On the Chemical Conversion of Lignin and Lignin Streams \textit{via} Reductive Routes

Dissertation

zur Erlangung des Grades eines Doktors der Naturwissenschaften

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Referent: Dr. Roberto Rinaldi

Korreferent: Prof. Dr. Martin Muhler
Preface
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<table>
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<tbody>
<tr>
<td>2-MeTHF</td>
<td>2-Methyl tetrahydrofuran</td>
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<tr>
<td>2-PrOH</td>
<td>2-Propanol</td>
</tr>
<tr>
<td>4-O-5</td>
<td>Biphenyl ether linkages</td>
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<tr>
<td>ATR-IR</td>
<td>Attenuated Total Reflectance Infrared Spectroscopy</td>
</tr>
<tr>
<td>BTX</td>
<td>Benzene, toluene, xylene</td>
</tr>
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<td>CP-MAS</td>
<td>Solid-state nuclear magnetic resonance</td>
</tr>
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<td>Da</td>
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<tr>
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<td>MCH</td>
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<td>Mechanocatalytic Precipitate Lignin</td>
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<td>pCA7</td>
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<td>SR</td>
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CHAPTER 1

Overview

Catalysis plays a critical role in the production of commodity chemicals from crude oil.\textsuperscript{1} Heterogeneous catalysis is key to approximately 90\% of such processes in the petroleum refinery.\textsuperscript{2} Biomass is expected to be a sustainable carbon source that can replace oil within the current refinery scheme.\textsuperscript{3-5} Several similarities can be drawn between the petrochemical processes and biofuel production.\textsuperscript{6} However, the great differences in composition between crude oil and biomass make utilization of biomass challenging.\textsuperscript{7} The high oxygen content leads to poor quality fuels and for this reason (hydro)-deoxygenation processes have to be applied. Deoxygenation of biomass can be achieved \textit{via} hydrogenation and hydrodeoxygenation (HDO). In both circumstances, a hydrogenation catalyst is required in order to activate hydrogen, which is then added to the substrate. Raney Ni is an inexpensive skeletal metal catalyst. By using concentrate sodium hydroxide solutions, this heterogeneous catalyst is produced \textit{via} the partial leaching of aluminum from an Ni-Al (1:1) alloy. Skeletal Ni catalysts have been employed for several types of reaction, including hydrogenation, transfer hydrogenation,\textsuperscript{8} hydrogenolysis,\textsuperscript{9,10} and dehydrogenation.\textsuperscript{11} In this thesis, Raney Ni is investigated as an H-transfer catalyst for hydrogenolysis and hydrodeoxygenation of lignin, which is one of the major components of
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lignocellulosic biomass. The goal is selective deconstruction of lignin into intermediates for the production of value-added chemicals.

In *Chapter Two*, an introduction of biomass composition and structure is provided. The primary existing fractionation processes of lignocellulosic biomasses are succinctly reviewed. Furthermore, the state-of-the-art utilization of biomass-derived commodities and catalytic processes recently developed for the production of chemicals from lignin are introduced.

In *Chapter Three*, hydrogenolysis reactions of lignin are described. Raney Ni is selected as a hydrogenation, catalyst and molecular hydrogen (H₂) is added to the lignin structure in order to depolymerize lignin into corresponding monomers. Together with hydrogenolysis, which leads to the production of *ortho*-methoxyphenols, hydrogenation of the ring occurs and cyclohexanols are obtained. Lignin feedstocks were obtained from an organosolv process and from the mechanocatalytic depolymerization of wood. A comparison of processes performed on these raw materials shows that the conversion is higher for the organosolv lignin compared to lignin obtained *via* the mechanical catalytic depolymerization of wood (MCP-L). The difference in reactivity may be related to the poor solubility of MCP-L in organic solvents (*e.g.* acetone). However, other factors may also influence the conversion of lignin (*e.g.* carbohydrate content and condensation).

In *Chapter Four*, the procedure for mechanical catalytic depolymerization of wood is improved. The saccharification step is performed in the presence of 2-methyl tetrahydrofuran (2-MeTHF) water mixture. Lignin is mostly extracted into the organic layer (2-MeTHF), whilst carbohydrates (*e.g.* cellulose and hemicellulose) are depolymerized into monomers and recovered in aqueous phase. The obtained lignin (E-L) exhibits high solubility in organic solvents and, therefore, higher reactivity than MCP-L. Moreover, hydrogenolysis reactions, performed in the presence of Raney Ni and H₂, leads selectively to *ortho*-methoxyphenols without saturation of the ring.
In Chapter Five, a low-temperature deoxygenation route,\textsuperscript{13} performed in the presence of Raney Ni and a solid acid catalyst, is applied to a variety of phenol in order to convert them into arenes. 2-Propanol (2-PrOH) is employed as the hydrogen source for the hydrogenation of phenol into cyclohexanol, which is dehydrated by the solid acid catalyst into cyclohexene. Raney Ni catalyzes the dehydrogenation of cyclohexene into benzene as a tandem process. The reaction conditions are optimized and applied to a lignin-derived bio-oil.\textsuperscript{14}

Finally, in Chapter Six, a new procedure for the selective conversion of phenol into arenes is described. Raney Ni alone catalyzes the selective conversion of phenol derivatives into arenes in the presence of alkanes, which can be also employed as a hydrogen source. The presence of a solvent with low basicity is strictly necessary for this reaction. Indeed, a solvent with high basicity (e.g. 2-PrOH, 2-MeTHF) could inhibit the Lewis acidic sites of Raney Ni and lead to hydrogenation of the ring. The stability of the catalyst is explored and enhanced by using stoichiometric quantities of alcohols. Furthermore, the reaction is successfully applied to the reaction of a lignin-derived bio-oil.
CHAPTER 2

State of the Art

2.1 Biomass composition and Lignin structure

The energy content of lignocellulosic biomass is sourced from sunlight. Plants are able to convert solar energy into chemical energy through photosynthesis. Carbon dioxide (CO₂) and water (H₂O) are converted into cellulose, hemicellulose and lignin. These biopolymers represent the most abundant renewable organic resource on earth. Far small amounts of proteins, lipids and other simple sugars are also incorporated into the plants together with inorganic compounds.¹⁵

Cellulose constitutes up to 50% of lignocellulose composition. It is a polymer of β-glucose linked by β-1,4-glycosidic bonds. Cellulose is insoluble in most common solvents due to of the strong inter- and intramolecular hydrogen-bonding network between -OH groups of the glucose units.¹⁶ ¹⁷ Therefore, the structure of cellulose is physically protected by its intrinsic crystallinity, and therefore, highly resistant against depolymerization and further chemical conversion. Nevertheless, new reactive media have been successfully applied to dissolve and depolymerize cellulose. In 2002, Rogers et al. introduced the use of dialkylimidazolium chloride ionic liquid as a solvent for cellulose,¹⁷ and more recently Rinaldi reported the
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instantaneous dissolution of cellulose in organic electrolyte solutions.\textsuperscript{18} Therefore, these researches have demonstrated that it is possible to disassemble the supramolecular structure of cellulose, activating it towards hydrolytic processes.\textsuperscript{16,19}

In contrast to cellulose, hemicellulose is composed of varied C$_5$ and C$_6$ sugars. Hemicellulose consists of linear and branched chains that render it more easily hydrolyzed compared to cellulose as the branched nature of this biopolymer prevents it from crystallization with a H-bonded supramolecular structure as those of cellulose.\textsuperscript{20}

Lignin constitutes up to 30% of biomass composition. It is primarily composed of para-propylated phenolic units and is the largest renewable source of aromatics on earth. Figure 2-1 describes the structure of wood and the distribution of lignin. The cell wall is composed of several layers whereby lignin concentration systematically decreases from the outer layer to the inner layer. Lignin in the outmost layer serves as a binding agent to hold the cells together whilst the lignin within the cell walls gives rigidity through chemical bonding with hemicellulose and cellulose microfibrils. Additionally, lignin offers several unique characteristics such as resistance to decay and biological attacks, UV absorbance, and water impermeability.\textsuperscript{21}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2-1.png}
\caption{Structure of wood and the distribution of lignin in the middle lamella (ML), primary wall (P) and secondary wall (S1, S2, S3) layers. Adapted from literature.\textsuperscript{21}}
\end{figure}
The characterization of lignin structure has benefited greatly from the development of new powerful tools for imaging lignin and analyzing its chemical structure. Early techniques employed for the evaluation of lignin structure include UV-Vis and infrared spectroscopies. Infrared spectroscopy has been employed as an indicator of the presence of band patterns corresponding to guaiacyl and syringyl units. Together with FTIR spectroscopic analysis, information about the structure of lignin has also been collected by chemical destructive techniques (e.g. acidolysis, thioacidolysis and nitrobenzene oxidation). In recent years, analysis of the lignin bonding motifs has been accomplished by using Nuclear Magnetic Resonance (NMR). Heteronuclear Single Quantum Coherence (HSQC)-type experiments have been designed for characterization of isolated lignin, or indeed the whole plant cell wall. Nevertheless, the polymeric structures of lignin are still poorly defined, incorporating many different varieties of linkage (although the alkyl aryl β-O-4 ether linkages are often most abundant). The primary monomeric units contained in lignin are: \( p \)-coumaryl alcohol (1), \( p \)-coniferyl alcohol (2) and \( p \)-sinapyl alcohol (3) (abbreviated once they are incorporated into lignin as “H”, “G” and “S” units respectively), displayed in Figure 2-2.

![Figure 2-2](image)

**Figure 2-2** The three primary lignin monomers; \( p \)-coumaryl alcohol (1), \( p \)-coniferyl alcohol (2) and \( p \)-sinapyl alcohol (3).

