Chapter 1

An Introduction to Catalytic Hydrotreatment of Pyrolysis Liquids
Introduction
Due to the depletion of fossil resources and environmental issues, e.g. global warming as a result of greenhouse gases emissions, there is an urgent need to identify, develop and implement alternative resources for energy, transportation fuel and chemicals. [1] Solar, wind, hydroelectric, geothermal activity and biomass are considered renewable and sustainable resources and are expected to (partly) replace fossil resources in the near future. [2] In this respect, lignocellulosic biomass, e.g. wood, agricultural waste, forest waste, (see Table 1) is of particular interest as it is the only sustainable resource containing renewable organic carbon. [3] Lignocellulosic biomass is a polymeric material composed of three main constituents: cellulose, hemicellulose and lignin. The composition of some typical biomass resources are shown in Table 1. [3] Cellulose is a linear polysaccharide with β-1,4 linkages of D-glucopyranose monomers. Inter- and intramolecular hydrogen bonding render it highly crystalline and as such has a high reluctance to hydrolysis reactions. Hemicellulose is a biopolymer consisting of a wide range sugars, *viz* five-carbon sugars (usually xylose and arabinose) and six-carbon sugars (galactose, glucose, and mannose). Compared to cellulose, hemicellulose is amorphous and highly branched, which makes it relatively easy to be hydrolyzed to monomeric sugars by acids. Lignin is a three-dimensional polymer consisting of propyl-phenol units with various types of linkages and is found in the cell walls of particularly woody biomass. [3] However, the use of biomass also has some drawbacks. For instance, collection is costly, various types of biomass show major differences in structure and composition, it has a low energy density compared to fossil resources, and often contains significant amounts of water and ash, as shown in Table 1. To overcome some of these drawbacks, it is crucial to develop commercially attractive ways to convert lignocellulosic biomass into a liquid product with a higher volumetric energy density and a lower level of contaminants. [4]
Table 1 Chemical composition, energy content and yield of various terrestrial biomass species (Adapted with permission from ref [3]. Copyright 2006 American Chemical Society)

<table>
<thead>
<tr>
<th>Biomass component</th>
<th>Corn grain</th>
<th>Corn stover</th>
<th>Switchgrass</th>
<th>Sugarcane</th>
<th>Sweet sorghum</th>
<th>Eucalyptus</th>
<th>Pine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Productivity (dry metric tons/ha-year)</td>
<td>7</td>
<td>13-24</td>
<td>8-20</td>
<td>73-87</td>
<td>43.8</td>
<td>40.0</td>
<td>11.6</td>
</tr>
<tr>
<td>Lower heating value (MJ/dry kg)</td>
<td>17.0</td>
<td>17.5</td>
<td>≈17</td>
<td>16.8</td>
<td>17.3</td>
<td>18.1</td>
<td>18.6</td>
</tr>
<tr>
<td>Energy inputs (MJ/dry kg)</td>
<td>1.35</td>
<td>1.20</td>
<td>0.346</td>
<td>2.82</td>
<td>5.57</td>
<td>7.43</td>
<td></td>
</tr>
<tr>
<td>Energy content (GJ/ha-year)</td>
<td>120</td>
<td>228-420</td>
<td>136-340</td>
<td>1230-1460</td>
<td>760</td>
<td>720</td>
<td>210</td>
</tr>
<tr>
<td>Energy content (boe/ha-year)</td>
<td>20</td>
<td>40-70</td>
<td>23-58</td>
<td>210-250</td>
<td>128</td>
<td>123</td>
<td>37</td>
</tr>
<tr>
<td>Representative components (dry wt%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Celluloses</td>
<td>3</td>
<td>36</td>
<td>40-45</td>
<td>22</td>
<td>35</td>
<td>48</td>
<td>46-50</td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td>6</td>
<td>23</td>
<td>31-35</td>
<td>15</td>
<td>17</td>
<td>14</td>
<td>19-22</td>
</tr>
<tr>
<td>Extractives (starches, terpenes)</td>
<td>72</td>
<td>6</td>
<td>0</td>
<td>43</td>
<td>23</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Lignins</td>
<td>2</td>
<td>17</td>
<td>6-12</td>
<td>11</td>
<td>17</td>
<td>29</td>
<td>21-29</td>
</tr>
<tr>
<td>Uronic acid</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Proteins</td>
<td>10</td>
<td>5-11</td>
<td>9</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>0.3</td>
</tr>
<tr>
<td>Ash</td>
<td>10</td>
<td>5-6</td>
<td>9</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Fast pyrolysis is considered as a very attractive technology for this purpose. The liquid product, known as pyrolysis liquids (PLs), bio-oil or bio crude, contains negligible amounts of ash and has a volumetric energy density 5 to 20 times higher than the original biomass. [5] In the following parts of this chapter, a short introduction on fast pyrolysis technology and the composition and properties of PLs will be reported.

1. Fast pyrolysis technology

Fast pyrolysis is a very versatile biomass conversion technology, which is carried out in the absence of oxygen at a temperature ranging from 450 to 600 °C under atmospheric pressure. A short vapor residence time (< 2 s) in combination with high biomass heating rates ensures a high yield of liquid product, which can be up to 70 wt% on dry biomass feed. [4] The process parameters of various pyrolysis technologies and the product distributions are shown in Table 2. Clearly, the liquid yields are highest when using fast pyrolysis technology.

Table 2 Comparison of thermochemical techniques (Adapted with permission from ref [6]. Copyright 2012 Elsevier)

<table>
<thead>
<tr>
<th>Mode</th>
<th>Conditions</th>
<th>Liquid</th>
<th>Solid</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast</td>
<td>~500 °C, short hot vapour residence time ~ 1 s</td>
<td>75%</td>
<td>12%</td>
<td>13%</td>
</tr>
<tr>
<td>Intermediate</td>
<td>~500 °C, hot vapour residence time ~ 10-30 s</td>
<td>50% in 2 phases</td>
<td>25%</td>
<td>25%</td>
</tr>
<tr>
<td>Carbonisation(slow)</td>
<td>~400 °C, long vapour residence time ~ hours to days</td>
<td>30%</td>
<td>33%</td>
<td>33%</td>
</tr>
<tr>
<td>Gasification</td>
<td>~750-900 °C</td>
<td>3%</td>
<td>10%</td>
<td>85%</td>
</tr>
<tr>
<td>Torrefaction(slow)</td>
<td>~290 °C, solids residence time ~ 10-60 min</td>
<td>0% unless condensed, then up to 5%</td>
<td>80% solid</td>
<td>20%</td>
</tr>
</tbody>
</table>

Process development activities in the field of fast pyrolysis culminated in the construction of successful (semi-) commercial scale plants in the US and Canada (Pyrovac, Dynamotive, Ensyn), Finland (Valmet), Germany (KIT) and the Netherlands (BTG, EMPYRO).

A successful example of PLs production by fast pyrolysis technology in the Netherlands is reported by the Biomass Technology Group (BTG). The company has developed proprietary pyrolysis technology with distinct advantages compared to conventional processes. The reactor technology (rotating cone) excludes the use of inert gases as required for fluidized bed reactors. Instead the biomass particles are fed and mechanically mixed near the bottom of the rotating cone with an excess sand.
Pyrolysis vapours pass through a cyclone and are quenched by cold PLs. The sand together with the char formed during the pyrolysis process are transported to a separate fluidized bed combustor where the char is combusted and the sand, re-heated to reactor temperature, is recycled to the pyrolysis reactor. A process flow diagram of BTG’s fast pyrolysis technology is shown in Figure 1.

![Process flow diagram of BTG’s fast pyrolysis process](image)

**Figure 1** Process flow diagram of BTG’s fast pyrolysis process [7]

In 2015, BTG designed and built a 5 t/h pyrolysis unit in Hengelo (the Netherlands), see Figure 2. The unit produces 22000 t/y of PLs from woody biomass waste, which will be used to replace natural gas in an industrial boiler of the dairy firm FrieslandCampina.
Fast pyrolysis technology is moving to maturity. The technology is on the verge of commercial exploitation, and large quantities of PLs will thus become available in the near future.

