Biobased chemicals from lignin
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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2015

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Chapter 1

Introduction
1.1 INTRODUCTION

The prospects of declining crude oil reserves, a steady increase in energy demand and concerns for the environment have intensified the search for renewable sources for energy generation, transportation fuels, materials and chemicals. Renewable electric energy is already commercialized in the form of wind-, solar, tidal-, and geothermal energy. However, it is expected that the transportation sector can be electrified only partly and that renewable replacements for diesel, gasoline, and kerosene will still be carbon based alternatives and thus produced from biomass. Currently, the commercial first generation bio-fuels are made from food crops, well known examples are bio-ethanol (from e.g. sugar cane, sugar beet, and starch) and bio-diesel (from vegetable oils and waste cooking oils) [1]. Ethical concerns related to the use of edible food sources for bio-fuels have led to an intensification in research and development activities on the use of more sustainable resources, like lignocellulosic (woody) biomass. The latter has high potential as a feed for bioenergy, second generation bio-fuels, and bio-based chemicals and performance products due to its high abundance at relatively low costs [2-4].

Figure 1.1. Pie chart of the major components of lignocellulosic biomass.

The last decade, a major proportion of the research on lignocellulosic biomass has focused on the development of second generation biofuels. Recently, focus has shifted to biobased chemicals and particularly the replacement for existing petrochemical products. The use of lignocellulosic biomass for chemicals production is not new. Currently, about 10 % of the carbon based chemicals is already produced from biomass, examples are oleochemicals and starch/cellulose derived products. However, these are mainly high molecular weight performance products and not the typical low molecular weight bulk/base chemicals. Early examples of biobased bulk chemicals from lignocellulosic biomass are methanol, acetic acid, and ethyl acetate from wood by continuous distillation [5]. Several approaches have been proposed to produce
biobased chemicals from biomass. Often used approaches involves modification of the biopolymer like starch, cellulose, or proteins while keeping the biopolymer intact. Examples of these are starch modifications by for example carboxymethylation or oxidation to obtain high added value starch products. An alternative approach involves breaking down the bio-polymers to low molecular weight building blocks, also known as platform chemicals or biomass building blocks. These are subsequently converted to secondary products, intermediates and finally to end products for introduction in the market [2, 3].

1.2 PLATFORM CHEMICALS FROM LIGNOCELLULOSIC BIOMASS

1.2.3 Valorisation of cellulose and hemi-cellulose
The chemical composition of lignocellulosic biomass depends on the source material, but woody biomass (wood, straw, grass, nuts) usually consists of cellulose (35-50 wt%), hemi-cellulose (20-30 wt%), and lignin (10-25 wt%), see Figure 1.1 for details. Cellulose and hemi-cellulose are biopolymers consisting of sugar monomers. While cellulose contains primarily glucose monomers, hemi-cellulose consists of mainly pentose sugar monomers like xylose and arabinose. A large number of valorisation technologies has been developed for cellulose and hemi-cellulose to generate a wide range of biobases platform chemicals, see Figure 1.2. Examples are fermentation, (e.g. lactic acid, succinic acid) and chemo-catalytic processes (furfural, sorbitol) [3].

![Figure 1.2. Pathways for the production of chemicals from cellulose and hemi-cellulose](image-url)
1.2.2 Lignin

Lignin is the third largest bio-polymer found in lignocellulosic biomass. It has a rigid structure and gives the plant tissue strength and hydrophobicity. The lignin content varies between plant species; for instance the lignin content of softwood (e.g. pine, spruce) is about 28 %, whereas it is about 20 % for hardwood (e.g. oak, birch) [6].

![Figure 1.3. The three building blocks of lignin; coumaryl, coniferyl, and syringyl alcohol.](image)

From a chemical perspective, lignin is an amorphous polyphenolic thermoset which is made in the plant/tree by radical coupling of three aromatic monomers, namely, coniferyl, sinapyl, and p-coumaryl alcohols (Figure 1.3) [7]. A highly complex three-dimensional polymer is formed with different types of linkages between the aromatic nuclei. Of these, the β-O-4, α-O-4, β-5, and 5-5 are the most common, see Figure 1.4 for details.

![Figure 1.4. Structural model of spruce lignin (softwood) based on Adler et al. [13], with added percentage of several linkages in soft-& hardwood [14].](image)
The main linkages (~70%) in lignin are C-O-C ether bonds (β-O-4 and a smaller amount of α-O-4) with the remaining ones primarily consisting of C-C double bonds (5-5 and β-5). The high number of aromatic fragments in lignin makes it an excellent feedstock for the production of aromatic biobased chemicals, like benzene, toluene, xylene, and alkylphenolics. This is widely recognized now and the topic has attracted considerable interest by academia and industry [8-12]. The major producer of lignin is the paper industry with an estimated yearly production of 50 million tons worldwide, which is primarily used for steam and power production [15, 16]. Two important processes are used in the paper industry, namely Kraft and sulphite pulping [17]. During sulphite pulping, the lignin is depolymerised and sulphonate groups are introduced upon the treatment with various salts of sulphurous acid. Kraft pulping uses alkaline conditions (sodium sulphite) to solubilize the lignin.

Lignin may also be isolated by advanced lignocellulosic biomass pre-treatment techniques like steam explosion [18, 19], and organosolv processes. In the latter, the biomass source is treated with a mixture of an organic solvent (e.g. ethanol) and water under pressure to separate the lignin from the other biopolymers [20-22].

1.2.3 Valorisation of lignin
Lignin is an interesting renewable source for aromatic chemicals like benzene, toluene, xylene (also known as BTX), and phenolic compounds (see Figure 1.5). These are important base chemicals which are commercially applied as intermediates for a wide range of other derivatives like styrene, benzoic acid, cyclohexane, and isophthalic acid [2].

Figure 1.5. Examples of chemicals from lignin [2].
Another interesting class of chemicals from lignin are alkyl substituted phenolics. The parent compound phenol is globally produced at a level of about 8 Mt/y (2008) and is a widely used as a base chemical for the production of bisphenol-A, an important monomer for polycarbonate synthesis (48 %), phenolic resins e.g. phenol formaldehyde resins (25 %), cyclohexanone production (the feed for caprolactam production) (11 %), and for conversion to other base chemicals [23]. The production of renewable aromatic and phenolic compounds from lignin thus would have a beneficial effect on the carbon footprint of the petrochemical industry.

1.3 LIGNIN UPGRADING TECHNOLOGY

Lignin valorisation to low molecular weight aromatics and phenolics requires

Table 1.1. Bond dissociation enthalpies (BDE) for lignin linkages.