Functionalization of the aromatic ring is the distinguishing feature amongst these building blocks. \( p \)-Coumaryl alcohol (1) incorporates no methoxy (-OMe) substituents, \( p \)-coniferyl alcohol (2) contains an -OMe on one ortho position, while
both ortho positions are methoxylated in the p-sinapyl alcohol (3). Typically, both the overall abundance of lignin as well as the ratio between these monomers differ between species of plant. For example, in lignin of sugarcane bagasse, all three monomers are present in considerable quantities. In contrast, softwood species, e.g. pine, are mostly derived from p-coniferyl alcohol (G-units). In the case of hardwood, p-coniferyl (G-units) and p-sinapyl alcohols (S-units) are both present in ca. 50-70% and 25-50% abundances, respectively. In this biomass type, lignin incorporates only low levels of p-coumaryl alcohol (H-units, less than 5 %).

A section of the most common structural elements occurring in native lignins is shown in Figure 2-3. Enzymatic-initiated reactions are responsible for generating radicals, which subsequently undergo solution-like polymerization via cross-coupling reactions. The β-O-4 linkage is typically the most abundant linkage in the lignin structure, although the quantity of β-O-4 linkages varies greatly between different plants. The β-O-4 moiety is obtained by coupling of the phenolic –OH to the β position of the double bond of the propyl chain. Alternatively, the –OH can be also added to the α position, affording the α-O-4 linkage (although free α-O-4 structure are now know not to exist). Along with the most abundant linkage β-O-4, other varieties of ether linkages occur in the structure of lignin. The five-membered ring of the phenylcoumaran unit comprises both α-O-4’ and β-5’ linkages. Resinol structures are formed via β-β couplings, whilst dibenzodioxin linkages are obtained from the coupling of two oligomers.
2.2 Fractionation processes for lignocellulosic biomass

Due to its complexity, it is not trivial to isolate lignin without significantly modifying its structure and properties. Likewise, it is not trivial to define to which extent the polymer was modified. Moreover, pulping processes have so far been tuned to isolate cellulose whilst little attention has devoted to the fate of lignin. As a consequence, lignin has been commonly isolated as part of a liquor rich in degraded lignin, to which researchers have tried for decades to find applications. In this section, the most significant pulping processes will be reviewed. The conversion of lignin, isolated from these processes, to a value-added product in commercially-scalable processes still represents a significant challenge.36

2.2.1 Kraft lignin

Pulping processes have been developed in order to obtain a strong fibers of cellulose that can be used in the paper industry.37 The main process employed for the separation of lignin from wood is the Kraft process, applying NaOH and Na2S, which effectively breaks the linkages between lignin and cellulose, providing high purity cellulose.38 However, the obtained Kraft lignin contains sulfur, making the catalytic
conversion very challenging, since sulfur act as a poison to many catalysts. Thus, the obtained lignin is generally burned in order to supply energy to the system and for the recovery of the chemical (NaOH and Na₂S).

2.2.2 Lignosulfonates

The production of acid sulfite pulp proceeds similarly to Kraft pulping, except that different chemicals are used in the cooking liquor. In place of the caustic solution used to dissolve the lignin of wood, sulfurous acid is employed. To buffer the cooking solution, a bisulfite salt of sodium, magnesium, calcium, or ammonium can be used. Digestion is carried out at high temperature and under high pressure, in either batch mode or continuous digesters, and in the presence of a sulfurous acid/bisulfite cooking liquid. During this process, lignin is sulfonated, degraded and solubilized. Different functional groups are incorporated in this variety of lignin, for example phenolic hydroxyl groups, carboxylic acid and sulfur containing groups. The sulfur content of lignosulfonates obtained from sulfite pulping is substantial (e.g. 4–8%), rendering lignosulfonates soluble over almost the entire pH range. Also, the average molar mass of both sulfonated lignin fragments as well as the molar mass of the phenolic monomers of lignosulfonate is higher than that of Kraft lignin. Interestingly, the (apparent) average molecular weight of lignosulfonate from softwood (e.g. 60,000 Da) is significantly higher than that of the lignosulfonate from hardwood (e.g. 12,000 Da).

2.2.3 Organosolv lignin

Organosolv process has been developed as an alternative method to Kraft and lignosulfonate processes to separate the holocellulosic fraction from lignin. A primary advantage is that under careful conditions, the lignin framework may be isolated in close to native form, that is, with a large quantity of β-O-4 linkages still present in the polymeric chain. For instance, when reacted with phloroglucinol under acid conditions an Organosolv lignin gives a purple coloration. This suggests that a
portion of the cinnamaldehyde end units characteristic of lignin in its native state are still incorporated in the technical Organosolv lignin. Organosolv process typically consists of the extraction of lignin from wood using an organic solvent, carried out at temperature of approximately 200 °C. Hydrolysis of the acetyl functionalities in the hemicellulose brings about a decrease in the pH, due to the formation of acetic acid, which catalyzes the acid hydrolysis of the carbohydrate-lignin complex and extracts lignin into the organic media. For this reason, Organosolv processes are described as autocatalytic. Mixtures of water together with an alcohol (e.g. ethanol) are employed as the extraction media. After solvent evaporation, lignin is recovered as a solid. The process is sulfur free and the obtained lignin shows greater potential for subsequent catalytic upgrading to chemicals. Cellulose remains as a solid pulp after delignification. The primary drawback of this process is the high cost associated with solvent recycling and, until now, no Organosolv process has reached commercial scale.

2.3 Lignin as a source of energy

Although substantial global deposits of fossil energy resources still exist, they are unquestionably finite. In the long-term, therefore, the transition to an energy supply based on renewable sources of energy must be achieved. Such a change in the classical refinery scheme is gradually ongoing. The increasing interest and use of bio-based products is also justified by the dependence of developed countries (e.g. European countries) on imported fossil fuels in an instable oil and gas market, due to politically and socially unstable suppliers.

A comparison of the use of primary sources of energy, of the ratio of domestic supply to imports for Germany in 2003 and 2013, and relative shares in 2013 is shown in Figure 2-4. Germany has to import most of its energy fuel. Accordingly, Germany imports ca. 98 % of its crude oil and 88 % of its natural gas. However, the use of renewable energetic sources is increasing in the decade between 2003 and 2013 wherein 12 % of the currently energetic demand is supplied by renewable resources.
Liquid bio-fuels are used as replacements for conventional the fossil fuels, gasoline and diesel. Liquid bio fuel can be categorized as first, second and third generation. The first generation refers to ethanol produced from sugar or starch that is extracted from sugarcane, wheat, sugarbeet or maize. The produced ethanol can be blended in gasoline at fraction as high as 25% employed as a replacement for diesel, nevertheless it would be in competition with food supply. To avoid competition of bio-fuels with food crops, second generation bio-fuel involves the production of ethanol from waste lignocellulose (e.g. crop waste). Similarly, the production of third generation bio-fuels does not compete with food crops because it utilizes triglycerides accumulated by microalgae for the production of biodiesel.

![Primary Energy Consumption 2013](http://www.bgr.bund.de/EN/Themen/Energie/energie_node_en.html)

**Figure 2-4** Comparison of the use of primary sources of energy and of the ratio of domestic supply to imports for Germany in 2003 and 2013, and relative shares in 2013. Reprinted from: http://www.bgr.bund.de/EN/Themen/Energie/energie_node_en.html.

2.3.1 Hydrodeoxygenation processes

Lignin is currently supplied as a by-product of the pulp/paper industry and is anticipated to be soon available in even larger quantities via the emerging technology of 2nd generation cellulosic ethanol production. The energy contents of biomass feedstock scale linearly with the lignin content. Indeed, the high oxygen-content of...
cellulose and hemicellulose decreases the heating value of these substrates. Therefore, lignin can be regarded as a valid alternative substrate to carbohydrate-based feedstocks for the production of liquid fuels. However, due to the complex structure and the presence of a broad variety of complex linkages between the monomers, the conversion of lignin to value-added compounds is substantially more difficult than that of carbohydrates. Relative to liquid fuels (e.g. diesel), lignin has a lower carbon and hydrogen content and more oxygen. C and H tend to raise the heating value of a fuel whilst oxygen reduces it. It is therefore clear that for the conversion of lignin into liquid fuels, one of the critical consideration, is deoxygenation.

Hydrodeoxygenation (HDO) of phenol, a simple lignin model compound, has been studied as a promising strategy for the targeted production of alkanes or arenes from lignin. In both circumstances two catalysts are employed in ‘tandem’: a metal catalyst for hydrogenation in conjunction with an acid catalyst for dehydration. Hydrogen is added to phenol to decrease the oxygen content. Figure 2-5 shows the possible pathways for the hydrogenation of phenol.

![Figure 2-5 Reaction pathways for the hydrogenation of phenols.](image)

If pathway ‘a’ is followed, saturation of the ring occurs followed by hydrogenolysis of the C–O bond, leading to the formation of cyclohexane. High selectivity towards alkanes under low severity conditions is possible by employing a noble metal supported on carbon as the hydrogenation catalyst, in cooperation with
phosphoric acid as the acid catalyst.\textsuperscript{50} By contrast, hydrogenolysis of the phenolic – OH substituent converts the phenol to benzene and water. A further saturation step to form cyclohexane is possible, but not desirable, when nickel or noble metals are used.\textsuperscript{51,52} However, three equivalents of molecular hydrogen (H\textsubscript{2}) are required for pathway “a” whilst equimolar H\textsubscript{2} is required for complete pathway ‘b’ to benzene. Therefore, due to the high cost associated with the production of hydrogen,\textsuperscript{53} the selective deoxygenation of phenol to benzene is the more attractive route.

A catalytic route for the tandem dehydroxylation of phenol to benzene, performed over Raney Ni and a \( \beta \)-zeolite catalyst, was recently demonstrated.\textsuperscript{54} This system is advantageous because the necessary input of hydrogen (provided by 2-PrOH \textit{via} a transfer hydrogenation reaction) is stoichiometric and not in excess. Moreover, no external pressure is required. Arenes obtained from lignin can be easily included in the existing industrial processes such as the BTX (benzene, toluene, xylene) process chains.

