TiO <sub>2</sub>	Hydrolysis at 400 °C, 100 bar H <sub>2</sub> for 4 h	78% yield of biooil	[84]
5	Kraft lignin	NiMo/MgO-La <sub>2</sub> O <sub>3</sub>	Hydrolysis at 350 °C, 100 bar H <sub>2</sub> for 4 h	26% yield of monomeric cyclic hydrocarbon	[15]
6	Kraft lignin	Limonite (FeO(OH)·nH <sub>2</sub> O)	Hydrolysis at 450 °C, 100 bar H <sub>2</sub> for 4 h	34% yield of aromatic hydrocarbons	[85]
7	Kraft lignin	10NiMoP/AC	Hydrolysis at 400–500 °C, 100 bar H <sub>2</sub> for 4 h	71% yield of biooil	[61]
8	Kraft lignin	NiMoP/SiO <sub>2</sub>	Hydrolysis at 400 °C, 100 bar H <sub>2</sub> for 2 h	68% yield of biooil, (52% sel. of monomeric compounds and 31% sel. of alkylphenols)	[2]
9	Pinewood	W <sub>2</sub> C/γ-Al <sub>2</sub> O <sub>3</sub>	Hydrolysis at 500 °C, H <sub>2</sub> ambience for 30 s	17% BTX, 18% alkyl benzenes, 15–17% of naphthalenes	[87]
10	Lignin extracted from Chinese fir	NixMo/ZrO <sub>2</sub>	Hydrolysis at 400 °C under atmospheric H <sub>2</sub>	18–19% yield of aromatics and 6% cycloalkanes	[88]
11	Industrial (Etek) lignin	Fe/ZrO <sub>2</sub>	Hydrolysis at 400 °C under atmospheric H <sub>2</sub>	65–67% Sel. of non-oxygenated aromatics (BTX)	[89]
12	Stem wood	Pt/TiO <sub>2</sub>	Hydrolysis at 600 °C under H <sub>2</sub>	35–37% yield of biooil	[90]
13	Kraft lignin	Y zeolite	Hydrolysis at 400 °C, 35 bar H <sub>2</sub> for 5 h	21% yield of biooil	[91]
14	Kraft lignin	NiMo/Y zeolite	Hydrolysis at 400 °C, 35 bar H <sub>2</sub> for 5 h	31% yield of biooil	[91]
15	Pine sawdust	NiMo/HZSM-5	Hydrolysis at 320 °C and 50 bar H <sub>2</sub>	24 wt.% of yield w.r.t dried biomass	[92]

## 6. Key Observations of Lignin Hydrolysis

Hydrolysis is a suitable method to produce non-oxygenated cyclic hydrocarbons which have the potential to replace conventional gasoline through improved research in this area.

- Hydropyrolysis is an industry-relevant process, it does not require solvent/medium which leads to low operation costs, and it is techno-economically viable.
- Generally, the non-catalytic pyrolysis resulted in oxygenated aromatic compounds including alkenyl-, aldo-, keto-, and carboxy-substituted compounds.
- In the acid-catalyzed hydropyrolysis of lignin, the HZSM-5 showed good activity for the biooil, which consists of a mixture of compounds such as phenols, alkyl-phenols, methoxyphenols, and non-oxygenated aromatics.
- The addition of base to acid-catalyzed lignin hydropyrolysis improves the cleavage of methoxy groups in the methoxyphenolic compounds and reveals a high amount of non-oxygenated compounds. Moreover, the additional base suppressed the condensation/polymerization (in between formed monomeric aromatics during acid-catalyzed hydropyrolysis) reaction and avoids the solid/char/polyaromatics formation.
- The Pd/C catalyst showed a high yield of biooil (81%), consisting of alkyl-cyclohexanones as major components. However, the Pd-containing bimetallic catalysts such as Pd-Fe and Pd-Co catalysts showed a high quantity of non-oxygenated aromatics, predominantly benzene and alkyl benzenes.
- The Ru-based catalysts showed a high yield (75–78%) of biooil, consisting of alkyl/hydroxyl phenols, non-oxygenated aromatic compounds (alkyl-substituted benzenes, benzene, toluene, xylenes, naphthalenes), and cycloalkanes.
- The Ni-containing bimetallic catalysts extensively reported for hydropyrolysis of lignin and the catalytic system's synergetic effect play important roles. For example, in the Ni-Mo bimetallic catalytic system, the Mo metal initiates the cleavage of methoxy moieties in the methoxyphenolics, and the Ni metal promotes the cleavage of hydroxyl moieties in the phenolic compounds and also initiates the hydrogenation of the benzene ring. The combined properties of bimetallic catalyst provided a good yield of monomeric non-oxygen-containing aromatic/alicyclic hydrocarbons.
- The oxophilicity character of metal (for example, Mo and Fe) interacts with oxygenated aromatic compounds, which leads to the closer distance between the catalyst active sites and the oxygenated reactant. Thus, the strategy enhances the hydrodeoxygenation capacity of lignin-oxygenates.