<table>
<thead>
<tr>
<th>Lignin compounds</th>
<th>BDE (KJ/mol)</th>
<th>Lignin compounds</th>
<th>BDE (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2.20 ±16&lt;sup&gt;b&lt;/sup&gt;</td>
<td>369 ±4&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>235 ±4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>398 ±4&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>263 ±4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>419 ±4&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>292 ±5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>427 ±4&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>281 ±1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>430 ±8&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>289 ±2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>435 ±4&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>332 ±7&lt;sup&gt;c&lt;/sup&gt;</td>
<td>463 ±4&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>334 ±4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>482 ±12&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>356 ±4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>488 ±12&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>358 ±4&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> BDE results from Benson [24], <sup>b</sup> Calculated BDE values from Parthasarathi et al. [25], <sup>c</sup> Calculated BDE values from Kim et al. [26].
depolymerisation of lignin. However, this is not sufficient, as the aromatic nuclei in lignin are heavily substituted, e.g. with at least a three carbon side chain with multiple substituents and additional methoxy- and hydroxyl groups. For aromatics production, full deoxygenation is required, for alkylphenolics methoxy group removal is essential. Lignin contains a large amount of ether bonds and thermodynamic calculations indicate that these bonds have the lowest bond dissociation energy. As such, they are in principle the most reactive of all bonds within the structure (Table 1.1). The main challenge is to cleave the remaining (up to 30 %) C-C linkages, which have a much higher bond dissociation energy.

Lignin conversions to low molecular weight compounds has been achieved by various (catalytic) methodologies (Figure 1.6) and can be classified according to process severity (pressure and temperature). Examples are lignin pyrolysis and catalytic versions thereof [8, 27], hydrothermal liquefaction in sub- or super critical water [28], and related versions in organic solvents in the absence or presence of catalysts (catalytic) solvolysis [29, 30]. Lignin conversion at milder conditions (< 300 °C) have also been developed, examples are enzymatic breakdown by enzymes (lignin peroxidase) [31, 32], oxidative depolymerisation [12, 33], and base catalysed depolymerisation [34, 35].

The focus of this thesis will be on lignin upgrading by catalytic hydrotreatment and catalytic solvolysis [9, 36]. Details will be discussed in the following sections.

Figure 1.6. Various thermochemical pathways and process parameters (P, T) for the depolymerisation of lignin [37]. Reproduced with permission.
1.4 CATALYTIC HYDROTREATMENT OF LIGNIN

Catalytic hydrotreatment is a process where a feed, here lignin, is reacted with hydrogen in the presence of a catalyst at elevated temperatures and pressures. Typical reaction temperatures are between 200 and 450 °C and hydrogen pressures between 50 and 250 bar. The hydrogen during the reaction can be supplied ex-situ by the addition of molecular hydrogen or formed in-situ by the use of hydrogen donating compounds (e.g. isopropanol or formic acid). Catalytic hydrotreatment of lignin aims for i) depolymerisation of the lignin to lower molecular weight fragments by cleavage of ether and C-C bonds, and ii) (partly) removal of bound oxygen for the production of phenolics and aromatics. A simplified reaction for the catalytic hydrotreatment of lignin to phenol is given in eq. 1.1.

\[
\text{C}_6\text{H}_{6.36}\text{O}_2 + 0.82 \text{H}_2 \rightarrow \text{C}_6\text{H}_6\text{O} + \text{H}_2\text{O} \quad (\text{eq. 1.1})
\]

The elemental composition of the lignin source given in eq 1.1 (C₆H₆.36O₂) is that of a typical technical lignin (Alcell lignin) and will be different for other types of lignin. Graphically, the catalytic hydrotreatment reaction can be represented in a van Krevelen plot [38]. Here, the molar oxygen/carbon ratio is shown on the y-axis and the hydrogen/carbon molar ratio on the x-axis. When aiming for alkylphenolics, the O/C ratio should be reduced by oxygen rejection, in the form of water or CO/CO₂. For aromatics, the O/C ratio should be reduced to zero.

Figure 1.7. van Krevelen plot with relevant products and the deoxygenation route for lignin, adapted from Kersten et al. with additional data from Schorr et al. [39, 40].

Various types of reactions may take place when performing the catalytic hydrotreatment of lignin, see Figure 1.8 for details. Examples are hydrogenation, hydrodeoxygenation, cracking, hydrocracking, decarbonylation and decarboxylation.
In addition, re-polymerization reactions of highly reactive intermediates, ultimately leading to char, may also occur to a certain extent and should be taken into consideration.

\[
\begin{align*}
\text{Cracking:} & \quad R_1 \overset{O}{\longrightarrow} R_2 \quad \rightarrow \quad R_1 \overset{H}{\longrightarrow} + \overset{O}{\longrightarrow} R_2 \\
\text{Decarboxylation:} & \quad \overset{O}{\longrightarrow} R_1 \quad \rightarrow \quad R_1 \overset{H}{\longrightarrow} + \overset{CO}{\longrightarrow} \\
\text{Decarboxylation:} & \quad \overset{O}{\longrightarrow} R_1 \overset{OH}{\longrightarrow} \quad \rightarrow \quad R_1 \overset{H}{\longrightarrow} + \overset{CO_2}{\longrightarrow} \\
\text{Hydrocracking:} & \quad R_1 \overset{R_2}{\longrightarrow} + \overset{R_2}{\longrightarrow} + \overset{H_2}{\longrightarrow} \rightarrow \quad R_1 \overset{R_2}{\longrightarrow} + \overset{H_3C}{\longrightarrow} \overset{R_2}{\longrightarrow} \\
\text{Hydrodeoxygenation:} & \quad R_1 \overset{OH}{\longrightarrow} + \overset{H_2}{\longrightarrow} \quad \rightarrow \quad R_1 \overset{H}{\longrightarrow} + \overset{H_2O}{\longrightarrow} \\
\text{Hydrogenation:} & \quad \overset{O}{\longrightarrow} R_1 \overset{H}{\longrightarrow} + \overset{H_2}{\longrightarrow} \rightarrow \quad R_1 \overset{OH}{\longrightarrow} \\
\text{Demethoxylation:} & \quad R_1 \overset{CH_3}{\longrightarrow} + \overset{H_2}{\longrightarrow} \rightarrow \quad R_1 \overset{H}{\longrightarrow} + \overset{CH_3OH}{\longrightarrow} \\
\text{Hydrogenolysis:} & \quad R_1 \overset{CH_3}{\longrightarrow} + \overset{H_2}{\longrightarrow} \rightarrow \quad R_1 \overset{OH}{\longrightarrow} + \overset{CH_4}{\longrightarrow}
\end{align*}
\]

Figure 1.8. Examples of reactions occurring during the catalytic hydrotreatment of lignin.

Studies on the catalytic hydrotreatment of lignin have been reported in the literature and will be reviewed in the following sections. A distinction is made between experimental studies in batch, mainly exploratory catalyst screening studies, and process studies in (semi)continuous set-ups. For batch studies, a distinction is made between studies using an external solvent and those in the absence of an external solvent, in the latter case, molten lignin and, in a later stage of the reaction, in combination with low molecular weight products, served as the solvent for the reaction. Model studies using molecular weight model components like anisole, phenol, or guaiacol will not be reviewed here, the reader is referred to recent reviews on this topic [9, 10].