2.3.2 \textit{Thermal degradation processes}

One alternative approach (to the production of liquid fuels from lignin) for the conversion of biomass into energy is the thermal degradation of lignocellulosic material. Gasification, direct combustion and pyrolysis are included within the category of thermal degradation processes.

Gasification is the thermochemical conversion of biomass into gaseous fuels by means of partial oxidation of the biomass at high temperatures. This process allows for the production of synthesis gas (CO and H\textsubscript{2}). Gasification also produces hydrocarbons, particularly in the lower temperature ranges.\textsuperscript{55}

Biomass can be also burned directly in waste-to-energy plants in the absence of any chemical processing, to produce steam for subsequent production of electricity. However, the remnant ash exhibits a high surface area and represents a hazard.\textsuperscript{15}
Pyrolysis is the thermal degradation of a lignocellulosic feedstock in the absence of oxygen (in order to avoid the combustion) into gas, liquid and a solid char. Pyrolysis is generally distinguished as “slow” or conventional and “fast” pyrolysis. In the conventional slow pyrolysis, biomass is heated to ca. 500 °C with a low heating rate (<10 °C/min). These conditions are favorable for the formation of char.56 In fast pyrolysis, temperature up to 500 °C are reached in very short reaction times (up to 2 s).57 The fast pyrolysis process affords high yields of liquid (up to 75 wt%), 15-25 wt% yields of solid char, and 10-20 wt% of non-condensable gases.58 Pyrolysis liquids are composed of depolymerized cellulose, hemicellulose and lignin. Rapid heating and rapid quenching “freezes in” the highly reactive intermediate derived from the fast degradation of hemicellulose, cellulose and lignin. It is possible to increase the quality of the pyrolytic bio-oil by combining pyrolysis with catalysis. The presence of the zeolite catalyst ZSM-5 leads to the pyrolysis of biomass into gasoline and renewable chemicals including benzene, toluene and xylenes in an one-step process.59 The addition of a catalyst generally brings about a decrease in coke formation, along with an increase in the quantity of extractable organic matter. Generally, a high quantity of catalyst is necessary for the catalytic fast pyrolysis. Therefore, high stability of the catalyst is critical. Coke formation and blockage of the active sites of the catalyst is a commonly-encountered reason for catalyst fouling. One drawback of the resultant pyrolytic bio-oil is the high content of oxygenated functional groups (e.g. carboxylic acid, aldehyde, alcohol), decreasing the stability of this oil over the time.

2.4 Catalytic hydrogen transfer reactions for the conversion of lignocellulosic feedstocks into chemicals

Several catalytic routes have been developed to convert lignocellulosic biomass into a mixture of compounds that show potential to replacing petroleum-based raw materials.60 As a source of renewable aromatic species, lignin can be depolymerized into ortho-methoxyphenols or alternatively converted into arenes to be consumed as a
fuel or fuel additive. Both depolymerization and deoxygenation processes required hydrogenolysis and hydrogenation, in order to decrease the molecular weight and the oxygen content, respectively.

Molecular hydrogen ($H_2$) has been employed together with a hydrogenating catalyst for these purposes.\textsuperscript{61-63} Pd/C is perhaps one of the most employed catalysts for the conversion of bio-derived phenols into alkanes using $H_2$.\textsuperscript{50,64} More recently, Selective hydrogenation of phenol into cyclohexanone can be achieved under atmospheric pressure of $H_2$ using palladium nanoparticles supported on mesoporous carbon nitrides.\textsuperscript{65}

Rinaldi and Wang highlighted that the activity of Raney Ni for the hydrogenation of Organosolv lignin with $H_2$ is enhanced in non-polar solvents (e.g. alkanes), whilst primary alcohols with basic properties, e.g. methanol, markedly reduce the catalytic activity towards hydrogenation of aromatic products.\textsuperscript{66} In that study, they show that catalytic performance similar to Pd catalyst can be obtained through the rational choice of reaction solvent.

Hydrogen transfer reaction is an alternative hydrogenation route, associated with a number of advantages compared to the use of $H_2$.\textsuperscript{67} Molecular hydrogen easily ignites and presents considerable risks, particularly on the large scale; the use of hydrogen donors obviates these drawbacks in that no gas containment is needed, no $H_2$-resistant pressure vessels are necessary, and simple stirring of the reaction solutions is typically sufficient. Moreover, it is possible to select and design the most appropriate hydrogen donor to give specificity to the reaction and enhance the selectivity of the reduction.\textsuperscript{68}

In the early 1950’s, Braude \textit{et al.} performed a pioneering investigation in the field of hydrogen transfer.\textsuperscript{69} Palladium was initially selected as the catalyst, since a decreasing activity was observed in the order $Pd > Rh > Ni > Pt$ for the transfer hydrogenation of 2-methylbuta-1,3-diene, employing 2-methylhydroquinone as the
hydrogen donor. Nonetheless, the hydrogen transfer reaction generally required longer reaction times and greater catalyst loadings compared to the corresponding conventional hydrogenation with H₂. Therefore, the use of a cheap Ni-based catalyst is preferred to the more expensive noble metals (e.g. Pd, Pt).

Different hydrogen donors such as cyclohexene, 1,4-cyclohexadiene, tetralin, hydrazine, formic acid and formates or alcohols have been investigated as hydrogen donors. Further advantages are gained when the products of the decomposing donor have large negative enthalpies of formation. For example, formic acid is converted into CO₂ and hydrazine into N₂, which provide added reactivity of these substances as hydrogen donors. 2-Propanol is among the most favored hydrogen donor solvents. It is an inexpensive, and nontoxic, solvent. It possesses good solvent properties, and is transformed into acetone, which is relatively benign and trivial to remove from the reaction medium via fractional distillation.

Due to the complex composition of lignocellulosic biomass, attempts to selectively convert cellulose, hemicellulose and lignin into specific or tailored chemicals are often unsuccessful. Instead, a broad range of products is usually formed. Hydrogen transfer methods have emerged as an efficient and selective tool for the reduction of biomass derived molecules in the presence of hydrogen donors. Ru/C as the catalyst and 2-PrOH as the hydrogen donor have been employed for the conversion of cellulose to sugar alcohols. In a different study, xylitol of high purity was produced from hemicellulose under mild conditions using 2-PrOH as the hydrogen source in the presence of a Ru/C catalyst. Other authors have demonstrated that Raney Ni catalyzes the transfer hydrogenation of ethyl levulinate (with 2-PrOH) into γ-valerolactone with a very low catalyst loading, at 298 K for 120 min. For the same type of reaction, Rinaldi et al. demonstrated that by carrying out a hydrogen transfer reaction with 2-PrOH, instead of the conventional hydrogenation with H₂, the hydrogenation and lactonization steps involved in the conversion of alkyl levulinates to γ-valerolactone can be decoupled owing to the thermodynamics
of reaction.\textsuperscript{74} Formic acid is another valid candidate to serve as a hydrogen source for the valorization of biomass-derived cellulosic feedstock.\textsuperscript{75-77}

As a simple model compound for lignin, phenol is hydrogenated in the presence of 2-propanol and Raney Ni, affording cyclohexanol yields of up to 99 \% at 80 °C after three hours.\textsuperscript{52} These extremely mild conditions can also be applied for the hydrogenation and deoxygenation of several phenolic models as well as bio-oil. Recently, we introduced a method for the catalytic upstream biorefining of lignocellulose into holocellulose and depolymerized lignin oil.\textsuperscript{78} Wood is subjected, in a batch reactor in a mixture of water and 2-PrOH (70/30 vol/vol), to Raney Ni in temperature range between 160-220 °C. Raney Ni is able to catalyze the hydrogenolysis of ether bonds by an H-transfer mechanism.\textsuperscript{66} 2-PrOH is employed as the H-donor in this circumstance, and during the process lignin fragments are released in the solution. Acidic media, due to the deacetylation of the hemicellulose with consequent formation of acetic acid, is responsible for the depolymerization and repolymerization of the lignin fragments.\textsuperscript{79} Reactive aldehyde functions incorporated in the lignin structure are primarily responsible for the repolymerization.\textsuperscript{80,81} The presence of the hydrogenation catalyst enables to hydrogenation of the highly reactive aldehyde functionality as they are realized into solution (as a result of the depolymerization of lignin). Simultaneously, hydrogenolysis of the $\beta$-O-4 and $\alpha$-O-4 linkages occurs. Hence, monomeric phenols are mostly obtained in solution. The spent catalyst can be easily separated from the mixture of reaction since Raney Ni is magnetic. After filtration and evaporation of the solvent a lignin bio-oil is obtained. The cellulosic fraction of the wood is obtained as a holocellulosic pulp. The enzymatic hydrolysis of this pulp is comparable to the pulp obtained \textit{via} Organosolv processes.

Recently, it was demonstrated that the conversion of phenol into benzene is possible in a one-pot process when a nearly stoichiometric quantity of 2-PrOH is employed.\textsuperscript{54} Raney Ni catalyzes the transfer hydrogenation of phenol to
cyclohexanol. Subsequently, the intermediate cyclohexanol is dehydrated over a solid acid catalyst (H-BEA-35) yielding cyclohexene, which is then converted into benzene via aromatization of the ring (transfer dehydrogenation). Hence, cyclohexene is employed as the hydrogen donor for continuous hydrogenation of phenol by Raney Ni. Benzene was achieved in 90% yield at 160 °C in 4 hours.

H-transfer hydrogenation has been selected as a mild hydrogenation protocol that can efficiently convert phenolic compounds to cyclohexanone under economical and energy-efficient conditions. One route to cyclohexanone production from phenol involves hydrogenation to form cyclohexanol, followed by dehydrogenation to give cyclohexanone.82-84 Alternatively, formic acid, a component of bio-oil, and sodium formate has been selected as H-donors for the selective hydrogenation of phenol into cyclohexanone. New Pd-based catalysts have been developed for this purpose.85,86

Figure 2-6 summarizes the main products originating from the conversion of lignin in H-transfer reaction.