2. The composition of pyrolysis liquids
Lignocellulosic biomass is composed of three main biopolymers: cellulose, hemicellulose, and lignin. Decomposition of these primary building blocks during fast pyrolysis leads to the formation of significant amounts of mono- and oligomeric, oxygenated functional molecules. Examples are organic acids, aldehydes, ketones, esters, alcohols, furans, sugars and phenolics, see Figure 3 for details. The total amount of low molecular weight GC detectables in PLs is around 45-65 wt%, the amount of oligomeric compounds, including sugar and lignin oligomers, is estimated to be around 15-25 wt%. The remainder is water, either feedstock moisture or reaction water. [8]
Figure 3 Typical products formed from the pyrolysis of the three main building blocks of lignocellulosic biomass (Adapted with permission from ref [9]. Copyright 2014 Royal Society of Chemistry)

For cellulose pyrolysis, the most abundant volatiles are levoglucosan, furans and light oxygenates (such as glycolaldehyde and formic acid). The mechanism of levoglucosan formation from cellulose involves the cleavage of a glycosidic linkage between pyranose rings to form a glucosyl cation, which is stabilized by the formation of a 1,6-anhydride. The subsequent cleavage of the glycosidic bond linking the anhydride to the end of the polymer chain yields levoglucosan, see Scheme 1 for details.
Scheme 1 Mechanisms of formation of levoglucosan and glucose during fast pyrolysis (Adapted with permission from ref [10]. Copyright 2012 Royal Society of Chemistry)

The formation pathways to furanics and other light oxygenates is less straightforward. [11] Proposed reaction pathways for the formation of C1-C6 organic compounds from glucose are shown in Scheme 2.

Scheme 2 Mechanism of formation of various C1–C6 organic compounds starting from glucose (pyranose form) (Adapted with permission from ref [10]. Copyright 2012 Royal Society of Chemistry)
The pyrolysis products from hemicellulose can be classified into three main categories: i) low-molecular-weight compounds, e.g. formic acid, acetic acid, acetaldehyde, and acetol, ii) furan/pyran ring derivatives and iii) anhydrosugars [12], see Scheme 3 for details. Patwardhan et al. [12] reported that a double dehydration product of xylose, the most abundant building block of hemicellulose, was the major product.[3]

Scheme 3 Proposed reaction scheme, showing primary pyrolysis reactions of switchgrass hemicellulose (Adapted with permission from ref [12]. Copyright 2011 Wiley)

For lignin pyrolysis, the main products are volatile compounds (e.g. methanol, acetone, and acetaldehyde), mono-phenols (e.g., phenol, guaiacol, syringol, and catechol), and polysubstituted phenols, see Scheme 4 for details. [13]
Breaking of the β-O-4 linkage by a radical mechanism is considered to be the primary step of the depolymerisation of the lignin structure. Free radical reactions will lead to the formation of lignin monomers such as vanillin and 2-methoxy-4-methylphenol, while the recombination of free radicals lead to the formation of oligomeric products and/or char. Patwardhan et al. [14] reported that volatile monomeric compounds are the primary products of lignin pyrolysis, whereas secondary reactions of such monomers lead to the formation of oligomers.

3. Properties of pyrolysis liquids
The presence of various oxygenated organics has a major impact on product properties of PLs. A comparison of typical properties of PLs and crude oil is shown in Table 3.
Table 3 Comparison of typical properties of PLs and crude oil (Adapted with permission from ref [15]. Copyright 2014 Royal Society of Chemistry)

<table>
<thead>
<tr>
<th>Composition</th>
<th>PLs</th>
<th>Crude oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (wt%)</td>
<td>15-30</td>
<td>0.1</td>
</tr>
<tr>
<td>pH</td>
<td>2.8-3.8</td>
<td>-</td>
</tr>
<tr>
<td>Density (kg·L⁻¹)</td>
<td>1.05-1.25</td>
<td>0.86-0.94</td>
</tr>
<tr>
<td>Viscosity 50 °C (cP)</td>
<td>40-100</td>
<td>180</td>
</tr>
<tr>
<td>HHV (MJ·kg⁻¹)</td>
<td>16-19</td>
<td>44</td>
</tr>
<tr>
<td>C (wt%)</td>
<td>55-65</td>
<td>83.86</td>
</tr>
<tr>
<td>O (wt%)</td>
<td>28-40</td>
<td>&lt;1</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>5-7</td>
<td>11-14</td>
</tr>
<tr>
<td>S (wt%)</td>
<td>&lt;0.05</td>
<td>&lt;4</td>
</tr>
<tr>
<td>N (wt%)</td>
<td>&lt;0.4</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ash (wt%)</td>
<td>&lt;0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>H/C</td>
<td>0.9-1.5</td>
<td>1.5-2.0</td>
</tr>
<tr>
<td>O/C</td>
<td>0.3-0.5</td>
<td>~0</td>
</tr>
</tbody>
</table>

### 3.1 Acidity of pyrolysis liquids

PLs are acidic in nature (pH < 3) because of the presence of around 3-6 wt% of volatile organic acids mainly from the degradation of the hemicellulose fraction. Examples are formic acid, acetic acid, and glycolic acids. Other compounds like phenolics, fatty and resin acids also have a certain acidity. The total acid number (TAN) is the preferred indicator for acidity in PLs. The determination of total acid number is generally carried out by a titration method using a basic solution, e.g. KOH or NaOH. [16] The acidic properties of PLs are a major drawback as it potentially leads to corrosion in pipelines and storage vessels.

### 3.2 Heating value of pyrolysis liquids

The typical heating value of PLs is between 16 and 19 MJ/kg, which is around half of that of crude oils (44 MJ/kg). The low heating value of PLs results from the presence of oxygenated organic molecules (28-40 wt% on dry basis) and water (15-30 wt%), see Table 3 for details. Due to the higher density (1.05-1.25 kg/L compared to 0.86-
0.94 kg/L for crude oil), the heating value of PLs on a volumetric basis is about 60% of that for crude oil. [17]

### 3.3 Stability of pyrolysis liquids

PLs are known to age during storage [18] and this aging process is accelerated at elevated temperature [5, 19]. Unlike crude oils and derivatives, PLs contain a significant amount of reactive oxygenated functional molecules, which can react to form larger molecules during handling or storage and at elevated temperature (polymerization). Other transformations upon storage involve etherification and esterification reactions. Water is formed as a byproduct for all these reactions. Aging has a negative effect on product properties, and for instance leads to an increase in the viscosity and water content.

Figure 4 shows the main chemical compositional changes of PLs during aging [20]. A clear increase in water insolubles is observed after 12 months of storage. Reactive carbonyl-containing molecules, e.g. aldehydes and ketones, are expected to play a major role in the aging of PLs. This is supported by the aging tests given in Figure 4, which shows that the amounts of carbonyl compounds decreases monotonously in time.

![Figure 4 Main changes in forestry residue PLs during storage](adapted with permission from ref [20]. Copyright 2011 American Chemical Society)
Figure 5 gives a detailed comparison of the composition of PLs derived from pine wood and the product oil after a high pressure thermal treatment (HPTT) using a fractionation method. [5, 19] Upon heating, sugars (indicated as ether-insolubles) are partly converted to water insolubles and water. This observation is rationalised by assuming that the anhydrosugars, e.g. levoglucosan, are initially hydrolysed to sugar monomers like glucose, which in acidic media and elevated temperatures, further dehydrate to 5-HMF and repolymerization products thereof like humin type of oligomers and polymers. [21]

![Figure 5 Composition of a typical pine PLs and high pressure thermal treatment products from PLs (HPTT) according to a fractionation method [5]](image)

4. **Characterization of PLs by solvent fractionation**

As depicted in paragraph 2 of this chapter, PLs are complex mixtures, composed of water, various volatiles and nonvolatile, oligomeric components from both sugar and lignin fractions. For the determination of the moisture content of PLs, a Karl Fischer titration is typically used. Quantification of monomeric components (Figure 3) is best done using gas chromatography (GC) or high performance liquid chromatography (HPLC) techniques. However, oligomeric compounds (15-25 wt% of PL) are nonvolatile, so analysis is not possible by conventional GC techniques. An alternative procedure involves solvent fractionation prior to detailed analyses. An example is a method developed by Oasmaa et al. [22], see Scheme 5 for details,
which was successfully used for the characterization of PLs and their hydrogenated product oils. [5, 23] Solvent fractionation combined with conventional analysis techniques, e.g. GC, NMR, GPC, and HPLC, gives a very good understanding on the molecular composition of PLs.