1.4.1 Catalytic hydrotreatment of lignin in batch set-ups using an external solvent

An overview of relevant studies on the catalytic hydrotreatment of various lignin sources in batch set-ups using an external solvent is given in Table 1.2 (entries 1-10). Typical reaction conditions are relatively harsh, with temperatures between 175-450 °C, pressures between 20 and 220 bar, and reaction times between 0.25 and 18 h (typically 1-4 h). Various solvents have been explored with a wide range of polarity (from dodecane to water). Both noble metal based supported catalysts (Pd, Rh, Ru, Pt) as well as non-noble metal systems based on Ni (Ni on alumina and carbon, Raney Ni, NiMo on alumina), Cu (Cu on CrO), Co (CoMo on alumina) and Fe (Fe$_2$O$_3$, red mud) have been explored. In most studies, though not all, the product (oil) yield is reported. Detailed characterisation in terms of molecular composition is often not provided. In the following, the individual entries in Table 1.2 will be discussed briefly.
Table 1.2. State of the art for the catalytic hydrotreatment of lignins in batch set ups using molecular hydrogen.

<table>
<thead>
<tr>
<th>#</th>
<th>Feed</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>T (°C)</th>
<th>Time (h)</th>
<th>P (bar)</th>
<th>Liquid phase products</th>
<th>Oil (wt% on lignin intake)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethanol-benzene extracted Aspen lignin</td>
<td>Dioxane</td>
<td>Cu-CrO</td>
<td>260</td>
<td>18-22</td>
<td>220-400</td>
<td>Methanol (28% isolated yield) 4-n-propyclohexanol (isolated yield 11%) 4-n-propyclohexanediol-1,2 and 3-(4-hydroxy-cyclohexyl)-propanol (together 29%)</td>
<td>70, sum of fractions</td>
<td>[41]</td>
</tr>
<tr>
<td>2</td>
<td>Maple/Spruce wood lignin</td>
<td>Dioxane/Water 1:1 NaOH (3%)</td>
<td>Raney nickel</td>
<td>173</td>
<td>5-6</td>
<td>34-200</td>
<td>4-ethylguaiacol (2.16 wt% on lignin) 4-ethylsyringol (16.4 wt% on lignin) homo vanillyl alcohol (8.2 wt% on lignin) 4-ethylcy-clohexanol (1.87 wt% on lignin)</td>
<td>66</td>
<td>[42]</td>
</tr>
<tr>
<td>3</td>
<td>Organosolv Lignin</td>
<td>1-Methyl-naphthalene</td>
<td>Ni/Mo, CoMo/γ-Al₂O₃</td>
<td>404-428</td>
<td>1</td>
<td>70</td>
<td>Only combined phenolics yield reported, between 0-10 wt% on lignin. Main products are phenol and cresols</td>
<td>n.d.</td>
<td>[43]</td>
</tr>
<tr>
<td>4</td>
<td>Rye Straw Lignin</td>
<td>Tetralin</td>
<td>Red Mud (S), CoMo/γ-Al₂O₃</td>
<td>400</td>
<td>4</td>
<td>150</td>
<td>10% of phenol on carbon basis, Gasoline (16.2%) and heavy oil fraction (37.9) after distillative work-up</td>
<td>75-78 (sum of the liquid fractions, C-based)</td>
<td>[44]</td>
</tr>
<tr>
<td>5</td>
<td>Spruce lignin</td>
<td>Dioxane/ water (1:1)</td>
<td>Pd, Rh, Ru/C, Ru/Ru/Al₂O₃</td>
<td>195</td>
<td>5</td>
<td>35</td>
<td>Phenolic compounds like, phenol, guaiacol, 4-methyl-guaiacol, ethylguaiacol, 4-n-propylguaiacol, dihydroconiferyl alcohol.</td>
<td>16-25 (Chloroform soluble product)</td>
<td>[45, 46]</td>
</tr>
<tr>
<td>6</td>
<td>White birch lignin</td>
<td>Water, dioxane (1%) H₃PO₄</td>
<td>Ru,Pd,Rh,Pt/C</td>
<td>200</td>
<td>4</td>
<td>40</td>
<td>Monomeric and dimer fraction. Monomeric fraction consist of guaiacylpropane (0.6-9.9 wt%), guaiacylpropanol (0.5-5.3 wt%), syringylpropanol (1.1-3.48 wt%), and syringylglycol (0.2-15.7 wt%)</td>
<td>-</td>
<td>[47]</td>
</tr>
<tr>
<td>7</td>
<td>Pyrolytic Alcell lignin oil</td>
<td>Dodecane</td>
<td>Ru/C</td>
<td>350</td>
<td>1</td>
<td>100</td>
<td>Cyclocalkanes, alkylated cyclohexanols, linear/branched alkanes</td>
<td>-</td>
<td>[27]</td>
</tr>
<tr>
<td>8</td>
<td>Organosolv Cornstalk lignin</td>
<td>65% vol Ethanol/Water</td>
<td>Ru/C, Pt/C, Ru/C/Pd/C</td>
<td>225-300</td>
<td>0.5-3</td>
<td>20</td>
<td>Main identified products: 4-ethylenol (3.1 wt% ethylphenol and 1.3 wt% 4-ethylphenol on lignin intake)</td>
<td>Liquid yield of up to 76%</td>
<td>[48, 49]</td>
</tr>
<tr>
<td>9</td>
<td>Alkali lignin</td>
<td>1:1 Ethanol/Water, and pure ethanol</td>
<td>Ru/Al₂O₃,Pt/C, Ru/C, Ni/Al₂O₃, Ni/C</td>
<td>200-450</td>
<td>0.25-6</td>
<td>50</td>
<td>Products identified but not quantified on the basis of lignin intake. Major components based on GC area for ethanol/water: diethyl-phenol, 2-ethyl-5-propy-phenol, hexanoic acid, 3-methyl penta-noic acid</td>
<td>Liquid product yields for ethanol/water: between 52 and 89</td>
<td>[50]</td>
</tr>
<tr>
<td>10</td>
<td>Organosolv lignin</td>
<td>1:1 Ethanol/water and pure ethanol</td>
<td>Ru/Al₂O₃, Ni/C</td>
<td>300-350</td>
<td>2</td>
<td>50</td>
<td>No detailed product composition reported</td>
<td>Liquid product yields for ethanol/water between 66 and 92</td>
<td>[51]</td>
</tr>
<tr>
<td>11</td>
<td>Multiple lignin sources</td>
<td>none</td>
<td>Fe,Oₓ, Raney Nickel, Pd/C</td>
<td>350-450</td>
<td>0-2</td>
<td>30-120</td>
<td>Products identified with GC and mainly phenols, guaiacols, substituted cyclohexanes</td>
<td>Liquid product yield between 15-66</td>
<td>[52]</td>
</tr>
<tr>
<td>12</td>
<td>Multiple lignin sources</td>
<td>none</td>
<td>Ni/Mo on AIS, zeolites, Cr₂O₃ on Al₂O₃, and mixtures thereof (S) and non-(S) form</td>
<td>395-430</td>
<td>20-60</td>
<td>90-100</td>
<td>Monocyclic aromatics: 6.1-10.8 wt% on lignin Phenols: 4.7-9.4 wt% on lignin Polycyclic aromatics: 1.3-2.2 wt% on lignin</td>
<td>Liquid product yield between 49-63</td>
<td>[53]</td>
</tr>
</tbody>
</table>