**Figure 2-6** Selective pathways for the catalytic depolymerization of lignin into chemicals via hydrogen transfer.

Hydrogen transfer reactions can definitely broaden the possibility for valorization of lignin-derived phenolic mixtures. Cyclohexanone is widely consumed in the industrial production of caprolactam and adipic acid,87,88 which are the
monomers for manufacturing Nylon-6, Nylon-66, and polyamide resins.\textsuperscript{85} Defunctionalization of lignin into simple aromatic species may prove to be a lucrative way for the conversion of lignin into high-value aromatics and fine chemicals (e.g. phenols, cresol). Moreover, the large quantities of residual lignin isolated from pulping processes can be fed into the production of higher-volume, lower-value bulk chemicals.\textsuperscript{89} The global production of benzene, toluene and xylene (BTX) in 2012 was 80 million tons per year,\textsuperscript{90} sufficient volumes so as to warrant large-scale utilization of lignin.
CHAPTER 3

Hydrogenation of lignin obtained from the mechanocatalytic upstream biorefining

In this chapter, the hydrogenation of the solid residue obtained from the saccharification of water-soluble lignocellulose (hereforth called MCP-L) with molecular hydrogen (H₂) in the presence of Raney Ni as a hydrogenation catalyst will be described. To compare the chemical reactivity of MCP-L to other varieties of lignins, hydrogenation of an Organosolv Lignin (OS-L) was also performed. MCP-L and OS-L were obtained from three different biomass feedstocks: beechwood, pinewood and sugarcane as examples of hardwood, softwood and grasses, respectively. The samples were initially characterized to obtain a deeper understanding of the precise structure of such lignins. Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR), Thermogravimetric Analysis (TGA) and Elemental Analysis were performed on the lignin samples. GC×GC-MS analysis of the products from thioacidolysis was performed to compare quantities of remnants β-O-4 linkages incorporated in the lignins produced by the two processes. Finally, hydrogenolysis reactions were performed on the lignin samples at 200 °C and 300 °C and the liquid product (LP) and solid residue (SR) of reaction were analyzed. MCP-L yields lower quantities of LP compared to the OS-L at 200 °C, whilst at 300 °C no differences were
observed in the conversion and the selectivity of the products for the two varieties of technical lignin.

3.1 Introduction

For comprehensive valorization of a lignocellulosic biomass feedstock, lignin has to be converted into value-added chemicals. Due to its nature, the depolymerization of lignin into monomers is an attractive route for the production of phenols and methoxyphenols, because these aromatic compounds have a high market value and can be utilized for many industrial processes. Hydrogenolysis is an economically feasible route for the depolymerization of lignin into aromatic compounds owing to the relatively low demand of hydrogen by this process. The primary ‘drawback’ of hydrogenolysis of lignin into phenols is that cyclohexanols are often formed as side products in significant quantities. After hydrogenolysis of the ether bonds of the lignin feedstock, ortho-methoxyphenols may undergo demethoxylation followed by saturation of the ring. Alternatively, lignin can be used as a feedstock for the production of liquid fuel although the intrinsically high oxygen content must be reduced for this purpose. For instance, lignin has been converted via hydrodeoxygenation (HDO) into mixtures of alkanes, useful as fuel or fuel additives, under relatively mild condition. Nevertheless, because of the high demand of hydrogen for full saturation of the ring this route is not economically attractive and, therefore, the HDO of phenols to arenes is more desirable.

Notably, the conversion of lignin does depend not only on the catalyst or catalyst system but also on the chemical nature of the lignin stream itself.

Recently, the mechanocatalytic route for the depolymerization of biomass into ‘water-soluble lignocellulose’ (WSL) was introduced. The overall process together with the appearance of the conversion of wood upon mechanocatalytic process and saccharification is described in Scheme 3-1.
Scheme 3-1 Schematic representation of the method for fractionation of plant biomass into water-soluble monosaccharides and lignin (adapted from literature), and the appearance of the conversion of wood upon mechanocatalytic process and saccharification.

The three-step process represented in Scheme 3-1 is able to fractionate wood into a solid lignin and sugar monomers. The first step is impregnation of the substrate (e.g. wood, cellulose) with a stoichiometric amount of acid in a low boiling point solvent (e.g. diethyl ether). After solvent evaporation, the acid is dispersed on (the surface of) the substrate. In the second step, the acid-impregnated substrate is subjected to solid state depolymerization, via use of a ball mill. During ball milling, kinetic energy is transferred to the lignocellulose substrate and, simultaneously, the
acid is homogeneously distributed throughout the substrate. The process has been described as ‘mechanocatalytic’ because the energy afforded by the collision of the balls with the substrate is needed for overcoming the activation energy for the conformational change of the polymer, promoting access to the β-1,4-glycosidic bond. The contact of the glycosidic oxygen with the H⁺ species is necessary in order to catalyze the depolymerization of cellulose. The third step consists of saccharification, wherein the water-soluble holocellulose fraction of the substrate after ball milling is depolymerized by heating to 145 °C. At this temperature, hydrolysis of the saccharide fraction is obtained while lignin precipitates as solid residue. By simple filtration, it is then possible to separate the lignin from the carbohydrates.

In this Chapter, the properties of the lignin precipitates from beechwood, pinewood and sugarcane (as examples of hardwood, softwood and grasses, respectively) are presented. Most importantly, the reactivity of the lignin precipitates towards reductive processes is examined, comparing the performance of processing of lignin precipitates and organosolv lignins in the presence of Raney Ni and H₂ pressure.

3.2 Characterization of the lignin precipitates

To better understand the chemical reactivity of the technical lignin feedstocks, preliminary characterization of the structure is needed. Lignin is an aromatic and considerably oxygenated polymer composed of monolignols with a 4-propylphenol backbone, bonded together typically by ether bonds, involving the phenolic –OH units and the propyl chains. The differences in monomer distribution and the prevalence of different linkages are responsible for the high diversity in lignin structure. Moreover, the different extraction processes, affording different isolated ‘technical’ lignin, can contribute to substantial changes in structure and can be responsible for the formation of new carbon-carbon bonds between phenolic units during the fractionation process rending the lignin structure more recalcitrant to
further depolymerization. Different analytic techniques are needed for a full characterization of lignin; however, characterization of MCP-L in liquid phase is rendered difficult because of the low solubility in conventional solvents. In this chapter, therefore MCP-L lignin has been characterized using Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR), Thermogravimetric Analysis (TGA) and Elemental Analysis in order to obtain a deeper understanding of the structure. A comparison to an OS-L is also described.

Figure 3-1 shows a comparison between the fingerprint region of the ATR-IR spectra of the MCP-L and analogues extracted with an organosolv processes (OS-L). The continuous lines refer to OS-L, while the dashed lines denote to MCP-L samples (from pinewood, sugarcane and beechwood). Peak assignment is summarized in Table 3-1.

In each set of spectra, the fingerprint region is very similar, indicating that the precipitates are indeed mostly formed of lignin. Surprisingly, the “core” of the structure of the lignin precipitates did not differ from that of the corresponding Organosolv lignins. The two varieties of lignin (MCP-L and OS-L) have similar functional groups as revealed by the presence of the similar stretching frequencies.
Figure 3-1 Attenuated Total Reflectance Infrared (ATR-IR) spectra of lignins from pinewood OS-L (a) and MCP-L (b), beechwood OS-L (c) and MCP-L (d), sugarcane OS-L (e) and MCP-L (f).
Table 3-1 Assignment of the ATR-IR spectra for Fig. 1

<table>
<thead>
<tr>
<th>Peak</th>
<th>Range</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wavenumber/cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1738-1709</td>
<td>C=O stretch in unconjugated ketones</td>
</tr>
<tr>
<td>2</td>
<td>1605-1593</td>
<td>Aromatic skeletal vibration plus C=O stretch</td>
</tr>
<tr>
<td>3</td>
<td>1515-1505</td>
<td>Aromatic skeletal vibration</td>
</tr>
<tr>
<td>4</td>
<td>1470-1460</td>
<td>C-H deformation</td>
</tr>
<tr>
<td>5</td>
<td>1430-1422</td>
<td>Aromatic skeletal vibrations combined with C-H</td>
</tr>
<tr>
<td>6</td>
<td>1330-1325</td>
<td>S ring</td>
</tr>
<tr>
<td>7</td>
<td>1270-1266</td>
<td>G ring plus C=O stretch</td>
</tr>
<tr>
<td>8</td>
<td>1166</td>
<td>C=O in ester group</td>
</tr>
<tr>
<td>9</td>
<td>1125-1128</td>
<td>Aromatic C-H in-plane deformation</td>
</tr>
<tr>
<td>10</td>
<td>1035-1030</td>
<td>Aromatic C-H in-plane deformation, plus C-O</td>
</tr>
<tr>
<td>11</td>
<td>990-966</td>
<td>(trans) -HC=CH- out of the plane deformation</td>
</tr>
<tr>
<td>12</td>
<td>860-850</td>
<td>Aromatic C-H out-of-plane deform</td>
</tr>
<tr>
<td>13</td>
<td>835-834</td>
<td>C-H out-of-plane in position 2 and 6 of S, and in all positions of H unit</td>
</tr>
</tbody>
</table>

To determine the thermal stabilities of lignin, Thermogravimetric Analysis (TGA) was performed. Figure 3-2 shows the percentage mass loss in weight % when the lignin samples (8 mg) were heated from 40 °C to 1000 °C (5 °C min⁻¹), under an argon atmosphere.
Hydrogenation of lignin obtained from the mechanocatalytic upstreaming biorefining

Figure 3-2 Thermogravimetric analysis (TGA) of technical lignins from beechwood (a), pinewood (b) and sugarcane (c) produced via mechanocatalytic depolymerization (MCP-L) or organosolv extraction (OS-L).