Scheme 5 Example of a solvent fractionation protocol for PLs [23]

Seven distinct fractions were obtained using this solvent fractionation scheme and include a) water, b) extractives, c) acids, alcohols, d) aldehydes, ketones, and lignin monomers, e) sugars, f) low-molecular-weight lignin, and g) high-molecular-weight lignin. The detailed composition of each fraction is provided in Table 4.
Table 4 Chemical composition of reference pine PLs and its fractions [8]

<table>
<thead>
<tr>
<th>COMPOUND TYPES</th>
<th>wt % (wet basis)</th>
<th>wt % (dry basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WATER-SOLUBLES</td>
<td>75-85</td>
<td></td>
</tr>
<tr>
<td>Acids, alcohols</td>
<td>5-10</td>
<td>36.0 6.0 0 58.0</td>
</tr>
<tr>
<td>Ether-solubles</td>
<td>5-15</td>
<td>60.0 6.0 0.1 33.9</td>
</tr>
<tr>
<td>Ether-insolubles</td>
<td>30-40</td>
<td>46.0 6.3 0.3 47.4</td>
</tr>
<tr>
<td>Water</td>
<td>20-30</td>
<td>0 11.1 0 88.9</td>
</tr>
<tr>
<td>WATER-INSOLUBLES</td>
<td>15-25</td>
<td>66.2 6.6 0.3 26.9</td>
</tr>
<tr>
<td>n-Hexane-solubles</td>
<td>2-6</td>
<td>77.4 10.4 0 12.2</td>
</tr>
<tr>
<td>DCM-solubles</td>
<td>5-10</td>
<td>88.1 6.7 0.4 24.7</td>
</tr>
<tr>
<td>DCM-insolubles</td>
<td>2-10</td>
<td>degraded lignin</td>
</tr>
</tbody>
</table>

5. Biorefinery concepts for pyrolysis liquids

PLs can be used as the input for a biorefinery, similar to the use of crude oil in an oil refinery. A PLs based biorefinery concept is shown in Scheme 6. In this concept, PLs are valorized in an integrated process for the production of heat, power, biofuels and bio-based chemicals.

PLs obtained from fast pyrolysis of biomass may be combusted in boilers, diesel engines, gas turbines and stirling engines for heat and power generation. Research activities have been carried out by VTT Energy (Finland), MIT (USA), Orenda Aerospace Corporation (Canada), ZSW (Germany), etc. and have been reviewed by Czernik and Bridgwater. [18, 24]

Gasification of PLs and further processing of the product synthesis gas in Fischer-Tropsch processes has been investigated and claimed to be technically and economically feasible [25-29]. Catalytic steam reforming of PLs or fractions thereof to syngas using a conversion strategy analogous to catalytic steam reforming of alcohols and oxygenated aromatics has been studied. The syngas is rich in CO₂, and
Chapter 1

contained hydrogen as well as minor amounts of CO and CH₄. [29] By adjusting the H₂/CO ratio by including a water-gas shift reaction, production of Fischer-Tropsch fuels, DME, and alcohols was claimed to be feasible.

PLs contain substantial amounts of valuable oxygenated compounds, some of them are actually existing bulk chemicals. Examples are organic acids (formic acid, acetic acid and glycolic acid), glycolaldehyde, anhydrosugars, phenolics, etc. Solvent extraction is widely used for the separation and isolation of individual chemicals from PLs. Rasendra et al. [30] reported that reactive extraction of organic acids, particularly acetic acid, from the aqueous phase of PLs is technically feasible by using a long chain aliphatic tertiary amine. The best results were obtained with tri-n-octylamine (TOA) in 2-ethyl-hexanol (40 wt%) giving 84% acetic acid recovery at equilibrium conditions at room temperature. Other organic acids, e.g. formic acid and glycolic acid, were also co-extracted with 92% and 69% efficiency, respectively.

The same reactive extraction system was used by Vitasari et al. [31-33] to extract glycolaldehyde from the aqueous phase of PLs. It was shown that an amine is not essential and the highest yields of glycolaldehyde was obtained using 2-ethyl-1-hexanol as the solvent. Bennett et al. [34-37] reported that a simple water extraction is a convenient way to obtain levoglucosan from PLs. Optimization of the water-to-oil ratio, temperature and contact time yielded an aqueous phase enriched in levoglucosan. Wang et al. [38] reported the extraction of monophenolics from the water-insoluble fraction of PLs by a multiple step extraction using aqueous acids and bases combined with dichloromethane.

The above mentioned products obtained by various extraction procedures can be used directly or further processed to high value chemicals. For example, glycolaldehyde is a precursor for ethylene glycol by hydrogenation [39] and the hydrolysis of levoglucosan gives glucose, which can be fermented to fuel ethanol [40].
PLs upgrading to either a stabilised oil or a transportation fuel by catalytic hydrotreatment has been studied extensively. For instance, in the European 6th Framework project BIOCOUP [42], the main objective was to develop processes/catalysts for the catalytic hydrotreatment of PLs to stabilised oils with a reduced oxygen content range (~ 10 wt%), to be used as a co-feed with e.g. vacuum gas oil (VGO) in existing fluidized catalytic cracking (FCC) units. The stabilised product oil can also be processed further by a deep hydrotreatment to hydrocarbons that can be used as a transportation fuel.

Upgrading of PLs by a catalytic hydrotreatment is the core objective of the research described in this thesis. In the following, the process and the status of catalyst development will be reviewed and discussed.

### 6. Catalytic hydrotreatment process

The major objectives of the catalytic hydrotreatment process are to reduce the oxygen content, increase the H/C ratio, reduce the molecular weight and to improve the thermal stability of PLs. Other thermal processes have been developed for PLs upgrading, examples include a high pressure thermal treatment (HPTT) and zeolite cracking (see Table 5 for details). Among all these upgrading technologies, catalytic hydrotreatment is considered the most promising because it yields a product with a higher H/C ratio compared to HPTT and char formation is much lower when compared to zeolite cracking. [43]

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**Scheme 6 Possible biorefinery concept for PLs [41]**
Table 5 High temperature processes for PLs upgrading [43]

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>HPTT</th>
<th>Zeolite cracking</th>
<th>Hydrotreatment/HDO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coke formation</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>473-623</th>
<th>573-873</th>
<th>523-673</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15-30</td>
<td>No</td>
<td>10-30</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>High, 26-39 wt%</td>
<td>Low, &lt; 5 wt%</td>
</tr>
</tbody>
</table>

6.1 Reactor configurations

Catalytic hydrotreatment of PLs is carried out in the presence of a hydrogenation catalyst at elevated temperatures (523-673 K) under high pressure hydrogen (10-30 MPa). A simplified representation is given in Scheme 7.

\[
CH_{1.47}O_{0.56} + 0.44 H_2O + 0.319 H_2 \\
\rightarrow 0.647 CH_{1.48}O_{0.11} + 0.183 CH_{3.02}O_{1.09} + 1.164 H_2O
\] (1)
Chapter 1

The catalytic hydrotreatment of PLs has been reported in batch autoclaves and continuous reactor configurations, particularly in packed bed reactors. In batch reactors, operating conditions as well as the concentrations of all species are time dependent. The experiments are often carried out in a closed system and hydrogen consumption is not compensated for. As such it is difficult to assess catalyst activity (often taken as an average over the batch time) as well as catalyst stability. Moreover, heating and cooling down of the batch reactor content using conventional heating often has a timescale in the order of > 15-30 min, particularly when reaction temperatures up to 400 °C are used. Isothermal conditions throughout an experiment are thus not met and this may affect quantification of catalyst performance. In contrast, continuous experiments are performed in a steady state mode with by far time dependencies of concentrations and temperatures.

A major difference in catalytic experiments using heterogeneous catalysts between batch and continuous set ups also includes the size of the catalyst particles. It is often in the micrometer range for batch slurry systems and up to several millimeters in a continuous packed bed reactor to reduce pressure drops. This will have a major impact on catalyst performance, particularly for the faster hydrotreatment reactions (e.g. aldehyde reduction) using larger particle as intra-particle mass transfer limitations may affect the overall reaction rates to a large extent. Notwithstanding these differences, the continuous reactor experiments provide valuable insight in catalyst stability as well as the suitability of a particular continuous reactor set-up for subsequent scale-up studies.