n.d. = not determined.
Early reports on the catalytic hydrotreatment of lignin involve the use of CuCrO as the catalyst (Table 1.2 entry 1) [41]. Experiments were performed at 260 °C with 220 bar of initial hydrogen pressure at room temperature (up to 400 bar at reaction temperature) with reaction times up to 22 h in dioxane (Scheme 1.1). After reaction, the products were distilled in fractions and analysed (melting- and boiling point and elemental analysis). The main compounds found in the lower boiling fractions were 4-propylcyclohexanol and 4-propylcyclohexandiol-1,2 (11 wt% on lignin), two type of glycols (28 wt% on lignin), and methanol (27 wt% on lignin). Higher boiling point fractions (33 wt% on lignin) were first dehydrated over alumina at 400 °C and further hydrogenated with Raney nickel (200 °C, 3 h, 300 bar hydrogen) to give a mixture primarily consisting of hydrocarbons (CₙH₂ₙ₋₂, CₙH₂ₙ₋₄) (6-8 wt% on lignin).

Scheme 1.1.

In 1948, Pepper et al. reported the use of Raney nickel as catalyst for the hydrotreatment of organosolv maple lignin in dioxane-water solutions (1:1) containing NaOH (3 %) [42], see Table 1.2 entry 2 and Scheme 1.2. The reactions conditions were relatively mild (173 °C, 206 bar of initial H₂ pressure, 6 h) and led to the complete conversion of the lignin. Main identifiable compounds were 4-ethylguaiacol (2.2 wt% on lignin), 4-ethylsyringol (15.4 wt% on lignin), and homovanillyl alcohol (6.2 wt%). Compounds were identified by boiling- and melting points.

Scheme 1.2.

In 1988, typical hydrodesulphurisation (HDS) catalysts like sulphided NiMo and CoMo on alumina were applied for organosolv lignin hydrotreatment in 1-methylnapthalene (1:2 ratio) [43], see Table 1.2 entry 3. Best results regarding total phenolic yields were achieved with sulphided CoMo/Al₂O₃ catalyst at 404 °C, 69 bar of H₂ at start of the experiment, and a reaction time of 1 h. The reported combined phenolic yield was
10.0 wt% on lignin when using a continuous flow of hydrogen, the main product being phenol (30 %) and cresols (40 % on total phenolics).

\[ \text{Organosolv lignin} \xrightarrow{1\text{-Methylnapthalene 1:2}} \text{Phenol + Cresols} \]

\[
\begin{align*}
\begin{array}{c}
\text{OH} \\
\text{OH}
\end{array}
& \\
\text{Phenol} & \text{Cresols}
\end{align*}
\]

\[ \text{Organosolv lignin} \xrightarrow{1\text{-Methylnapthalene 1:2}} \text{Phenol + Cresols} \]

\[
\begin{align*}
\begin{array}{c}
\text{OH} \\
\text{OH}
\end{array}
& \\
\text{Phenol} & \text{Cresols}
\end{align*}
\]

Scheme 1.3.

Klopries et al. (Table 1.2 entry 4) explored the conversion of rye straw lignin with sulphided red mud and sulphided CoMo with tetraline as the solvent [44], see Scheme 1.4. After reaction, the oil phase was collected, washed with water to isolate phenolic content and subsequently fractionated using distillation. The best results regarding product yields were achieved with sulphided red mud at 400 °C, with an initial pressure of 150 bar H₂ for 4 h reaction time. This resulted in 19.1 % carbon conversion to permanent gases, 16.2 % to a gasoline distillate fraction, 21.3 % of phenol, 37.9 % of a heavy oil fraction, and 5.5 % of char. It is not clear whether phenol is isolated or if this fraction consist of a mixture of phenolics.

\[
\begin{array}{l}
\text{Rye straw} \\
\text{lignin} \\
\text{Tetraline} \\
\text{Red mud (S),} \\
\text{Gasoline} \\
\text{Phenol} \\
\text{Heavy oil} \\
\text{Char}
\end{array}
\]

\[
\begin{align*}
\text{Tetraline} & \quad \text{400 °C, 150 bar H₂, 4 h} \\
\text{Gasoline} & \quad 16.2 \text{ C}\% \\
\text{Phenol} & \quad 21.3 \text{ C}\% \\
\text{Heavy oil} & \quad 37.9 \text{ C}\% \\
\text{Char} & \quad 5.5 \text{ C}\%
\end{align*}
\]

Scheme 1.4.

In the late 1960’s, noble metal catalyst like palladium, platinum, rhodium, and ruthenium were introduced for the catalytic hydrotreatment of lignin. Pepper et al. reported the use of noble metal catalyst like Pd, Rh, and Ru on carbon or alumina for the hydrotreatment of extracted spruce lignin in a dioxane/water 1:1 solution [45, 46], see Table 1.2 entry 5. The most interesting catalyst was Rh/C which gave the largest amount of a chloroform soluble fraction (~23-26 wt%). The main compounds detected after an diethylether extraction were 4-\textit{n}-propylguaiacol and dihydroconiferylalcohol (Scheme 1.5, GC-FID).

\[
\begin{array}{c}
\text{Extracted spruce} \\
\text{lignin} \\
\text{Dioxane/water 1:1} \\
\text{Raney Ni, Rh/C,} \\
\text{Rh/Al₂O₃, Pd/C} \\
\text{Gasoline} \\
\text{Phenol} \\
\text{Heavy oil} \\
\text{Char}
\end{array}
\]

\[
\begin{align*}
\text{Dioxane/water 1:1} & \quad 195 °C, 35 \text{ bar H₂, 5 h} \\
\text{Gasoline} & \quad 16.2 \text{ C}\% \\
\text{Phenol} & \quad 21.3 \text{ C}\% \\
\text{Heavy oil} & \quad 37.9 \text{ C}\% \\
\text{Char} & \quad 5.5 \text{ C}\%
\end{align*}
\]

Scheme 1.5.
The catalytic hydrotreatment of ethanol-benzene extracted birch wood lignin using Ru/C, Pd/C, Rh/C, and Pt/C was investigated by Yan et al. [47], see Table 1.2 entry 6. Reactions were performed in water, either pure or in combination with phosphoric acid (1 %) and/or dioxane (1:1 v/v), at 40 bar of initial H$_2$, at 200 °C, for 4 h. After reaction, the suspension was filtered and the liquid phase was analysed by GC and GC-MS. The emphasis was on the quantification of the individual components in the monomer and dimer fraction. Highest amounts of the monomer fraction were found for Pt/C (46.4 wt% on lignin) using dioxane/water/phosphoric acid as the solvent. The main components were 4-propylsyringol, 4-propylnuaiacol, dihydroconiferylalcohol and syringylpropanol, see Scheme 1.6 for details.