All samples (Fig. 2) exhibit a similar decomposition profile, whereby the onset of thermal decomposition occurs at approximately 200 °C. At temperature of 300 °C each of the samples underwent ca. 10% weight loss. At the end of the experiment, the % mass loss was in the range 55-60%. This observed behavior of OS-L is in agreement with previous reports. The derivative curves highlight that for beechwood OS-L and MCP-L the highest mass loss rates occur at approximately 357 °C, therefore, both lignins behave similarly upon heating of the samples. Conversely, for pinewood and sugarcane the derivative curve of OS-L has a maximum ca. 20-30 °C earlier the derivative curve of MCP-L. Hence, the extreme degradation rate was recorded at the lower temperature for OS-L than MCP-L for these two varieties of lignin.
Elemental compositions of the substrates were also determined. Figure 3-3 shows the Van Krevelen’s diagram of the investigated lignins, in which the molar ratio of carbon/hydrogen and oxygen/carbon are reported. MCP-L has higher O/C ratio than the OS-L.

![Van Krevelen’s diagram of the technical lignin, OS-L and MCP-L.](image)

**Figure 3-3** Van Krevelen’s diagram of the technical lignin, OS-L and MCP-L.

The differences in the H/C ratio for beechwood lignins are small and within the measurement error. For pinewood, MCP-L has a higher H/C ratio than OS-L. In sugarcane samples, this difference is more pronounced. Sugarcane has a larger content of hemicellulose than beechwood and pinewood. Perhaps, degraded products from the hemicellulose fraction are responsible for this different behavior among the samples. For all the samples, the quantity of sulfur is below the limit of detection.

From the results, it can be concluded that the structure, composition and stability of the technical lignins obtained by organosolv and mechano-catalytic processes are similar. Differences primarily related to the elemental composition, whereby a higher quantity of oxygen is observed for the MCP-L compared to the OS-L, indicating a possible hydration of the structure during the saccharification step or a content of residual saccharides higher in the lignin precipitates than in the
corresponding OS-L. Although similar in structure (ATR-IR), MCP-L is less soluble in organic solvents compared to the OS-L. The difference in solubility suggests that the MCP-L is more condensed, higher molecular structures have been formed by the mechanocatalytic process,\textsuperscript{108} or even polysaccharide residues are present.

3.3 Thioacidolysis

In order to determine the quantities of uncondensed units remaining in OS-L and MCP-L thioacidolysis was performed on the beechwood, pinewood and sugarcane lignins. Thioacidolysis is an acid-catalyzed reaction performed in presence of a solution of dioxane-ethanethiol and boron trifluoride etherate.\textsuperscript{26} \(\beta\)-O-4 linkages are quantitatively cleaved by thioacidolysis whilst condensed units are not converted into monomers. Scheme 3-2 demonstrates the mechanism for the acid-catalyzed depolymerization of \(\beta\)-O-4 linkages into thioethylated monomers and it also shows the structures of the thioacidolysis products obtained from lignin. GC\texttimes{}GC-FID chromatograms of trimethylsilylated products from thioacidolysis of beechwood OS-L (a) and beechwood MCP-L (b) are highlighted in Figure 3-4.
Scheme 3-2 Schematic representation of the acid-catalyzed depolymerization of β-O-4 linkage into thioethylated monomers and the structures of thioacidolysis products from various isolated lignins.

Figure 3-4 GC×GC-FID chromatograms of trimethylsilylated derivated of beechwood OS-L (a) and MCP-L (b) after thioacidolysis.
The primary products identified by the thioacidolysis assay of beechwood samples were the thioethylated monomers from the aryl-glycerol-β-aryl ether structures derived from coniferyl (compound 6) and sinapyl alcohols (compound 7). Semi-quantitative analysis of the monomers obtained by thioacidolysis is rendered possible by GC×GC-FID. Table 3-2 displays the ratios of compounds 1, 2, 3, 4, 6 and 7 between OS-L and MCP-L for beechwood, pinewood and sugarcane. The yields of thioethylated monomers for OS-L and MCP-L are shown in Figure 3-5. Compounds 6 and 7 were isolated from OS-L in 221 and 662 μmol/g, respectively. This data is consistent with previous literature. Products X1 and X2 are not related to lignin but to other impurities (e.g. xylans).

Table 3-2 Ratio of compounds 1, 2, 3, 4, 6 and 7 isolated from OS-L and MCP-L.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Beechwood OS-L/MCP-L</th>
<th>Pinewood OS-L/MCP-L</th>
<th>Sugarcane OS-L/MCP-L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.37</td>
<td>2.62</td>
<td>1.41</td>
</tr>
<tr>
<td>2</td>
<td>0.71</td>
<td>0.46</td>
<td>0.72</td>
</tr>
<tr>
<td>3</td>
<td>13.45</td>
<td>-</td>
<td>11.05</td>
</tr>
<tr>
<td>4</td>
<td>1.37</td>
<td>-</td>
<td>0.37</td>
</tr>
<tr>
<td>6</td>
<td>2.24</td>
<td>0.98</td>
<td>1.04</td>
</tr>
<tr>
<td>7</td>
<td>3.41</td>
<td>-</td>
<td>1.39</td>
</tr>
</tbody>
</table>

In an Organosolv process, acidic conditions combined with high temperature (e.g. 180 °C) are known to partially cleave β-O-4 linkages. With respect to S-units, β-O-4 linkages are 3-4 times higher in the OS-L than in the analogous MCP-L and 2 times higher in quantity for G-units. Therefore, the mechanocatalytic process in our investigation is more effective than the comparable organosolv process in terms of the depolymerization of beechwood lignin, especially with respect to the S-units.
Figure 3-5 μmol/g of thioacidolysis products obtained from beechwood, pinewood and sugarcane, OS-L (a) and MCP-L (b).

Compounds 1 and 3 are originated from benzaldehyde end groups of the uncondensed G and S-units, respectively. Benzaldehyde end groups may be incorporated into the structure of the native lignin or may be produced upon fractionation process. Notably, far higher quantities of compounds 1 and 3 are incorporating into the OS-L sample compared to MCP-L. The benzaldehyde end-groups that could occur in the structure of the native lignin may be more stable during the mild acid conditions of the organosolv process, yet are likely unstable during the mechanocatalytic process leading to repolymerization of these functionalities into carbon-carbon bonded moieties.

Compounds 2 and 4 originate from the vinyl ether structures of uncondensed G and S-units, respectively. Compound 8 is derived from depolymerization of the uncondensed H-units. However, compound 8 is isolated only in trace quantities in the MCP-L and it is not incorporated in the OS-L. Therefore, beechwood lignin is composed of low quantities of H-lignin, or the H-units are linked primarily by carbon-carbon bonds.
Hydrogenation of lignin obtained from the mechanocatalytic upstreaming biorefining

Figure 3-6 shows the GC×GC-FID chromatograms of trimethylsilylated products from thioacidolysis of pinewood OS-L (a) and pinewood MCP-L (b).

![GC×GC-FID chromatograms](image)

Figure 3-6 GC×GC-FID chromatograms of trimethylsilylated derivated of pinewood OS-L (a) and MCP-L (b) after thioacidolysis.

Compound 6 is the primary product obtained from pinewood, which is understandable on the basis that pine is mostly composed of guaiacyl structures. For OS-L, the content of compound 6 in the mixture was 135 μmol/g. The ratio of compound 6 is approximately 1.0 between the two varieties of lignins. Surprisingly, these observation suggest that the mild acidic conditions of the organosolv process (pH 4.5) are sufficient to bring about the depolymerization of G-units in pinewood to an equal extent as the stronger sulfuric acid used during the mechanocatalytic process. Benzaldehyde end units, which may be found in native structure of lignin or are possibly related to a partial liberation of such structures on mild acid treatment, are detected in large quantity in the OS-L, whilst for MCP-L benzaldehyde end units are incorporated in only trace quantities, as previously observed for beechwood. Conversely, vinyl ether structures (2) are incorporated in MCP-L to a far great extent than in OS-L.

The GC×GC-FID chromatograms of trimethylsilylated products from thioacidolysis of sugarcane OS-L (a) and sugarcane MCP-L (b) are shown in Figure 3-7.
The primary products of the thioacidolysis performed on sugarcane samples were the thioethylated monomers arising from the aryl-glycerol-β-aryl ether structures derived from coniferyl (compound 6) and sinapyl (compound 7) alcohols, respectively, obtained in GC-yields of 37.2 and 162 μmol/g in OS-L. HSQC data, discussed in the following section of this thesis, confirm that small quantities of the H-units are incorporated in sugarcane OS-L and ‘WSL’. Therefore, the H-units incorporated in the lignin samples are likely to be linked by carbon-carbon bonds. Indeed, p-coumaryl alcohol, incorporated in the H-units, is potentially very reactive towards electrophilic aromatic substitution. This is because the hydroxy group, -OH, is a strongly activating, ortho-/para- directing substituent. However, because the para position is blocked by a hydroxypropyl chain, ortho substitution occurs. Similar to pinewood, the G-units are affected in the same manner in the two processes (indicated by a ratio of compound 6 close to one). Conversely, the stability of the S-units is higher in the organosolv process than in the mechanocatalytic process. This finding suggests that stronger acids are required for depolymerization of the S-units than G- and H-units. Compound 11, arising from ferulate units, is quantitatively produced from both kind of lignins with a ratio OS-L/MCP-L of 1.5.30

Figure 3-5 shows the μmol/g of thioacidolysis products obtained from OS-L and MCP-L, which gives an idea regarding of cleavable linkages in each material.
Beechwood OS-L yields three times higher quantities of monomers than MCP-L. Much lower yields of thioacidolysis products are obtained from pinewood and sugarcane lignins. This finding is in agreement with previous reports, where low yields of thioacidolysis products are observed for straw samples, indicating that lignins from grasses may have more carbon-carbon linkages or a higher content of residual carbohydrates than hardwood lignins. Moreover, for sugarcane and pinewood, the quantities of thioacidolysis products are comparable between the lignins isolated by the two processes. Beechwood is mostly composed of S-Lignin which is more stable during acid conditions and leads to higher quantities of thioacidolysis products. Conversely, the G- and H-units, which largely can be found in the structures of pinewood and sugarcane lignins, easily brings about condensation reactions that lower the yields of monomers. This finding highlights that the quality of the substrate obtained by a fractionation process of biomass is highly influenced by the structure of the material in the native state.