Due to the thermal instability of PLs as depicted in section 3 of this chapter, the direct hydrotreatment of PLs at elevated temperatures (> 300 °C) is not the best choice as polymerization of thermal labile components in PLs result in the formation of considerable amounts of char/humins. To avoid this, a two-step hydrotreating process for the upgrading of PLs was developed by both Elliott and Venderbosch et al. and is characterised by a low and high temperature step. [5, 45, 46] A schematic representation of a packed bed set-up for the catalytic hydrotreatment of PLs using a staged concept is shown in Figure 6.
In the low temperature stage (around 200 °C), thermally labile components are hydrogenated to compounds with improved stability. In the high temperature stage (up to 400 °C), further hydrodeoxygenation of stabilised products and hydrocracking occurs, leading to products with reduced oxygen contents and lower molecular weights. In this staged concept, char formation is considerably decreased, which has a positive effect on both operability as well as catalyst stability.

**6.2 Chemical reactions during catalytic hydrotreatment**

Catalytic hydrotreatment involves a number of reactions (Figure 7), which can be classified as hydrogenations, hydrodeoxygenations, decarbonylations, decarboxylations, cracking, hydrocracking and polymerization reactions.
Venderbosch et al. [5] investigated the catalytic hydrotreatment of PLs using a Ru/C catalyst in a 4 stage packed bed reactor, with different process severities, especially temperature, in the 4 stages [5]. The experiments revealed that catalytic hydrogenation and a thermal, non-catalytic polymerisation occur in a parallel mode in the initial phase of the hydrotreatment process, see Scheme 8 for details.
Polymerisation leads to the formation of higher molecular weight fragments which upon further condensation lead to char. This route is as such not preferred and the rate of polymerisation should be reduced as much as possible. The preferred pathway involves the hydrogenation of the thermally labile components in the PL feed to stable molecules that are not prone to polymerisation. Subsequent reactions (hydrogenations and hydrocracking) on a time scale of hours lead to products with reduced oxygen contents and ultimately to higher H/C ratios.

Among all the components in PLs, carbonyl-containing molecules and sugars (the so-called water soluble fraction or pyrolytic sugars) play a major role in polymerization reactions. Examples are reactions of monomeric sugars, which are known to form hydrochars upon heating. These reactions involve sugar dehydrations (e.g. glucose to HMF) accompanied by the formation of humin type of products [21].

**6.3 Reactivity of various component classes in pyrolysis liquids**

As mentioned earlier, PLs can be fractionated using various methods, among others solvent extraction. A simple method involves the addition of water to PLs, which will result in the formation of a brown precipitate (pyrolytic lignin) and a water fraction enriched in oxygenates. Catalytic hydrotreatment of the two fractions, supported by model component studies, has given valuable insights into the reactivity of various component groups. The water soluble fraction (pyrolytic sugars) is known to be by far more reactive at low temperature (< 200°C) than the water insoluble fraction (pyrolytic lignin). Carbonyl-containing molecules like small aldehydes and ketones in the water soluble fraction are readily converted, most likely hydrogenated, to the corresponding alcohols at temperatures below 180 °C. Examples are the hydrogenation of glycolaldehyde to ethylene glycol [39] and hydroxyacetone to 1,2-propanediol [48]. Sugar monomers like glucose are known to be hydrogenated at...
temperatures as low as 80 °C to among others sorbitol [49-51], but higher temperatures (around 250 °C) are required for the full conversion of anhydrosugars, e.g. levoglucosan [52, 53], and sugar oligomers [54, 55]. The pyrolytic lignin fraction is less reactive and hydrocracking reactions occur at temperatures above 300 °C, resulting in mono-phenolics followed by hydrocarbon formation by hydrodeoxygenation reactions [53]. Among all components classes in PLs, organic acids (except formic acid) are the most persistent and temperatures higher than 400 °C are required to observe reactivity [53]. An overview of the reactivity of various organic component classes is given in Figure 8 [53].

Figure 8 Reactivity of the various organic component classes in PLs versus reaction temperature [53]

The high reactivity of the water soluble fractions was further confirmed by Wildschut et al. [56] Carbonyl-containing molecules and sugars are readily converted using Ru/C as the catalyst at 350 °C in 4 h, while no significant changes were observed for
the water insoluble, pyrolytic lignin fraction, indicated as the DCM-insolubles in Figure 9. [56] The total amounts of hydrocarbons increased at prolonged reaction times at the expense of carbonyl-containing molecules and sugars.

![Figure 9 Composition of PLs and hydrotreated product oils (Ru/C, 350 °C, 200 bar) at various reaction times using solvent–solvent extraction [56]](image)

Thus we can conclude that in order to obtain stabilised oils with good thermal stability, the catalyst should possess a high activity for carbonyl-containing and sugar components of PLs.

### 6.4 Application of product oils from catalytic hydrotreatment reactions

The typical products from a catalytic hydrotreatment reaction include a gas phase, an oil phase, an aqueous phase and char. For hydrotreatments below about 180°C, the organic and aqueous phases are miscible and form one liquid phase. For the oil phase, a high energy density, high H/C ratio, a good thermal stability, a limited amount of organic acids and a high solubility in apolar solvents is preferred. The actual oxygen content of the product oil can be tuned, for instance to the 10 wt% range (for co-feeding purposes in existing FCC units) and to less than 1 wt% for direct use as a transportation fuel, by adjustment of the process severity.

### 7. Catalysts development for the catalytic hydrotreatment of pyrolysis liquids

PLs are complex mixtures of monomeric and oligomeric molecules, with a high diversity in molecular structures. Examples are carboxylic acids, aldehydes, ketones,
sugars, and lignin monomers and oligomers. In addition, the water content of PLs is reported as high as 30 wt%. These features put serious constraints on the design of efficient catalysts for the hydrotreatment reactions. Catalysts developed for the hydrotreatment of various fossil (crude) oil fractions are not necessary suitable for use with PLs. A good catalyst should have a good hydrogenation activity for a broad range of organic compounds with different reactivities in the low temperature range, be stable in acidic water at elevated temperatures and removal of coke deposits should be possible, preferably by simple oxidative treatments. [57] Catalyst stability is thus of prime importance. Main deactivation mechanisms mentioned in the literature for catalysts used in catalytic hydrotreatment processes are: a) sintering of active metals, resulting in a decrease in surface area of active metals, b) leaching of active metals due to the presence of carboxylic acids in the PL feed, c) limited stability of the support material in acidic media under hydrothermal conditions, leading to a collapse of the structure of the catalysts, and d) accumulation of inorganic components from the PL feed on the catalysts surface that block the active sites. [58-60]

A range of catalysts have been reported in the literature for the catalytic hydrotreatment of PLs. [61] In the following part of this chapter, the results on the catalytic hydrotreatment of PLs derived from lignocellulosic biomass using noble metal catalysts (e.g. Ru, Pt, Pd, Rh), and non-noble metal, mainly Ni based catalyst, are summarized. The catalytic hydrotreatment of PLs diluted by solvents like alcohols [62-65], decalin [66], 1-methylnaphthalene [67] and PL fractions including the water soluble [68] and water insoluble fraction [69, 70] are beyond the scope of this chapter. Model component studies are also not reported, details can be found in recent review papers from Wang [71] and Robinson [72].

### 7.1 Noble metal based catalysts

Supported noble metals (Pt, Pd, Ru and Rh) are widely used for industrial hydrogenation processes because of their high catalytic activity, allowing operation at low temperature and pressure, and good catalyst stability. [73] Besides, some noble metals are resistant to poisoning with O-, S- and N-containing compounds. [61] As such, noble metal based catalysts have been studied in detail in the last two decades. An overview of catalytic hydrotreatment studies of PLs using supported noble metal catalysts is given in Table 6. A distinction is made between batch and continuous
operation. Noble metals include Pt, Pd, Rh and Ru supported on various supports like activated carbon, TiO$_2$, Al$_2$O$_3$, ZrO$_2$.

### 7.1.1 Studies in batch set-ups

Wildschut et al. [74] reported the catalytic hydrotreatment of PLs using Ru/C (commercial and homemade catalysts) in a batch reactor set-up (Table 6, entry 1). The catalytic hydrotreatment of PLs using a commercial Ru/C catalyst at 350 °C and 200 bar hydrogen yielded about 55 wt% of an oil phase with a H/C ratio of 1.24. Solids/char formation was in the order of 3 wt%. After 2 catalyst recycle runs, the oil yield decreased to around 30 wt% with an H/C ratio of 1.08, whereas the amounts of char increased to 20 wt%, indicative for substantial catalyst deactivation. Furthermore, nine Ru/C catalysts were synthesized using different Ru precursors (RuCl$_3$, Ru(NO)$_3$(NO$_3$)$_3$ and Ru(acac)$_3$) and Ru loadings (1, 3 and 5 wt%) to determine the effect of catalyst precursor on catalyst performance for the hydrotreatment of PLs (350 °C, 200 bar for 4.3 h). The best results with respect to hydrogenation activity, as expressed by the H/C ratio of the product (1.32), were obtained for the catalyst prepared with RuCl$_3$ (5 wt%).