![Scheme 1.6.](image)

The catalytic hydrotreatment of a lignin pyrolysis oil obtained by fast pyrolysis of Alcell lignin was explored with Ru/C in dodecane as the solvent at 350 °C with 100 bar H$_2$ for 1 h [27], see Table 1.2 entry 7. The main components in the feed, syringols (3.3 wt%), methoxybenzenes (5.7 wt%), alkylated phenolics (7.0 wt%) were hydro(-deoxy) genated to alkylated cyclohexanols (8.6 wt%), and cyclic- and linear alkanes (2.7 wt%), Scheme 1.7.

![Scheme 1.7.](image)

Ye et al. (Table 1.2 entry 8) studied the use of Ru/C, Pt/C, and Pd/C for the hydrotreatment of organolsolv cornstalk lignin in 65 vol% ethanol-water mixtures (250 °C, 20 bar hydrogen, 1.5 h) [48]. The liquid and solid reaction products were quantified using a distillation/extraction protocol. Typical liquid yields were between 69 and 76 %. The highest yield (76 wt%) was achieved with Ru/C at 250 °C, 90 min reaction time, and 20 bar of H$_2$. 4-Ethylphenolics, the target products of this study, were obtained in yields of up to 3.1 wt% for 4-ethylphenol and 1.3 wt% of 4-ethylguaiacol on lignin intake (Scheme 1.8).
INTRODUCTION

More recently, Cheng et al. converted alkali lignin in pure ethanol and water/ethanol mixtures with Pt/C, and Ni or Ru on alumina or carbon as the catalysts at 200-450 °C, 50 bar H₂ and reaction times up to 6 h (Table 1.2 entry 9, Scheme 1.9) [50]. Best yields (14.8 wt% on lignin) for reactions in ethanol were obtained with the Pt/C catalyst. Main components were esters (~44 % peak area), phenolic compounds (~19 % peak area) and alcohols (~10 % peak area). The liquid product yield was substantially better when using ethanol/water mixtures (1 to 1) and yields up to 89 % were obtained using Ru/C. Monomeric phenolic compounds were the primary products (~65 % GC peak area) and include 2-ethyl-5-propylphenol, diethylphenol, 3-ethyl-5-methylphenol, and 2-ethyl-5-methylphenol.

In subsequent studies, Cheng et al. depolymerised organosolv lignin in water-ethanol (1:1 v/v) and pure ethanol with Ni/C, and Ru/Al₂O₃ [51], see Table 1.2 entry 10. The reaction temperature determined to a large extent the liquid product yield and molecular weight distribution of the depolymerised lignin. Optimum results considering both depolymerised lignin yield (81 %) and lowest molecular weight (Mₙ 181 g/mol) were achieved with a Ni/C catalyst at 340 °C with 50 bar of H₂ and a 1:1 v/v water-ethanol mixture. The molecular composition of the depolymerised lignins was not reported.

1.4.2 Catalytic hydrotreatment of lignin in batch in the absence of a solvent using molecular hydrogen

The studies reported in the previous paragraph were all performed in the presence of a solvent and using molecular hydrogen. However, for large scale processing, the use of an external solvent is best avoided to reduce extensive solvent recycling. For catalytic hydrotreatment studies in batch at elevated temperatures, the use of a solvent is not necessary as most lignins are known to melt above 200 °C and as such may act as the solvent. In addition, the lower molecular weight products may, at a later stage of the reaction, also serve as a solvent. A potential drawback of the absence of
the solvent is a higher rate of repolymerisation reactions ultimately leading to char. Such repolymerisation reactions are expected to occur to a larger extent in more concentrated solutions.

Meier et al. performed experiments with mainly organocell lignin using Pd/C, red mud, Raney Nickel, and NiMo on several supports as the catalyst in the absence of a solvent [52], see Table 1.2 entry 12. After reaction, the oil was isolated after extraction of the reactor content with dichloromethane. The highest oil yield (80.6 wt% on lignin intake) was obtained with Pd/C (380 °C, 100 bar initial H₂, for 15 min reaction time). The total GC detectables in the oil was about 11.5 %, indicating that the majority of the products is of higher molecular weight and not sufficiently volatile for GC detection. The main compounds were methyl-, and ethylcyclohexanones together with minor quantities of phenols, guaiacols, and catechols, see Scheme 1.10 for details (total 8.8 wt% on lignin intake). The product composition of the oil is a function of the catalyst employed. For instance, with NiMo, cyclohexanones were absent and higher amounts of phenolics were detected (3.68 wt% on lignin). Process optimisation studies with the NiMo catalyst led to GC detectable fractions of up to 37.8 wt% (22 wt% on lignin), with a phenol content of 6.4 wt% (3.7 wt% on lignin).

Scheme 1.10.

Oasmaa et al. performed catalytic hydrotreatment reactions using a (non-)sulphided NiMo/Al₂O₃ catalyst and several lignin sources at elevated temperatures (395-400 °C) and pressures (90-101 bar H₂) in the absence of an external solvent (Table 1.2 entry 11) [53]. Best results were obtained with Pine Kraft lignin hydrotreated at 430 °C for 60 min with a mixture of sulphided NiMo on alumina and Cr₂O₃ on alumina (1:1), see Scheme 1.11. For this catalyst composition, the oil consisted of 10.8 wt% of monocyclic aromatics and 9.4 wt% of phenols on lignin intake (GC), the main phenolic compounds being phenol, methylphenol, and ethylphenol.

Scheme 1.11.
### Table 1.3. State of the art for catalytic hydrotreatment of lignin using external hydrogen in continuous set ups.