3.4 Hydrogenolysis of lignins. Characterization of the liquid (LP) product of reaction

To compare the reactivity of OS-L and MCP-L in a heterogeneous catalytic system, the lignin feedstocks were processed by hydrogenolysis. Hydrogenolysis of lignin was performed at 200 and 300 °C in the presence of H\textsubscript{2} (70 bar), using Raney Ni as hydrogenating catalyst. 2-PrOH was selected as the solvent because Raney Ni is highly active in the presence of secondary alcohols. Moreover, lignin is slightly soluble in 2-PrOH while practically insoluble in non-polar solvents (e.g. alkanes). Therefore, the small lignin fragments, which arise from hydrogenolysis and thermolysis of lignin, may be solubilize in 2-PrOH upon formation, lowering the quantities of lignin that decompose into coke during the process. After reaction, the fraction of the lignin products which was solubilized in 2-PrOH, was separated from the solid residue (SR) by filtration. After evaporation of the solvent, the yield of
liquid product (LP) of reaction was determined by weight. Figure 3-8 shows the obtained percentages of LP and SR compared to the starting material.

![Bar chart showing the obtained percentages of LP and SR compared to the starting material.]

**Figure 3-8** Yield of liquid product (soluble in the solvent of reaction at room temperature) and solid residue after reaction. Reaction condition: Substrate: 430 mg, Raney Ni: 125 mg, 2-PrOH (13 mL, solvent), H₂: 70 bars (at room temperature), 200 °C, 8 hours.

The yields of the products (Fig. 8) demonstrate that MCP-L seems to be less reactive than OS-L analogues. For beechwood and pinewood, MCP-L yields a quantity of liquid products 20% less than OS-L. For sugarcane, the yields of LP are comparable for the two varieties of lignin.

A plot of the yields of liquid products obtained from hydrogenolysis and the yields of thioacydolysis products is shown in Figure 3-9. For beechwood, the degree of conversion of lignin in a heterogeneous system may be correlated to the sum of products that arises from thioacidolysis. Indeed, OS-L yields proportionally higher quantities of monomers in the two processes (thioacidolysis and hydrogenolysis).
compared to MCP-L. For pinewood and sugarcane, a no linear correlation in the two processes was found. Notably, the thioacidolysis yields from pinewood OS-L and MCP-L were the same, whilst the liquid products of OS-L were the double than the MCP-L. Therefore, the relationship between the quantities of uncondensed units and the catalytic conversion is deeply influenced by the structure of the substrates and, from the results obtained from pinewood and sugarcane, the yield of thioacidolysis does not seem to be useful as a predictor of performance in the hydrogenolysis of lignin.

**Figure 3-9** Plot of the yields of liquid products (soluble in the solvent of reaction at room temperature) and yields of thioacidolysis products.

In order to evaluate the degree of hydrogenation and deoxygenation occurring during the reaction, Elemental Analysis of the liquid products (LP) and solid residue (SR) of reaction was performed. Figure 3-10 compares Van Krevelen’s diagram of the starting material with the products of reaction.
Figure 3-10 Van Krevelen’s diagram of organosolv (OS) and precipitated (MCP) lignins: starting material, solid residue (SR) and liquid product (LP). a) Beechwood lignin; b) Pinewood lignin; c) Sugarcane lignin.

Generally, the liquid products exhibit a higher H/C ratio and lower O/C ratio compared to the starting materials. This finding demonstrates that both hydrogenation and hydrodeoxygenation processes occur during the reaction. Interestingly, the H/C ratio is higher for the MCP-L LP compared to the OS-L LP whilst the O/C ratio is similar in the two samples, between 0.28 and 0.24. However, MCP-L has a higher O/C ratio that OS-L, therefore, this observation indicates that the higher hydrogenation and deoxygenation degree was achieved for MCP-L compared to OS-L.
In addition to the investigation of elemental analysis composition, depolymerization of lignin during the hydrogenolysis was evaluated using GPC and comparing to the starting material. The results are shown in Figure 3-11. The chromatogram of the MCP-L refers only to the part of the sample soluble in THF, the solvent utilized for this analysis.

**Figure 3-11** Gel permeation chromatograms (GPC) of the starting material (OS-L and MCP-L) and the liquid product (LP) of reaction. a) Beechwood; b) Pinewood; c) Sugarcane.

For beechwood, the molecular weight of the LP of reaction is lower compared to the starting material. This clearly demonstrates a net depolymerization of the
lignin under the reaction condition. Moreover, the MPC-L LP exhibits a lower molecular weight than the OS-L LP.

For pinewood samples (Fig. 3-11b), the MCP-L LP has a similar molecular weight distribution to the starting material, whilst a decrease in molecular weight of OS-L is obtained after reaction. For sugarcane (Fig. 3-11c), the OS-L LP has a lower molecular weight distribution compared with the starting material. Conversely, for MCP-L the reaction leads to a higher molecular weight product than the starting material. This finding is particular interesting because it highlights that molecular weight is not the only determining parameter for the solubility of lignin. For sugarcane MCP-L, the LP is completely soluble in the solvent of reaction despite the higher molecular weight compared to the partially-insoluble starting material. Presumably, the low solubility of the MCP-L starting material in organic solvents is determined by comparatively condensed structure or it may be related to the presence of carbohydrate-linked residues to the structure of lignin.

In order to better evaluate the quality of the LP, GC×GC-MS analysis was performed. The identification and quantification of the volatile fraction of the sample may be achieved using this technique. Qualitative analysis was achieved using a mass spectrometer (MS) detector while quantification of the products was undertaken with a flame ionization (FID) detector.

The GC×GC-FID chromatograms of beechwood OS-L LP (a) and MCP-L LP (b) are shown in Figure 3-12. A suggested pathway for hydrogenolysis of the β-O-4 linkage, catalyzed by Raney Ni, is shown in Scheme 3-3. A table with the GCxGC yields for selected products (cyclohexanols, methoxyphenol and 4-(3-hydroxypropyl)-phenols) is also reported (Table 3-3).
Hydrogenation of lignin obtained from the mechanocatalytic upstreaming biorefining

**Figure 3-12** GC×GC-FID chromatograms of beechwood lignin liquid products (LP): a) OS-L LP; b) MCP-L LP.

**Scheme 3-3** Suggested pathway for conversion of lignin into aliphatic monomers.

\[
\begin{align*}
\beta-O-4 & \quad \xrightarrow{\text{step 1}} \quad 1 \\
R= R'= H \text{ or } -\text{OMe} \\
R''= -\text{CH}_3, -\text{CH}_2\text{CH}_3, -\text{CH}_2\text{CH}_2\text{CH}_3
\end{align*}
\]
Table 3-3 Ratio between selected products isolated from OS-L and MCP-L.

<table>
<thead>
<tr>
<th>Beechwood OS-L/MCP-L</th>
<th>Pinewood OS-L/MCP-L</th>
<th>Sugarcane OS-L/MCP-L</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>1.6</td>
<td>0.8</td>
</tr>
<tr>
<td>0.7</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>0.8</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

R = -CH₃; -CH₂CH₃; -CH₂CH₂CH₃
R’ = H; -OMe

For beechwood lignin (Fig. 3-12), 4-(3-hydroxypropyl)-2,6-dimethoxyphenol 1, likely derived from depolymerization of the S-Lignin (step 1, of Scheme 3-3), is the primary product of reaction. Cleavage of the 3-hydroxypropyl unit of this compound (step 2, of Scheme 3-3) leads to the formation of 2. 4-(3-hydroxypropyl)-2-methoxyphenol is also present in the mixture of reaction because beechwood is also partially composed of G-Lignin. Cleavage of the 3-hydroxypropyl chain leads to the formation of 4-alkylguaiacol products. 4-alkylcyclohexanols are obtained from a minor reaction pathway via combined demethoxylation and saturation of the aromatic ring (step 3, Scheme 3-3). Phenol species were not observed in the mixture of reaction. Therefore, these phenols appear to be highly reactive towards subsequent conversion to cyclohexanols. Moreover, from hydrogenolysis of OS-L and MCP-L similar quantities of methoxyphenols are obtained. However, much higher GC yields were quantified for OS-L.
Hydrogenation of lignin obtained from the mechanocatalytic upstreaming biorefining

GC×GC-FID chromatograms of the pinewood LP are shown in Figure 3-13.

![GC×GC-FID chromatograms of pinewood lignin liquid product (LP): a) OS-L LP; b) MCP-L LP.](image)

4-alkylcyclohexanols and 4-alkylmethoxyphenols are the only detected products of the hydrogenolysis of OS-L. Low yields of methoxyphenols are obtained by hydrogenolysis of OS-L compared to the MCP-L. Conversely, a the quantity of cyclohexanols formed upon reaction of OS-L are slightly higher than in MCP-L (Table 3-3). Therefore, after hydrogenolysis of the β-O-4 linkages, methoxyphenols are quantitatively converted into cyclohexanols for the OS-L (step 3, Scheme 3-3). The low yield of volatile products for OS-L may be due to the low abundance of β-O-4 linkages in this variety of lignin, as already highlighted by thioacidolysis (Fig. 3-7). Exclusively guaiacyl-derived monomers are detected because pinewood lignin is primarily composed of G-Lignin. Hydrogenolysis of the MCP-L (Fig. 3-13b) leads to higher quantities of volatile molecules compared to the OS-L, predominantly guaiacols.