Elkasabi et al. [75] studied the catalytic hydrotreatment of PLs from switchgrass (320 °C, 145 bar of H$_2$ for 4 h) using Pt, Ru, or Pd on carbon catalysts in a batch autoclave (Table 6, entry 2). Organic product yields between 36.2-46.6 wt% were obtained. Pt/C performed the best in terms of hydrogen consumption and deoxygenation level (O/C ratio of 0.15).

Mercader et al. [76] reported the catalytic hydrotreatment of PLs and fractions thereof at different temperatures (220, 270 and 310 °C) under a constant total pressure of 190 bar using a 5 wt% Ru/C catalyst in a batch autoclave (Table 6, entry 3). Around 53-58 wt% of product oil with oxygen contents between 26.7-15.6 wt% were obtained. The oils from the PL fractions were evaluated by co-processing with an excess of fossil feeds in catalytic cracking and hydrodesulfurisation (HDS) lab-scale units. All co-processing experiments were conducted successfully without operational problems.
Table 6 Overview of catalytic hydrotreatment of PLs using supported noble metal catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>PLs</th>
<th>Reactor type</th>
<th>Catalyst</th>
<th>Condition</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Beech wood derived PLs</td>
<td>Batch</td>
<td>Ru/C</td>
<td>350 °C, 200 bar, 4 h</td>
<td>[74]</td>
</tr>
<tr>
<td>2</td>
<td>Switchgrass derived PLs</td>
<td>Batch</td>
<td>Ru/C, Pt/C, Pd/C</td>
<td>320 °C, 145 bar, 4 h</td>
<td>[75]</td>
</tr>
<tr>
<td>3</td>
<td>Forest residue derived PLs</td>
<td>Batch</td>
<td>Ru/C</td>
<td>220-310 °C, initial H₂ pressure of 100 bar followed by 190 bar for 4 h</td>
<td>[76]</td>
</tr>
<tr>
<td>4</td>
<td>White oak derived PLs</td>
<td>Batch</td>
<td>Ru/C, Pt/C, Pd/C</td>
<td>320 °C, 128 bar, 15 h</td>
<td>[77]</td>
</tr>
<tr>
<td>5</td>
<td>Corn stover derived PLs</td>
<td>Batch</td>
<td>Ru/C, Pd/C</td>
<td>200 or 300 °C, 125 bar, 4 h</td>
<td>[78]</td>
</tr>
<tr>
<td>6</td>
<td>Beech wood derived PLs</td>
<td>Batch</td>
<td>Ru/C, Ru/TiO₂, Ru/Al₂O₃, Pt/C and Pd/C</td>
<td>250 °C, 100 bar, 4 h and 350 °C, 200 bar, 4 h</td>
<td>[79]</td>
</tr>
<tr>
<td>7</td>
<td>Pinewood derived PLs</td>
<td>Batch</td>
<td>Pt/ZrO₂, Pd/ZrO₂, Rh/ZrO₂, RhPt/ZrO₂, RhPd/ZrO₂ and PdPt/ZrO₂</td>
<td>350 °C, 200 bar total pressure, 4 h</td>
<td>[80]</td>
</tr>
<tr>
<td>8</td>
<td>Beech wood derived PLs</td>
<td>Batch</td>
<td>Ru/C</td>
<td>350 °C, 200 bar total pressure, 1-6 h</td>
<td>[56]</td>
</tr>
<tr>
<td>9</td>
<td>Forest residue derived PLs</td>
<td>Batch</td>
<td>Ru/C</td>
<td>230-340 °C, 4 h, 290 bar total pressure</td>
<td>[81]</td>
</tr>
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<td>10</td>
<td>Oak derived PLs</td>
<td>Semibatch</td>
<td>Pd/C, Pd/char, Pt/char, and Ru/char</td>
<td>150-280 °C for stabilization, 340-400 °C for hydrodeoxygenation, 69-169 bar</td>
<td>[82]</td>
</tr>
<tr>
<td>11</td>
<td>Mixed wood derived PLs, 2nd corn stover derived PLs, Poplar derived PLs (hot-filtered)</td>
<td>Continuous</td>
<td>Pd/C</td>
<td>1 stage packed bed reactor First stabilization: 0.25 LHSV, 340 °C, 138 bar Then HDO: 0.2 LHSV, 405 °C, 103 bar</td>
<td>[83]</td>
</tr>
<tr>
<td></td>
<td>Forestry residue derived PLs</td>
<td>Continuous</td>
<td>Ru/C</td>
<td>Two fixed bed reactors  Stabilization: WHSV of 3.3 h⁻¹, 100 °C, 200 bar  HDO: WHSV of 3.3 h⁻¹, 150-360 °C, 200 bar</td>
<td>[84]</td>
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</tr>
<tr>
<td>13</td>
<td>Pine wood derived PLs</td>
<td>Continuous</td>
<td>Ru/C</td>
<td>4 stages packed bed reactor in series  Temperature: 175/225/375/400, WHSV 5.4 kg oil kg⁻¹ cat h⁻¹, 241 bar</td>
<td>[5]</td>
</tr>
<tr>
<td>14</td>
<td>Pine wood derived PLs</td>
<td>Continuous</td>
<td>Ru/C + (NiMoS/γ-Al₂O₃, CoMoS/C)</td>
<td>2 stages packed bed reactors in series  Temperature: 170 °C in the 1st stage and 250 to 400 °C in the 2nd stage  LHSV: 0.19 LₚL/(Lₜₐtₐ) 75-150 bar</td>
<td>[85]</td>
</tr>
<tr>
<td>15</td>
<td>Wood derived PLs</td>
<td>Continuous</td>
<td>Ru/TiO₂</td>
<td>2 stages packed bed reactors in series  120-160 °C, 10.3 MPa, liquid hourly space velocity of 0.40 h⁻¹</td>
<td>[86]</td>
</tr>
<tr>
<td>16</td>
<td>Pine derived PLs</td>
<td>Continuous</td>
<td>Ru/C</td>
<td>81-83 °C, 84 bar, LHSV: 0.48-0.95 L/L/hr</td>
<td>[87]</td>
</tr>
</tbody>
</table>
Mullen et al. [77] reported the mild batch hydrogenation of the PLs produced from white-oak at 138 bar H₂ and 320 °C over Ru/C, Pd/C and Pt/C catalysts (Table 6, entry 4). The results revealed that Ru and Pd catalysts were more effective than Pt for deoxygenation reactions. The highest H/C ratio of 1.87 and lowest O/C ratio of 0.32 was obtained using the Ru/C catalyst.

Capunitan et al. [78] studied the hydrotreatment of corn stover PLs and distilled fractions thereof using noble metal catalysts such as Ru and Pd on carbon support at 125 bar, 4 h reaction time and two different temperatures (200 °C and 300 °C) in a batch reactor (Table 6, entry 5). Results showed that Ru performed better than Pd at higher temperature (300 °C) giving a deoxygenation level of about 25–26%. In addition, higher yields (54–67 wt.%), higher H/C molar ratios (1.46–1.48) and lower O/C molar ratios (0.065–0.08) were obtained using Ru. Analysis of the chemical composition of the products indicated that the major reactions involve hydrogenation of ketones to alcohols. The hydrotreated product from the distillate fraction with Ru as the catalyst at 300 °C gave the lowest oxygen content (7.0 wt.%). Product properties were determined, and for instance the water content was 2.6%, the acidity was 5.3 mg KOH/g sample, and the heating value was 40.2 MJ/kg, which makes the product a potentially interesting feed for co-processing with crude oils in existing refineries.

Wildschut et al. [79] investigated the hydrotreatment of PLs using a series of heterogeneous noble-metal catalysts include Ru/C, Ru/TiO₂, Ru/Al₂O₃, Pt/C, and Pd/C. The reactions were carried out at two temperatures (250 and 350 °C) and pressures (100 and 200 bar) in a batch autoclave. Among all the noble metal catalysts studied, the Ru/C catalyst was found to be superior to other catalysts with respect to oil yield (up to 60 wt%) and deoxygenation level (up to 90 wt %) (Table 6, entry 6).