<table>
<thead>
<tr>
<th>#</th>
<th>Feed</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>T (°C)</th>
<th>WHSV</th>
<th>P (bar)</th>
<th>Major products</th>
<th>Oil (wt%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Multiple lignin sources</td>
<td>Lignin tar, phenols</td>
<td>FeS, CuS</td>
<td>350-400</td>
<td>1-2 h&lt;sup&gt;b&lt;/sup&gt;</td>
<td>150-300</td>
<td>Products distilled in fraction, monophenol fraction up to 50 wt%&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Up to 95%</td>
<td>[54]</td>
</tr>
<tr>
<td>2</td>
<td>Kraft lignin</td>
<td>Phenol/water/methanol</td>
<td>FeS with modifiers (prepared in situ)</td>
<td>300-450</td>
<td>1 h&lt;sup&gt;b&lt;/sup&gt;</td>
<td>50-150</td>
<td>Products distilled in fractions. Main products C&lt;sub&gt;6&lt;/sub&gt;-C&lt;sub&gt;8&lt;/sub&gt; Phenols, cresols</td>
<td>Up to 98%</td>
<td>[55]</td>
</tr>
<tr>
<td>3</td>
<td>Kraft Lignin</td>
<td>-</td>
<td>Fe γ-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; (S)</td>
<td>440</td>
<td>0.3-0.6 g lignin/(g cat.h)</td>
<td>40-135</td>
<td>For hydrotreatment step: Gas/water: 43 wt% on lignin. Liquid product was distilled in fractions: Light oil: 14.0 wt% on lignin Phenols: 37.5 wt% on lignin Heavy oil: 11.0 wt% on lignin</td>
<td>62.5</td>
<td>[21, 56]</td>
</tr>
<tr>
<td>4</td>
<td>Pyrolytic lignin</td>
<td>-</td>
<td>CoMo/γ-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; (S)</td>
<td>400-415</td>
<td>0.51-1 g lignin/(g cat.h)</td>
<td>140</td>
<td>Light organic phase (60-64 wt% on lignin) mainly comprising of aliphatic and aromatic hydrocarbons</td>
<td>60-64</td>
<td>[57]</td>
</tr>
<tr>
<td>5</td>
<td>Organocell lignin</td>
<td>Lignin slurry oil</td>
<td>NiMo (S)</td>
<td>375-450</td>
<td>2 h&lt;sup&gt;a&lt;/sup&gt;</td>
<td>75-180</td>
<td>Only monomeric phenolics quantified, up to 12.8 wt% on lignin</td>
<td>28-83</td>
<td>[58, 59]</td>
</tr>
<tr>
<td>6</td>
<td>BCD lignin</td>
<td>Alcohol water mixture</td>
<td>CoMo/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;, NiMo, NiW (S)</td>
<td>350-385</td>
<td>2 h&lt;sup&gt;b&lt;/sup&gt;</td>
<td>100-150</td>
<td>Alkylated phenols, alkoxy-phenols, alkylbenzenes, branched paraffins up to 25 wt%</td>
<td>Up to 75</td>
<td>[60, 61]</td>
</tr>
</tbody>
</table>

<sup>a</sup> wt% on lignin intake, <sup>b</sup> for batch reactor set-up, residence time in the continuous set up not provided, <sup>c</sup> batch data, <sup>d</sup> batch time for the liquid phase.
Despite the fact that the catalytic hydrotreatment of lignins has been studied already since the 40’s of the previous century, it appears that most studies are very exploratory in nature viz., use a large number of catalysts, a wide range of process conditions and a range of lignin feeds (variations in origin (hard and softwood), and lignin extraction methods (alkaline, organosolv)). This makes it hard to draw general conclusions regarding the best catalyst and reaction conditions. Detailed, systematic optimization studies regarding product liquid yields are lacking and feed composition-product relations and catalyst-product relations have not been determined. As such, it is very difficult to assess which catalysts are most suitable for the catalytic hydrotreatment of lignin when aiming for the highest yields of valuable bulk chemicals like aromatics and alkylphenolics.

1.4.3. Catalytic hydrotreatment of lignin in continuous set-ups.

As stated earlier, most studies on lignin hydrotreatment are exploratory in nature and have been carried out in batch set ups. Investigations using dedicated continuous set-ups are scarce and an overview is provided in Table 1.3. In most cases, either cheap Fe catalysts or HDS catalysts (CoMo, NiMo) are used, whereas studies with supported noble metal catalysts have not been reported to date. Lignin feeding was performed either in the solid state or as a liquid. In the latter case, the lignin feed was dissolved in an organic solvent or a liquid reaction product. Typically harsh conditions are used, temperatures between 250 and 450 °C and pressures between 70 and 450 bar. In most cases, both the solid phase and liquid phase are fed continuously. In one example in Table 1.3 (entry 5), the hydrogen is fed continuously while the liquid phase was operated in batch.

An early patent on the conversion of several types of lignin was reported by the Japanese Noguchi institute (Table 1.3 entry 1) [54]. The reactions were carried out in a mixture of lignin and lignin oil products as the solvent (and in some cases a co-solvent) using a cheap catalyst based on FeS in combination with a co-catalyst (most examples use CuS). Typically, the lignin to solvent ratio was between 100 and 200 %, temperatures between 350 and 400 °C, hydrogen pressures between 150 and 300 bar and reaction times between 1 and 2 h. Most reactions were carried out in a batch set-up and an oil and a water phase were obtained after reaction. Lignin oil yields up to 95 wt% were reported. The lignin oil was distilled, and four fraction with a boiling point i) below 100 °C (acetone, methanol), ii) between 190 and 230 °C (monophenol fraction) iii) between 230-260 °C (catechols) and iv) a fraction above 260 °C were collected. The yield of the monophenol fraction was reported to be as high as 51 %. However, a later patent by UOP claims that these high yields of monophenols could not be reproduced [55].

The authors also describe a continuous process for lignin liquefaction. It involves mixing the lignin with the catalyst and lignin oil solvent to form a paste. This paste is preheated to 250 °C and pumped into a reactor at a typical flow rate of 3 l/h. The reactor
is not mechanically stirred but hydrogen gas is introduced using a tube at the bottom of the reactor and this may result in some agitation. The liquefied reaction product is taken from the reactor by a weir system and collected. The gas phase is cooled and the liquid product is collected, whereas the gas phase is recycled. An overview of the set-up is given in Figure 1.9.

Figure 1.9. Schematic representation of the continuous reactor set-up provided by the Noguschi institute [54].

The residence time in the reactor is not given. The liquid product from the reactor is distilled in fractions with boiling points described above. When using a mixture of 200 parts of lignin as feed and 250 parts of lignin oil as the solvent, 6 parts of a fraction with a boiling point below 100 °C, 47 parts of a fraction boiling below 230 °C (monophenols), 4 parts of a fraction with a boiling point between 230 and 260 °C (catechols), and 17 parts with a higher boiling point were obtained. Unfortunately, a proper mass balance cannot be made with the data provided in the patent. However, the composition of the monophenol fraction is given and consists of 7 parts of o-cresol, 20.4 parts of p-cresol, 15.6 parts of 4-ethylphenol and 4 parts of 4-propylphenol (Scheme 1.12).