The GC×GC-FID chromatograms of sugarcane LP are shown in Figure 3-14. As for the pinewood samples, higher quantities of volatile products are detected for the MCP-L LP compared to the OS-L LP. As observed in the GPC analysis, MCP-L exhibit a lower molecular weight compared to the analogous OS-L, therefore fewer linkages must be break for the formation of volatiles products, enhancing the
probability to obtain monomeric units in solution. This observation likely accounts for the higher quantities of volatile products in sugarcane MCP-L LP (Fig. 3-14). Guaiacols and dimethoxyphenols are present in both samples whilst no demetoxylated phenols are detected. Compared to pinewood and beechwood, sugarcane incorporates higher quantities of \( p \)-coumaryl alcohol which upon reaction, is likely converted to phenol monomers and then eventually hydrogenated to cyclohexanols. Phenols are more reactive than methoxyphenols with respect to hydrogenation in the presence of Raney Ni, therefore\(^{52,117}\) this is one probable explanation for why simple phenols are not isolated in the mixture of reaction. Furthermore, the H-units in lignin may be more susceptible to recondensation reactions, compared to S and G-units, leading to the formation of recalcitrant C-C bonds and consequently likely decreasing the yield of volatile phenols upon reaction.

\[ \text{Figure 3-14 Relatively yield of liquid product (soluble in the solvent of reaction at room temperature) and solid residue after reaction. Reaction condition: Substrate: 430 mg beechwood lignin, Raney Ni: 125 mg, 2-PrOH (13 mL, solvent), H}_2: 70 \text{ bars (at room temperature), 300 °C, 8 hours.} \]

Partial inclusion of the solvent is found in the products of reaction of MCP-L. For certain individual product species obtained from hydrogenolysis of MCP-L a fraction was observed to be alkylated with an isopropyl unit at the phenolic \(-\text{OH}\) position. Surprisingly, these species are not encountered in the OS-L LP samples.
Hydrogenation of lignin obtained from the mechanocatalytic upstreaming biorefining

Heteronuclear Single Quantum Coherence (HSQC)-type experiments have been design for characterization of isolated lignin or the whole plant cell wall and analysis of the lignin bonding motifs can be accomplished by using this technique. The HSQC NMR spectra of OS-L and of the ‘water-soluble lignocellulose’ (WSL) obtained \emph{via} mechanocatalytic processing in the region of the ether linkages are shown in Figure 3-15.
Figure 3-15 Partial HSQC spectra highlighting the C3 side-chain region of lignin units derived from: a) Beechwood; b) Pinewood; c) Sugarcane. OS-L (Organosolv lignin) and WSL (water soluble lignocellulosic) are shown along the respective liquid product (LP) after hydrogenation of lignin at 200 °C.

The ‘WSL’ is completely soluble in dimethyl sulfoxide (DMSO), the solvent used for this analysis, while the MCP-L is only partially soluble in DMSO. Therefore, it was decided to use ‘WSL’ for comparison with the OS-L sample for NMR studies. The HSQC spectra of MCP-L LP and OS-L LP after hydrogenolysis at 200 °C are also shown.
The HSQC analysis indicates that phenolic units of OS-L are predominantly linked by β-O-4 (A), β-5 (B) and β-β (C) linkages, in agreement with previous reports. In the HSQC spectra of the WSL sample β-O-4 (A), β-β (C) and β-5 (B) linkages are barely detected. Although, other signals are present in the spectra, it is not possible to distinguish which signals correspond to the lignin fraction and which to the carbohydrate fraction. As previous reported by Rinaldi and co-workers, the mechanocatalytic process is similarly mild as a typical organosolv process concerning the depolymerization of lignin. However, isolation of lignin, via hydrolysis and subsequent precipitation, could in part hydrolyze the weak β-O-4 linkages. As already shown, the elemental composition of MCP-L is richer in oxygen compared to the OS-L. For beechwood, thioacydolysis of lignin samples demonstrated that MCP-L incorporates 2-3 times fewer β-O-4 linkages compared to the OS-L. Therefore, the greater extend of the hydrolysis at the ether bonds of MCP-L compared to OS-L could explain the higher O/C ratio in the MCP-L compared with OS-L. However, the same effect was not found for pinewood and sugarcane lignins, where the two kinds of lignins comprise similar abundances of uncondensed units.

In the HSQC spectra of the LP produced at 200 °C, new signals appeared, indicating that novel structures had formed. GPC analysis demonstrated that depolymerization of lignin occurs upon reaction with Raney Ni, hence partially cleaving the ether linkages. The LP obtained by hydrogenolysis of OS-L still incorporates considerable quantities of β-O-4 (A), β-5 (B) and β-β (C) linkages, as shown in the HSQC spectra. Therefore, the hydrogenolysis performed at 200 °C catalyzed by Raney Ni is not wholly effective for scission of these varieties of linkages for the OS-L.

Partial HSQC spectra of the aromatic region of the OS-L, ‘WSL’ and LPs after reaction at 200 °C are shown in Figure 3-16. Approximate quantities of S, G and H units in the OS and MCP lignin samples are listed below the spectra.
**Figure 3-16** 2D HSQC NMR spectra of the aromatic region of lignin. a) Beechwood; b) Pinewood; c) Sugarcane. OS-L (Organosolv lignin) and WSL (water soluble lignocellulosic) are shown alongside the respective liquid product (LP) after hydrogenation at 200 °C.
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Peak assessment was performed based on literature protocols.\textsuperscript{118,119} Semiquantitative analysis of the spectra is useful for quantifying and characterizing the lignins. Nevertheless, accurate quantitative analysis by HSQC is challenging and conclusion must be not overlooked.\textsuperscript{96} OS-L beechwood is mostly composed of S and G-units. However, the observed quantity of S-units found in the MCP-L samples was lower than that found for OS-L. This finding agrees with the results reported by Ragauskas et al. on the structural characterization of ball-milled switchgrass lignins obtained before and after dilute acid pretreatment.\textsuperscript{96,120} Pinewood OS-L and MCP-L were found to have a similar proportion of guaiacyl (G) and p-hydroxyphenyl (H) units, whilst S-units are absent.

The sugarcane OS-L and MCP-L exhibit a different ratio of G, S and H-units. Sugarcane OS-L was found to have a higher abundance of the S-unit (49\%) than G-Unit (43\%). Conversely, ‘WSL’ is mostly composed of G-units (54\%) and lower quantities of S-units (42\%). H-units are lower in abundance in the WSL (4\%) than OS-L (8\%). These differences indicate that the MCP-L has undergone structural modifications, which may include self-condensation. Compared to thioacidolysis, whereby only uncondensed S, G and H-units are quantifiable, by NMR is possible to quantify the entire sample. High quantities of p-coumarate (pCA\textsubscript{r}) and ferulate (FA\textsubscript{r}) units are incorporated into the sugarcane lignins, in agreement with previous chemical literature.\textsuperscript{121} Therefore, the “organosolv” and mechanocatalytic processes influence the composition of lignin extracted from pinewood and beechwood to a similar degree, whereas in the case of the sugarcane lignin major structure and compositional changes occur.

Interestingly, each all the LPs of reaction exhibit signals indicating the condensation of the units (Fig. 3-18). This phenomenon is more evident in the beechwood and sugarcane lignins after reaction, whereby structure formed from condensed S-unit exhibit a twin peak around 6.4/106.3 ppm (\(\delta_H/\delta_C\)). The condensation of the phenolic units has already been reported in literature by Ikeda et. al.\textsuperscript{122} This
signal is incorporated in the starting material of the mechanocatalytic processed wood, and emerges as a result of repolymerization/condensation reactions which can occur during the impregnation with acid and the subsequent mechanocatalytic depolymerization. Condensation reactions generate new carbon-carbon bonds. Nevertheless, fragmentation processes after condensation could in part compensate for the increase in molecular weight. However, during mechanocatalytic process, depolymerization may accounts a major role than repolymerization, as displayed from the experiment of the ‘artificial wood’ in the next chapter, where a lower molecular weight product is obtained upon acid impregnation and milling of OS-L. This phenomenon may explain why the molecular weight is not necessarily wholly responsible for the lower solubility of MCP-L in organic solvents. Indeed, the results of this investigation suggest that the formation of higher cross-linked structures may better explain the decrease of solubility and hence the lower conversion of the MCP-L compared to the OS-L in the hydrogenation reaction.

For beechwood, mechanocatalytic processing of biomass brings about cleavage of the β-O-4 linkages of lignin via acid-catalyzed ether bond hydrolysis decreasing the molecular weight of lignin. Simultaneously, hydrolysis may bring about an increasing of the oxygen content in the MCP-L, as revealed by elementary analysis. This aspect foremost distinguishes the MCP-L from the OS-L. Conversely, a similar degree of depolymerization of the uncondensed units is achieved for pinewood and sugarcane samples in the two fractionation processes. Raney Ni promotes depolymerization of the lignins, however, differing quantities of volatile products were obtained after hydrogenolysis for MCP-L and OS-L. The hydrogenolysis reaction of OS-L yields a higher quantity of liquid products compared to the MCP-L, nevertheless, other factors must be taken into account. Despite the higher conversion of the OS-L, due to the high solubility of this lignin in organic solvent, the extent of hydrogenation and deoxygenation is higher for MCP-L than for the OS-L.
Subsequently, the hydrogenolysis reaction of beechwood OS-L and MCP-L was repeated at the higher temperature of 300 °C, maintaining the other parameters of reaction as before in order to get information regarding the influence of reaction temperature. The percentage yields of LP and SR compared to the starting material are shown in Figure 3-17.

![Bar chart showing the yields of liquid product and solid residue for OS-Lignin and MCP-Lignin.](image)

**Figure 3-17** Relatively yield of liquid product (soluble in the solvent of reaction at room temperature) and solid residue after reaction. Reaction condition: Substrate: 430 mg beechwood lignin, Raney Ni: 125 mg, 2-PrOH (13 mL, solvent), H₂: 70 bars (at room temperature), 300 °C, 8 hours.