Ardiyanti et al. [80] reported the catalytic hydrotreatment of PLs from pinewood at 350 °C, 200 bar pressure for 4 h using mono- and bi-metallic catalysts based on Rh, Pt, Pd on a zirconia support in a batch set-up (Table 6, entry 7). Pd/ZrO₂ showed the highest activity, followed by Rh/ZrO₂. Upgraded oils with the best product properties were obtained with Rh/ZrO₂. For this catalyst, the TGA residue, which is a measure for coking tendency, was 13.4 wt% and the Mw of the upgraded oil (748 g/mol) was lowest. All noble metal catalysts showed higher activities per gram of metal than the benchmark catalyst CoMo/Al₂O₃. Hydrotreatment reactions at variable batch times
were performed using the Rh/ZrO$_2$ catalyst to gain insights in reaction pathways and showed the involvement of competitive hydrogenation and polymerisation pathways at the initial stage of the process. Temperature programmed oxidation (TPO) measurements of spent catalysts showed the presence of carbonaceous deposits on the catalyst (2–6 wt%). These deposits may be removed by oxidation at temperatures lower than 600 °C without changing the morphology of the catalysts. Wildschut et al. [56] reported the use of Ru/C (5 wt%) as a catalyst for the hyrotreatment of PLs at 350 °C and 200 bar pressure in a batch reactor set-up (Table 6, entry 8). Highest oil yields (65 wt%) were obtained after 4 h using a 5 wt% intake of catalyst on PL. Longer reaction times lead to a reduction of the oil yield due to the formation of gas phase components. A solvent–solvent extraction procedure was applied to gain insights into the molecular transformations during the catalytic hydrotreatment experiments. It appears that specifically the carbohydrate fraction is very reactive. The observations were rationalized by a set of reaction pathways for the various product phases.

Shell [81] patented a process for the catalytic hydrotreatment of PLs derived from forestry residue at 230-340 °C for 4 h under 290 bar total pressure using a Ru/C catalyst in a batch autoclave to produce biofuels (Table 6, entry 9). At low temperature (230-260 °C), a bottom oil in a yield of around 47-49 wt% was obtained with an oxygen content between 24.4-28.0 wt% and MCRT values between 9.1-11.7 wt%. At higher temperatures (300-340 °C), top oils in 48-50 wt% yield were obtained. The lowest oxygen content was 15.5 wt%, the lowest MCRT was 1.8 wt%, obtained at 330 °C.

French et al. [82] studied the catalytic hydrotreatment (150-280 °C for stabilization, 340-400 °C for hydrodeoxygenation, 69-169 bar) of PLs derived from oak using Pd/C (activated), Pd/char, Pt/char, Ru/char and a NiMo–S in a semibatch reactor to determine the effects of catalyst type on the quality of the product oils (Table 6, entry 10). The organic product yield ranged from 24-42 wt% (about 51-77% of the carbon in the feed) and the products showed a low oxygen content (5 wt%) and acidity.

7.1.2. Studies in continuous set-ups

Elliott et al. [83] reported the hydroprocessing of PLs from mixed wood in a fixed bed reactor using a Pd/C catalyst (Table 6, entry 11). Reactions were performed at a range of conditions (310 and 375 °C, 138 bar) and a LHSV between 0.18 and 1.12 h$^{-1}$. 

36
An oil phase was obtained in a yield of 0.62 g/g dry feed with a H/C ratio of 1.43 at 340 °C and a LHSV of 0.25 h⁻¹. The set-up was successfully operated for 8 to 102 h on stream.

Bi et al. [84] performed catalytic hydrotreatment studies of PLs from forestry residue in two fixed bed reactors (Table 6, entry 12). The reaction temperature in the first reactor was kept at 100 °C for stabilization, the second reactor was maintained at 150-360 °C. The pressure was set at 200 bar. Both the PL feed and product oils were analyzed by negative-ion ESI FT-ICR MS. The PL feed contained mainly O₂–O₁₈ species with double bond equivalent (DBE) values between 0 and 22. After catalytic hydrotreatment, the oxygen numbers reduced to O₁–O₁₀, and the DBE values also decreased. The amounts of major oxygen containing compounds such as carbonyls, carboxylic acids, ethers, carbohydrates, and alcohols considerably changed upon the hydrotreatment process. Hydrogenation of the carbonyls, carbohydrates, and furans occurred below 150 °C. Dehydration, hydrodeoxygenation, and dehydration–hydrogenation reactions were observed above 210 °C. Decarboxylation and decarbonylation required higher temperatures (>300 °C). Lignin polymers were depolymerized after reduction of the carbonyl and methoxy groups.

Venderbosch et al. [5] investigated the catalytic hydrotreatment of PLs in a 4 stage packed bed reactor at different process severities using the benchmark Ru/C catalysts (Table 6, entry 13). The results revealed that catalytic hydrogenation and thermal (non-catalytic) polymerization are parallel reactions, as shown in Scheme 8. Polymerization leads to the formation of higher Mw fragments, especially during the low temperature stabilisation step as shown in Figure 10. The TG residue, a good indicator for thermal stability of an oil sample, shows the same tendency as the Mw. This clear increase in Mw and TG residue in the stabilisation step points out that the initial activity of Ru/C is not sufficiently high to suppress the polymerization of thermally labile components, e.g. carbonyl-containing compounds and sugars. High Mw fragments with high TG residues will undergo further condensation reactions, ultimately forming char. This char may lead to catalyst deactivation and reactor plugging.
Figure 10 TG and Mw of the organic phases after catalytic hydrotreatment using Ru/C catalyst in 4 stages packed bed reactors [5].

The low initial hydrogenation activity of Ru/C type of catalysts was also confirmed by Elliott and co-workers (Table 6, entry 14) [85]. They reported the catalytic hydrotreating of PLs using a two stage packed bed reactor with a first catalyst bed composed of Ru/C for low temperature stabilization (at around 170 °C) and a second bed with sulfided CoMo or NiMo on Al₂O₃ for high temperature hydrocracking reactions (at around 400 °C) (Table 6, entry 13). The results revealed that the formation of higher Mw fragments and char in the first bed led to an increase in pressure drop over time and all tests were terminated in less than 100 h. In a subsequent study, hydrotreatment experiments were performed in the two stage packed bed reactor with a PL feed which was pre-hydrotreated at 140 °C using the same procedures [88]. The run was successful and a cumulative runtime of 1440 h was reported without major operational issues.

Wang et al. [86] investigated the low temperature stabilization of PLs derived from wood in a 2 stage packed bed reactor using a homemade Ru/TiO₂ catalyst at 120-160 °C (Table 6, entry 15). Hydrogen uptake was around 3.8-12.4 mmol/g PL for 48 h tests. Hydrogenation of the sugar fraction was confirmed by ¹³C-NMR; hydrogenation of smaller aldehydes and ketones was shown to take place by performing carbonyl content measurement. Hydrogenation reaction of sugars to
sugar alcohols, ketones and aldehydes to alcohols significantly improved the thermal stability of the PLs and allowed for better performance in the second high temperature, deep hydrotreatment step.

Elliot et al. [87] patented a process for stabilizing PLs with hydrogen as the reactant in the presence of Ru/C at low temperature (81-83 °C, 84 bar) in a trickle-bed (down flow) reactor configuration (Table 6, entry 16). The carbonyl content was reduced slightly from 4.2-7.0 for the feed to 3.1-3.4 (C %) for the product oil. Aging of the product oils was studied by monitoring the viscosity upon heating at 80 °C for 24 h. A viscosity increase of about 5.2 % was observed for the product oil compared to 42 % for the fresh PL feed.

As such, it can be concluded that noble metal based catalysts have been used successfully for the hydrotreatment of PLs. However, the catalysts are in general not sufficiently active in the initial stabilisation stage of the catalytic hydrotreatment of PLs and, combined with their high prices, the identification of cheap metal based catalysts with high hydrogenation activity for the thermally labile components in PLs in the low temperature stabilization step has been pursued actively.

### 7.2 Non-noble metal based catalysts

The first non-noble metal based catalysts explored for the catalytic hydrotreatment of PLs were typical hydrodesulphurization (HDS) catalysts, viz sulfided NiMo or CoMo/γ-Al2O3 [46, 69, 82, 89-91]. Close to quantitative deoxygenation levels have been reported [89]. A continuous supply of a sulfur-containing compound is required to keep the catalyst in the sulfided form, which is essential to maintain high catalytic activity. As such, these catalysts are less attractive for the hydrotreatment of sulfur-free biomass streams.