Scheme 1.12.
Further improvements on the Noguchi process and particularly on the monophenolic yield were reported by IOP in 1986 using Kraft lignin and a promoted iron sulphide as the catalyst (Table 1.3 entry 2). These improvements were mainly due to the use of a proper solvent (water, phenol, and a low aliphatic alcohol). Total amounts of monophenols were reported as high as 65 % and a cresol amount of about 45 %, though it is not clear what is the basis for these yields (on lignin feed or amount in one of the distillate fractions). The process consist of two separate stages. In the first step, the Kraft lignin is suspended in water/phenol and methanol and the in-situ prepared solid catalyst. The reaction is performed at temperatures between 300 and 450 °C and a hydrogen pressure between 50 and 150 atmosphere. The product is distilled and the fraction with a boiling point below 235 °C is collected. The remaining residue is the fed to a second reactor and used as a solvent for a second reaction with fresh Kraft lignin and catalyst. The product of the second reactor is distilled and the fraction with a boiling point below 235 °C is used as the substitute for phenol in the first reaction. The concept is not demonstrated on continuous scale and only examples in a batch set-up are provided in the patent. Lignin liquefaction yields were as high as 93 %, with cresols and substituted C₆-C₈ phenols as the main products. Unfortunately, full mass balances are not given, making it very cumbersome to quantify the exact yields of these products (see Scheme 1.13) [55].

Another landmark in the development of efficient catalytic hydrotreatment processes for Kraft lignin is the Lignol process (1983) from the Hydrocarbon Research Institute (HRI) [21, 56], see Figure 1.10 and Table 1.3 entry 3. The process aims to co-produce phenol and benzene. It involves the reaction of a lignin feed mixed with a process oil in an ebullated hydrocracking reactor followed by a thermal hydro-dealkylation step. The final product is fractionated to produce phenols and aromatics, along with a heavy alkylated material which is recycled to the hydrodealkylation reactor to increase the product yield.
The first reactor contains a sulfided Fe/y-Al₂O₃ catalyst and is operated at 440 °C and 70 bar of H₂ and a WHSV of about 0.3-0.6 g lignin/(g cat.h). It is claimed to produce about 37.5 wt% alkylated phenolics on lignin intake, the main phenolic compounds being phenol (6.6 wt%), m-cresol (11.9 wt%), p-cresol (9.7 wt%), 2,4-xylenol (7.0 wt%), p-ethylphenol (33.2 wt%), and p-propylphenol (20.0 wt%), see Scheme 1.14. Detailed information on the second stage reactor for hydrodealkylation of the alkylated phenolic mixture is not given, though it is said that about 60 mol% of the cresols can be dealkylated to phenol.

Scheme 1.14.

The advantages of the Lignol process compared to the Noguschi process are a lower amount of gas and liquid produced (42 wt% on lignin versus 45 wt%), a comparable amount of light distillate (14 wt% on lignin) a higher amount of phenol fraction (37.5 versus 21 wt% on lignin) and a lower amount of heavy oils.

Piskorz et al. (Table 1.3 entry 4) studied the catalytic hydrotreatment of pyrolytic lignin (a lignin isolated from fast pyrolysis oil from hog fuel) in a continuous packed bed reactor operated co-current upflow with the objective to obtain high yields of hydrocarbons for the transportation blending pool. The catalytic hydrotreatment was performed with sulphided CoMo/Al₂O₃ at 400-415 °C for a run time of 94-182 min at a
hydrogen pressure of 140 bar [57]. Typical WHSV's were between 0.51 and 1 g lignin/(g cat.h). The reactor effluent was cooled in two stages and the liquid products were collected. The total liquid product yield was about 81-85 %, consisting of light organics (60-64 wt%) and water (about 20 %). The light oil contained only 0.5 wt% of oxygen and consisted of about 62 % aliphatic, 38 % aromatics, see Scheme 1.15 for details. Main compounds identified by GC-MS were cyclohexane, methylcyclohexane, toluene, ethylbenzene, propylbenzene, and dodecane.

Scheme 1.15.

Meier et al. depolymerised organocell lignin in a semi-continuous setup with a continuous flow of hydrogen and batch wise operation of the liquid phase with the objective to maximise phenolics yields [58, 59], see Figure 1.11 and Table 1.3 entry 5. A range of reaction temperatures (375-450 °C), hydrogen pressures (75-180 bar), catalysts (sulphided NiMo, zeolite A, and none), and the use of several different slurry oils as solvent were tested. Lowest char formation (0.3 wt%) and highest oil yield (about 82 %) were achieved with sulphided NiMo at 375 °C, 180 bar, and 120 min batch time with organocell lignin mixed with a lignin derived slurry oil. Phenolics yields were up to 12.8 wt% on lignin intake (NiMo, 450 °C, 180 bar hydrogen) with the main phenolic compounds being cresols, xylanols, phenol, and guaiacol.

Scheme 1.16.

Figure 1.11. Schematic overview of the semi-continuous process set up of Meier et al. [58, 59].
### Table 1.4 State of the art for (catalytic) solvolysis of various lignins.

<table>
<thead>
<tr>
<th>#</th>
<th>Feed</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>T (°C)</th>
<th>Time (h)</th>
<th>Oil (wt%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Solids (wt%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Major products</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Enzymatic/hydrolysis lignin</td>
<td>FA, IPA, EtOH optional water</td>
<td>-</td>
<td>370-390</td>
<td>2-16</td>
<td>Not provided</td>
<td>16-30</td>
<td>Phenolics</td>
<td>[62]</td>
</tr>
<tr>
<td>2</td>
<td>Multiple sources</td>
<td>FA, IPA, EtOH, MeOH</td>
<td>-</td>
<td>380</td>
<td>8-54</td>
<td>82-130</td>
<td>n.d.</td>
<td>Phenolics (25-35 wt%)&lt;sup&gt;a&lt;/sup&gt; H/C 1.3-1.7 O/C 0.05-0.17</td>
<td>[29, 30]</td>
</tr>
<tr>
<td>3</td>
<td>Enzymatic/weak acid hydrolysis lignin</td>
<td>FA, IPA/EtOH</td>
<td>-</td>
<td>380</td>
<td>Overnight runs</td>
<td>Not provided</td>
<td>2-15</td>
<td>Aliphatic hydrocarbons/ Phenolics H/C 1.2-1.8 O/C 0.16-0.5</td>
<td>[63]</td>
</tr>
<tr>
<td>4</td>
<td>Various lignins</td>
<td>FA, water</td>
<td>Pd/C, Nafion SAC-13</td>
<td>300</td>
<td>2</td>
<td>-</td>
<td>10-20</td>
<td>Mixture of phenols, max 10.5 wt% Mainly guaiacol and catechols (pyrocate- chol and resorcinol)</td>
<td>[64]</td>
</tr>
<tr>
<td>5</td>
<td>Switchgrass lignin</td>
<td>FA, EtOH</td>
<td>Pt/C</td>
<td>135-800</td>
<td>1-20</td>
<td>Max. 21 wt% on lignin of GC identified products.</td>
<td>-</td>
<td>Main GC identified products: 4-propylguaiacol (8 wt% on lignin) 4-methylguaiacol (5 wt% on lignin) Homovanillyphenol (3 wt% on lignin) Phenolics, guaiacols H/C 1.3-1.2 O/C 0.33-0.15</td>
<td>[65]</td>
</tr>
</tbody>
</table>