## 7. Conclusions

Cyclic aromatic/alicyclic hydrocarbons may find important applications in the liquid transportation fuel sector. The cyclic hydrocarbons can be prepared from lignin by hydropyrolysis through hydrodeoxygenation and hydrogenation reactions. This review discussed the catalytic hydropyrolysis of lignin in the presence of H<sub>2</sub> as a hydrogen source. Multiple reactions are usually involved in the hydropyrolysis and produce several cyclic hydrocarbon concoctions, predominantly aromatic hydrocarbons. The lignin hydropyrolysis experiments are generally carried out in a Hastelloy (or) SS-made high-pressure and high-temperature static (or) continuous reactor. The obtained liquid products from the hydropyrolysis of lignin were analyzed by using various analytical tools including NMR, GC, GC-MS, GPC and CHNS.

The acid-catalyzed hydropyrolysis was conducted at 500–600 °C temperatures and yielded both oxygenated and non-oxygenated aromatic compounds with 40–50% selectivity. The HZSM-5 zeolite catalyst is extensively reported for acid-catalyzed lignin hydropyrolysis and plays a crucial role in this conversion, yielded a moderate to good amount of biooil. The addition of a base to the acid-catalyzed hydropyrolysis promotes high yield of aromatic hydrocarbons. The metal-supported catalytic hydropyrolysis reported at 300–450 °C temperatures and 1 bar H<sub>2</sub>–120 bar H<sub>2</sub> produced a high yield of non-oxygenated aromatic and alicyclic compounds such as benzene, toluene, xylenes, alkyl-benzenes, cyclohexanes, alkyl-cyclohexanes, cyclopentanes, and alkyl-cyclopentanes, etc. Several metals such as Ru, Pd, Cu, Co, Ni, Mo, and W were screened for lignin hydropyrolysis. However, the bimetallic catalyst consisting of Ni-Co was reported with the highest catalytic activity to obtain non-oxygenated cyclic compounds. The acidity and oxophilicity of the catalytic

supports were commonly reported for the metal-catalyzed lignin hydrolysis and can boost the catalytic activity of metals.

Only a few catalytic processes have been attempted thus far for the hydrolysis of lignin, but these are quite impressive and initiative. The lignin hydrolysis research is in the primary stage and there is a lot of scope for improving the process to produce cyclic hydrocarbons using different catalytic systems, especially supported metal catalysts. The design of suitable reactors and catalysts will play a key role in the lignin hydrolysis. According to the literature, the catalyst-to-lignin ratio is very high in lignin hydrolysis, thus recovery and recycling of the catalyst are very important, and are less studied. The techno-economics of the process and fuel efficiency of the obtained cyclic hydrocarbons have also been less investigated in the literature, which offer research scope for the future.

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