Investigations using non-sulfided noble metal free catalysts are mainly focusing on nickel, promoted by Cu, Fe, Pd or Mo, supported on activated carbon, TiO2, ZrO2, Al2O3 or SiO2. An overview of the results on the catalytic hydrotreatment of PLs using such catalysts is given in Table 7.

Ardiyanti et al. [92] reported the catalytic hydrotreatment of PLs using bimetallic Ni-Cu catalysts on various supports (CeO2–ZrO2, ZrO2, SiO2, TiO2, rice husk carbon, and Sibunite) at 350 °C, 200 bar total pressure in a batch autoclave (Table 7, entry 1). The metal contents ranged from 7.5 to 9.0 (Ni) and 3.1–3.6 wt.% (Cu) for the inorganic supports and 17.1–17.8 (Ni) and 7.1–7.8 (Cu) for the carbon supports. After reaction,
a product oil was isolated in yields between 35.9-45.5 wt% on PL feed. The product with the highest H/C ratio (1.43) and lowest TG residue (2.7 wt%) was obtained using Ni-Cu on TiO$_2$[92]. However, char formation was still high (4.1 wt%), indicating that the rate of hydrogenation in the initial stage of the process is not sufficiently high to suppress thermal polymerization.

Ardiyanti et al. [93] also performed catalytic hydrotreatment experiments for PLs using bimetallic NiCu/$\delta$-Al$_2$O$_3$ catalysts at 350 °C in a batch autoclave (Table 7, entry 2). The catalysts are characterized by various Ni/Cu ratios (0.32 to 8.1 w/w) at a fixed total metal intake of about 20 wt%. Hydrotreatment of PLs was performed for 1 h at 150 °C followed by 3 h at 350 °C, at 100 bar initial pressure and yielded an upgraded oil. Best performance was found for the catalyst with a Ni to Cu wt% ratio of eight. For this catalyst, hydrogen consumption was the highest (146 NL/kg PL feed), the oil had a high H/C ratio of 1.35, a low Mw of 500 g/mol, and a low TGA residue of 6.8 wt%.

Cheng et al. [94] reported the catalytic hydrotreatment of PLs from prairie cordgrass using 34 bar of H$_2$ at 350 °C in a batch autoclave (Table 7, entry 3). Supported Ni catalysts on activated carbon including Ni/AC, Ni-Fe/AC, Ni-Mo/AC and Ni-Cu/AC (6% metal content) were used. All catalysts gave product oils with improved properties compared to the PL feed (water content, pH, oxygen content, higher heating value and chemical compositions). The oxygen content was reduced from 68.81 % for the feed to 21.70–25.88% for the products. As a result, the higher heating value increased from 11.33 for the PL feed to 29.65 - 31.61 MJ/kg for the products. Ni/AC gave a product oil with 33% of hydrocarbons (C6–C12) in the gasoline range. For Ni-Mo/AC, a product oil with the highest content of gasoline blending alkyl-phenols (38%) was obtained.
Table 7 Catalytic hydrotreatment of PLs using nickel based catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>PLs</th>
<th>Reactor type</th>
<th>Catalyst</th>
<th>Condition</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Pine wood derived PLs</td>
<td>Batch</td>
<td>Ni-Cu/TiO$_2$, Ni-Cu/CeO$_2$-ZrO$_2$, Ni-Cu/ZrO$_2$, Ni-Cu/CRH, Ni-Cu/Sibunite, Ni-Cu/δ-Al$_2$O$_3$</td>
<td>110 bar H$_2$, 150 °C for 1 h and 350 °C for 3 h</td>
<td>[92]</td>
</tr>
<tr>
<td>2</td>
<td>Pine wood derived PLs</td>
<td>Batch</td>
<td>Ni-Cu/δ-Al$_2$O$_3$ with various Ni/Cu ratios</td>
<td>100 bar H$_2$, 150 °C for 1 h and 350 °C for 3 h</td>
<td>[93]</td>
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<tr>
<td>3</td>
<td>Prairie cordgrass derived PLs</td>
<td>Batch</td>
<td>Ni/AC, Ni-Fe/AC, Ni-Mo/AC, Ni-Cu/AC</td>
<td>34 bar H$_2$, 350 °C, 5 h</td>
<td>[94]</td>
</tr>
<tr>
<td>4</td>
<td>Pine sawdust derived PLs</td>
<td>Batch</td>
<td>Ni/HZSM-5</td>
<td>40 bar H$_2$, 240 °C, 3 h</td>
<td>[95]</td>
</tr>
<tr>
<td>5</td>
<td>Pine sawdust derived PLs</td>
<td>Batch</td>
<td>Reduced Ni-Mo/γ-Al$_2$O$_3$</td>
<td>200 °C, 2 h, 30 bar</td>
<td>[90]</td>
</tr>
<tr>
<td>6</td>
<td>Pine sawdust derived PLs</td>
<td>Batch</td>
<td>Reduced Ni-Mo/CNT</td>
<td>100–250 °C, 2–10 h, 50-60 bar</td>
<td>[96]</td>
</tr>
<tr>
<td>7</td>
<td>Pine wood derived PLs</td>
<td>Batch/Continuous</td>
<td>Ni-Cu/SiO$_2$,Ni-Cu/SiO$_2$ and Kaolin, Ni-Pd/SiO$_2$, Ni-Cu/SiO$_2$-ZrO$_2$-La$_2$O$_3$</td>
<td>120 bar H$_2$, 150 °C for 1 h and 350 °C for 3 h</td>
<td>[58, 43]</td>
</tr>
</tbody>
</table>
Zhang et al. [95] reported the catalytic hydrotreatment of PLs from pine sawdust using a 10 wt.% Ni/H-ZSM-5 (Si/Al = 38) catalyst at 240 °C in a batch autoclave (Table 7, entry 4). A single liquid phase was obtained after reaction, with a water content considerably higher than the PL feed (52.0 versus 38.3 wt%) due to hydrodeoxygenation and polymerization reactions. The pH of the product oil increased from 2.27 to 4.07, and the hydrogen content increased from 6.28 to 7.01 wt%. The decrease in acidity is advantageous from an application point of view. The spent catalyst was characterized by thermogravimetry analysis (TGA) and revealed the presence of large amounts (up to 36 wt%) of organic residues on the catalyst surface, likely formed by polymerization of reactive species in the PLs.

Xu et al. [90] reported the upgrading of PLs from pine sawdust using reduced Ni-Mo/γ-Al₂O₃ catalysts at 200 °C, 30 bar for 2 h in a batch autoclave (Table 7, entry 5). After reaction, a single phase oil was obtained with a water content of 59.0 wt%, compared to 46.2 wt% for the feed. The pH value increased from 2.16 to 2.84 due to the conversion of organic acids, which was confirmed by GC. The amount of aldehydes and ketones in the product oil was lower than for the PL feed (from 47.0 to 26.1%, GC peak area), whereas a slight increase in alcohol content was observed (23.0 for the feed to 25.6% in the product, GC peak area). The H content of the product oil was higher than the feed (6.93 wt.% versus 6.61 wt% for the feed).

Zhou et al. [96] studied the upgrading of PLs from pine sawdust using a reduced Ni-Mo/CNT catalyst at 100–250 °C under 5-60 bar hydrogen in a batch autoclave (Table 7, entry 6). After reaction, a single liquid product was obtained with a higher water content than the feed (from 42.8 to 51.8 %). The pH increased from 2.92 to 3.68, indicative for the conversion of organic acids under the prevailing conditions. The H content of the product (11.26%) was considerably higher than the feed (8.40%).

The use of novel bimetallic Ni-Cu/Pd catalysts for the catalytic hydrotreatment of PLs, referred to as Picula™ catalysts, was reported by Ardiyanti et al. [58]. The catalysts were prepared using a sol-gel method and are characterized by a high metal loading (i.e. Picula™ Cat D: 57.9 wt% Ni, 7 wt% Cu, and 35.1 % SiO₂, Table 7, entry 7 and Table 8 for details).
Catalytic hydrotreatment of pine wood derived PLs in batch autoclaves were performed (Table 7, entry 7 for details). The catalysts show clear advantages compared to the benchmark Ru/C catalyst. Examples are a low methane production rate as shown in Figure 11, which has a positive effect on the hydrogen consumption. The best performance was obtained using Picula\textsuperscript{TM} Cat B with Pd as the promoter, giving an oil phase with highest H/C ratio (1.51) and lowest TG residue (0.7 wt%). The results revealed that Pd is a better promoter compared to Cu for the Picula\textsuperscript{TM} catalysts studied. Further product analyses revealed that the reduced tendency for char formation is likely due to a higher hydrogenation activity of the Picula\textsuperscript{TM} catalysts for thermal labile components in PLs at low temperature (below 200 °C). As such, the rate of polymerization reactions is considerably suppressed.