<sup>a</sup> wt% on lignin intake.
A continuous process for the conversion of lignin to hydrocarbons and aromatics by catalytic hydrotreatment was patented by Shabtai et al. [60, 61], see Table 1.3 entry 6. A two stage approach is followed. The first stage involves a base catalysed (NaOH, KOH, etc) depolymerisation (BCD) of lignin in supercritical (260-310 °C) methanol or ethanol to yield a liquefied lignin (10 minutes). In this stage, high yields of mono-, di-, and tri-oxygenated aromatics are produced. The second step involves a catalytic hydrotreatment of the liquid depolymerised lignin mixture at severe reaction conditions (350-385 °C, 97-152 bar H₂) with the use of a sulphided CoMo/Al₂O₃ catalyst without the addition of a solvent. The main components found after 2 hours of reaction time were mono-, di-, and tri-alkylbenzenes (about 25 wt%). The process is demonstrated in a batch mode, continuous operation is not reported.

![Scheme 1.17](image)

**1.5 (CATALYTIC) SOLVOLYSIS OF LIGNIN**

Historically, the catalytic hydrotreatment of lignin uses ex-situ molecular hydrogen as hydrogen source for the reaction (vide supra). A relatively new and upcoming lignin conversion methodology uses an in-situ hydrogen donor. A well-known hydrogen donor is formic acid (FA), which is, either thermally or catalytically, converted to hydrogen and CO/CO₂. Commonly used solvents are alcohols, like ethanol, methanol, and isopropanol (IPA), which may also generate hydrogen upon heating in the presence of a catalyst. Kleinert and co-workers, pioneers in this research area, were able to convert lignin to a liquid product at 370-390 °C with reaction times of 2-16 h with only formic acid and an alcohol as the solvent in the absence of a catalyst (Table 1.4 entries 1-3) [29, 30, 62]. Lignin oil yields were between 60-90 %, with claimed phenolic yields on lignin intake between 25-35 wt%. Main phenolic compounds were primarily alkylated phenolics like 2-ethylphenol, thymol, and 2-ethyl-4,5-dimethylphenol (Scheme 1.18).

![Scheme 1.18](image)
Further work by Liguori et al. (Table 1.4 entry 4) showed that lignin solvolysis could be improved by the use of a supported noble metal catalyst (Pd/C) in combination with a strong solid acid (Nafion SAC-13) [64]. The reactions were carried out with various lignins and using formic acid and water as the solvent. The use of catalysts compared to the non-catalytic version allows reduction of the reaction temperature to 300 °C and a shorter reaction time (2 h). Typical products were monomeric phenolics like methoxyphenolics and (substituted) catechols (Scheme 1.19).

Scheme 1.19.

Recently, Xu et al. reported the use of Pt/C as the catalyst in combination with ethanol and formic acid for the depolymerisation of switchgrass lignin at 350 °C (Table 1.4 entry 5) [65]. The reaction products were analysed with GC and a maximum of 21 wt% on lignin of GC identified product were detected after 4 h reaction time. The main GC detectable compounds were 4-propylguaiacol (8 wt% on lignin), 4-methylguaiacol (5 wt% on lignin) and homovanillyl alcohol (3 wt% on lignin), see Scheme 1.20 for details.

Scheme 1.20.

1.6 THESIS OUTLINE

This thesis describes an experimental study on the valorisation of Alcell lignin to biobased products by catalytic hydrotreatment. The first part of the thesis focuses on the catalytic hydrotreatment of Alcell lignin, fractionated Alcell lignin, pyrolytic lignin, and relevant dimeric model components using mainly Ru/C as the catalyst. The main objective of this part is to gain insights in the relation between process conditions and starting lignin feed on molecular composition and the product properties of the resulting lignin oils. The last chapter of the thesis is focused on the use of catalytic solvolysis to valorise Alcell lignin with Ru/C as catalyst. Also here, relations between process conditions and molecular composition of the resulting lignin oils were determined. The study was performed in the framework of the Dutch national project...
In Chapter 2, a catalyst screening study on the catalytic hydrotreatment of Alcell lignin using different noble metal catalysts (Pd, Ru) and a non-noble metal catalyst (Cu) on different supports is reported. The catalysts were tested at similar reaction conditions (400 °C, 4 h reaction time, and with an initial hydrogen pressure of 100 bar) and the level of depolymerisation and selectivity towards desired monomeric compounds (aromatics, alkylphenolics) was determined. Subsequent detailed experimental studies were performed with Ru/C to determine the effect of process conditions on the final product composition.

An exploratory study on the catalytic hydrotreatment of two pyrolytic lignins (pine and forestry residue) using Ru/C as the catalyst is described in Chapter 3. The effect of lignin feed properties on the resulting product composition was established and compared with benchmark experiments using Alcell lignin. The reactions were performed in a batch set-up (400 °C, 4 h, 100 bar initial H₂ pressure). Based on the product composition, a global reaction network for the catalytic hydrotreatment of pyrolytic lignin with Ru/C is proposed.

Experimental research on the catalytic hydrotreatment of fractions of Alcell lignin, obtained by solvent extraction, using Ru/C as the catalyst (400 °C, 4 h reaction time, and with an initial hydrogen pressure of 100 bar) is provided in Chapter 4. Relevant product properties and composition of the lignin fractions and corresponding product oils were determined and rationalised.

A model compound study on the catalytic hydrotreatment of various dimeric lignin model compounds, (guaiacylglycerol-β-guaiacyl ether, 4-benzyloxy-3-methoxy-benzaldehyde, and 2,2’-biphenol) using Ru/C is reported in Chapter 5. The reactions were performed at 250 °C with 100 bar H₂ using n-dodecane as the solvent. A reaction network is proposed for each model compound and a reactivity order for the various lignin linkages is proposed.

In Chapter 6, a comparative study on the differences between catalytic solvolysis (in-situ hydrogen production) and catalytic hydrotreatment (ex-situ hydrogen addition) of Alcell lignin using Ru/C is reported. Distinct differences in product yields and compositions were observed and the extent of depolymerisation and selectivity towards the desired monomeric compounds were evaluated. Furthermore, the effect of process conditions like reaction time, and type of alcohol solvent on the catalytic solvolysis approach were explored and the results were rationalised by a reaction network.
REFERENCES

INTRODUCTION