Further catalytic hydrotreatment studies on PLs using noble metal free Picula\textsuperscript{TM} Cat D were performed in a continuous reactor configuration consisting of a packed bed reactor with 4 individual reactors arranged in a series configuration. Deactivation of the catalyst and clogging by char formation, a typical phenomenon for Ru/C, was not observed for the Picula\textsuperscript{TM} Cat D at extended times on stream [43].
From the above results, it is clear that the Picula™ catalysts show considerably better performance for the catalytic hydrotreatment of PLs compared to the benchmark Ru/C catalyst as well as the Ni based catalysts with low metal loadings. It was postulated that this good performance is due to a high activity for thermally labile carbonyl-containing molecules and sugars at low temperature (below 200 °C), thereby reducing the tendency for char formation.

The stability of the Picula™ catalysts was investigated for up to 400 h time-on-stream in a 4 stage packed bed reactor. Reactor clogging was not observed to a significant extent though some catalyst deactivation occurred. [43] Further characterization studies on spent and regenerated Picula™ catalysts (Ni-Pd/SiO₂) revealed that the regenerated catalysts have a considerably lower surface area compared to the fresh catalysts and also show some agglomeration of active metal nanoparticles, see TEM images in Figure 12. [58]
8. Conclusions

PLs contain substantial amounts of oxygenated molecules, e.g. carboxylic acids, aldehydes, ketones, sugars and lignin monomers and oligomers, etc. The presence of carboxylic acids renders the PLs acidic in nature. High water content and high oxygen content results in a relatively low energy density, and carbonyl-containing molecules and sugars are considered to be the main reason for the limited thermal stability during storage and coke formation when heating PLs.

Catalytic hydrotreatment is a promising technology for the upgrading of PLs. Tuning of the oxygen content of the product is possible by proper selection of process conditions. The use of the product oils for co-feeding in existing FCC refinery units (mixed with crude oil derivatives, e.g. vacuum gas oil, oxygen content around 10 wt%) or direct use as a transportation fuel (oxygen content less than 1 wt%) have been considered. However, polymerization may occur during the catalytic hydrotreatment of PLs, leading to the formation of larger Mw fragments, which react further to char, resulting in catalysts deactivation and reactor clogging. As such, it is of high importance to identify catalysts which have a high activity at relatively low temperatures to avoid polymerisation of reactive components. Various types of catalysts have been studied for
the catalytic hydrotreatment of PLs in the last decade. Noble metal based catalysts are expensive and show low hydrogenation activity, especially in the initial low temperature stabilisation step and these drawbacks limit their application as attractive catalysts for PL upgrading. Non-noble metal catalysts, mainly Ni based, have also been tested for the catalytic hydrotreatment of PLs. The results reveal that the activity of nickel based catalysts with a low metal loading (< 10 wt%) is still insufficient to fully eliminate char formation. Picula™ catalysts developed by our group in cooperation with BTG, the Netherlands and the Boreskov Institute of Catalysis (BIC, Russia) are characterized by a high metal loading, small metal nanoparticles and show higher activity in the low temperature range compared to noble metal based catalysts. Bimetallic catalysts also seem to have good potential and particularly Pd is shown to be a good promotor.

9. Thesis outline
The research described in this thesis involves the catalytic hydrotreatment of PLs and fractions thereof as well as model component studies using heterogenous catalysts. The overall objectives are the development of improved hydrotreatment catalysts, both with respect to activity and stability, as well as a better understanding of the molecular transformations taking place during the process. As such the thesis includes catalyst synthesis, preparation and characterisation studies, experimental hydrotreatment studies in both batch and continuous set-ups and the use of advanced analytical techniques for characterisation of PL feeds and products (for instance GC x GC and HSQC-NMR).

In Chapters 2 and 3, exploratory catalyst screening studies on the catalytic hydrotreatment of PLs using Ni based catalysts promoted by Cu, Pd and Mo are reported. In Chapter 2, studies on the catalytic hydrotreatment of PLs at temperatures between 80-410 °C using a Ni-Cu catalyst characterised by a high Ni loading (46 wt% Ni) in both batch and continuous set-ups are described. The effect of process variables on product yield, hydrogen consumption, coke formation and relevant product properties (total acid number, carbonyl number, H/C ratio, molecular weight distribution and TG residue) were determined. The objectives of this study were to gain insight in i) relevant product properties of the upgraded oils (such as flash point, viscosity, acidity and coking tendency) as a function of the reaction temperature and ii) the molecular
transformations taking place at the various temperatures to assess the reactivity of various component classes in the PLs. For the latter, the product oils were analysed using a range of (analytical) techniques, including advanced GC x GC, 1H-NMR, GPC, CAN, TAN and IR spectroscopy. The results for the batch and continuous experiments were compared and are discussed. Finally, catalyst characterization studies (BET, XRD, TEM, etc.) were carried out to assess changes in catalyst structure and composition during the hydrotreatment reaction.

In Chapter 3, studies on the catalytic hydrotreatment of PLs using Mo promoted Ni based catalysts at 350 °C, 140 bar H₂ for 4 h in a batch reactor are described. Organic carbon yields in the oil phase and relevant product oil properties (H/C ratio and TG residue) for the Mo based catalysts were compared with Cu and Pd promoted catalysts as well as a monometallic Ni catalyst and a benchmark Ru/C catalyst.

Experimental studies on the reactivity of the two main fractions of PLs, viz the sugar rich fractions and pyrolytic lignin fraction, are reported in Chapter 4 and 5. In Chapter 4, the catalytic hydrotreatment of specifically the sugar fraction of PLs over Ni based catalysts with various Ni contents (38-57 wt.%), promotors (Pd, Cu and Mo) and support materials (SiO₂, SiO₂-ZrO₂ and SiO₂-Al₂O₃) are provided. A monometallic Ni catalyst supported on SiO₂-Al₂O₃ was used as a reference catalyst to gain insights in promotor effects. All experiments were performed using isolated sugar fractions (pyrolytic sugars) from PLs as the starting material at 180 °C, 120 bar H₂ for 4 h in a batch reactor. The catalysts were characterised using a wide range of techniques (TEM, XRD, CO chemisorption, TPR) before and after reaction. Relevant properties of the hydrotreated products such as elemental composition, water content and molecular weight distribution were determined to evaluate catalyst performance. The best catalyst was also tested for the hydrotreatment of a 50 wt% pyrolytic sugar solution in water in a 4 stage continuous reactor set-up to gain insights in operational stability and to obtain sufficient amounts of product samples for detailed characterisation and further testing.

Chapter 5 concerns the catalytic valorisation of the pyrolytic sugar fraction from PLs using hydrotalcite based Cu-PMO catalyst in sc-MeOH and EtOH (275 °C, 50 bar H₂). The products were characterised by various techniques (GPC, TGA). In addition, model compound studies, using levoglucosan and D-cellobiose were performed to gain insights into the chemical pathways taking place during the hydrotreatment process. The catalyst
was characterized by various techniques, including XRD, NH$_3$-TPD, BET, and TEM. In addition, recycling tests were performed to determine catalyst stability.

In Chapter 6, a model component study is reported involving levoglucosan, the most abundant sugar derivative in PLs. Reactions were performed in water using a bifunctional Ru catalyst on a mesoporous carbon support (CMK-3). This support is characterized by a large surface area and a highly oxygen-functionalized surface containing acid sites. For comparison, hydrogenation of levoglucosan using a commercial Ru/C catalyst was also carried out. In addition, the scope of the catalytic reaction was investigated by performing reactions with disaccharides like cellobiose and sucrose. Various techniques (nitrogen physisorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), NH$_3$-temperature programmed desorption (NH$_3$-TPD) and H$_2$-temperature programmed desorption (H$_2$-TPD)) were used to gain insights in the texture and acidity of the Ru/CMK-3 catalyst. Finally, catalyst stability was investigated by performing a number of batch experiments with recycled catalyst.
References


Chapter 1