At the temperature reaction of 300 °C, the yield of LP was identical for OS-L and MCP-L, but this observation does not indicate that both lignins exhibit similar reactivity. TGA analysis demonstrated that lignin underwent a significant weight loss event (during temperature-ramped analysis) between 200 and 300 °C, due to likely thermolysis of the structure and vaporization of volatile decomposition products. Likely, performing the reaction at 300 °C provides efficient energy to the system so as to depolymerize lignin into small, soluble and reactive fragments, to a similar extend for both MCP-L and OS-L. Under these conditions, the intrinsic reactivity of lignin is disguised by the non-catalytic thermal processes occurring on lignin and releasing soluble products. As both lignins show similar thermal stability,
it is plausible to affirm that the extent of thermal depolymerization should be similar for both materials.

The GC×GC-FID spectra of the LP of reaction at 300 °C are shown in Figure 3-18.

[Figure 3-18 GC×GC-FID chromatograms of the liquid product (LP) of beechwood lignin after reaction at 300 °C: a) OS-L LP; b) MCP-L LP.]

Interestingly, in stark contrast to the reaction at 200 °C (Fig. 3-12 and 3-14), the volatile fraction of reaction performed at 300 °C is primary composed of cyclohexanols and cyclic alkanes. The conversion of an Organosolv Lignin into demethoxylated and saturated products is consistent with results reported in previous literature.66,124 The distribution of the products of reaction is similar for both varieties of lignin, indicating that the catalyst is similarly effective for hydrogenation of MCP-L and OS-L under the specified conditions. However, catalytic hydrogenolysis of MCP-L yields higher quantities of high-boiling point bicyclic compounds than OS-L. This finding highlights that MCP-Ls may have a more cross-linked structure that their OS-Ls counterparts with considerably high quantity of carbon-carbon linkages. Moreover, modification of the reaction temperature is a sensible strategy in order to selectively convert lignin into either methoxyphenols or saturated products.
3.5 Characterization of the Solid Residue (SR) of reaction

In the last part of this chapter, the results obtained from the characterization of the solid residue of reaction (SR) will be discussed. Because of the low solubility of the SR in organic solvents it is not possible to analyze it in liquid state. Nevertheless, comparison of the SR to the starting material will be done by C\textsubscript{13}-solid state NMR.

Figure 3-19 shows the C\textsubscript{13}-solid state NMR spectra of the starting material (in orange) with the solid residue (in blue) of reaction MCP-L SR and OS-L SR for beechwood (a), pinewood (b) and sugarcane (c), peaks assignments are based on literature.\textsuperscript{125-127}
Figure 3-19 Comparison between the CP-MAS 13C NMR spectra of the starting materials (in orange) with solid residues of reaction (SR, in blue). a) Beechwood; b) Pinewood; c) Sugarcane.
The main peak at 56 ppm in all the spectra is associated with the methoxy function of the methoxyphenols. S-Unit, G-Unit and H-Unit in beechwood SR and sugarcane SR were identified by the peaks at 105, 115 and 135 ppm, respectively. For pinewood, only the peak at 115 ppm, typical of the G-Unit, was identified. Signal at 73 ppm is associated with the presence of residual carbohydrates; this band was primarily found in the sugarcane and beechwood MCP-L and for pinewood OS-L. Lignin samples from certain sources can be expected to contain small amount of un-hydrolyzed ester linkages to organic acids. The same signal at 73 ppm was found in the sample after reaction. Therefore, the residual carbohydrates fraction may stay incorporated in the SR.

A peak in the alkyl region (40-20 ppm) appears in the spectra of pinewood lignin samples, and in a smaller extent, in the samples of beechwood and sugarcane lignin. After reaction, all the samples incorporate a broad peak in the alkyl region. The presence of this peak may explain the higher H/C ratio observed in the solid residue of reaction compared with the starting material, as identified in the Elemental Analysis (Figure 3-10). Indeed, this peak, usually absent in lignin, may be attributed to the formation of aryl propanol structure upon reaction, which may be obtained by etherification of the phenolic hydroxyl with 2-PrOH (the solvent employed during the hydrogenolysis reaction). Alternatively, formation of carbon-carbon bonds between the phenolic unit leads to cross linked structures thought sp3 carbon bridge bond. The presence of these sp3-carbons can explain the high field signals in the solids state NMR spectra. We can conclude that the solid residue is mainly composed of lignin but small amount of sugar where also found.

3.6 Conclusions

We have demonstrated that by hydrolysis of the WSL obtained utilizing the mechanocatalytic process, high quality lignin is obtained. A higher quantity of oxygen was found for MCP-L compared to an OS-L, indicating higher content of residual saccharides in the lignin precipitates comparing to the corresponding OS-L
or a possible hydration of the lignin structure during the saccharification step of the WSL. Further evidence for this possible phenomenon will be provided in the next chapter. Thioacidolysis assay, performed on the lignin samples, showed that the quantities of uncondensed structure in lignin are strongly dependent both on the fractionation procedure and the lignin structure. Indeed, the high quantities of S-lignin units in beechwood may prevent the acid-catalyzed depolymerization of the β-O-4 linkages during an organosolv process.

Catalytic depolymerization on the lignin samples was also performed. In presence of H₂, Raney Ni is effective for the depolymerization of lignin into methoxyphenols, and small quantities of cyclohexanols, at 200 °C. The catalytic depolymerization of lignin may be related to the quantities of uncondensed units for certain qualities of lignin and may explain the low conversion of MCP-L compared to OS-L in the hydrogenolysis at 200 °C. Nevertheless, catalytic hydrogenation at 300 °C yielded very similar results when performed on OS-L and MCP-L. At this temperature, the impact of the structure on the catalytic performance is negligible.
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CHAPTER 4

Extraction of lignin released from the saccharification of mechanocatalytically depolymerized wood in a biphasic system and its downstream processing.

In this chapter, extraction of the lignin from the hydrolysate of water-soluble lignocellulose (WSL, obtained from the mechanocatalytic process) in a biphasic system (H₂O/2-MeTHF) will be described. The aim of this study is to prevent the repolymerization of the lignin fragments liberated by the saccharification of mechanocatalytically depolymerized lignocellulose. The obtained Extracted Lignin (E-L) and the lignin precipitate (MCP-L), formed upon saccharification of mechanocatalytically depolymerized lignocellulose in a monophasic aqueous system (as described in Chapter 3), exhibit a lower molecular weight compared to an Organosolv Lignin (OS-L). β-O-4 and β-5 linkages are quantitatively hydrolyzed during the saccharification step for both E-L and MCP-L. However, E-L still incorporates the more stable β-β type of linkage, typical of native lignins, and carbonylic functional groups. As a result of the lower molecular weight and high solubility in organic solvents, E-L showed similar productivity of liquid products under a hydrogenolysis reaction compared to the solid precipitated lignin (MCP-L).
Interestingly, hydrogenolysis brings about the selective conversion of E-L to ortho-methoxyphenols at 200 °C, without any saturation of the ring.

4.1 Introduction

Mechanocatalytic processes are able to convert wood into a ‘water soluble lignocellulose’ (WSL), whereby lignocellulosic biomass is converted into solubilized holocellulose and lignin fraction. Following the mechanocatalytic treatment, a simple hydrolytic step in water suffices to fractionate the carbohydrates and separate them from lignin, which precipitate from solution. The obtained sugar monomers, in an acidified solution, may be used for a wide range of applications.129 Hydrogenation of sugars may lead sugar alcohols.130 Dehydrogenation of sugar monomers may afford important platform chemicals such as furfurals and γ-Valerolactone.131 Conversely, the chemistry of the mechanocatalytically depolymerized lignin is still far less well-understood, despite the potential as a raw-material for the production of chemicals and fuels.91

Precipitation of lignin during the saccharification step immediately after mechanocatalytic treatment brings about recondensation (as presented in Chapter 3) and inclusion of carbohydrate fragments into the MCP-L, lowering its solubility in common organic solvents. Therefore, MCP-L is typically less reactive that analogous technical lignins (e.g. OS-L) to depolymerization, despite its high purity and quality (sulfur-free lignin).

Leitner et al. reported an organic acid-catalyzed fractionation of lignocellulosic biomass in a biphasic system composed of water and 2-MeTHF.132,133 After acid pretreatment, the hemicellulose is depolymerized into C5 and C6-sugars, which are soluble in water. Cellulose precipitates in solution whilst lignin is partially extracted into the organic layer. This approach is capable of separating all three major components of biomass in an environmentally-benign manner because water and 2-
MeTHF are considered as green solvents\textsuperscript{134-136} (e.g. 2-MeTHF has found application as an alternative to chlorinated solvents for biphasic reactions).\textsuperscript{137}

The ability of a solvent to solubilize lignin has previously been explained in terms of defined solvent parameters.\textsuperscript{35,138} Lignin are commonly readily soluble in solvents that exhibit high hydrogen-bonding capabilities and with Hildebrand solubility parameters that approach a value of around eleven.\textsuperscript{115} Typically, mixtures of water and short-chain alcohols are employed as extraction media in the organosolv process to separate the cellulosic fraction from lignin.\textsuperscript{139,140} Indeed, a homogenous system is obtained when water is mixed with a low-molecular-weight alcohol (e.g. ethanol or propanol). Conversely, both 1- and 2-butanol, a phase separation phenomenon is observed. However, compared to 2-MeTHF, alcohols are not compatible with acid conditions because they easily undergo to dehydration.\textsuperscript{141,142} Therefore, despite the promising solvent properties of 1-butanol,\textsuperscript{143} aqueous mixture of 2-MeTHF have been preferred as organic media during saccharification of the WSL.

This chapter is organized as follow. Firstly, the effect of the mechanocatalytic process and the subsequent saccharification step on an organosolv lignin is investigated. Subsequently, the acid-catalyzed saccharification of WSL in a biphasic system is described. Finally, the extracted lignin (E-L) is characterized and reacted in heterogeneous catalytic system. A comparison to an organosolv lignin and MCP-L is also provided.

4.2 Effect of the mechanocatalytic process on an organosolv lignin

Both the mechanocatalytic process and the saccharification step lead to hydrolysis of the ether bonds, forming small lignin fragments. Indeed, GPC analysis of lignin (as described in Chapter 3) shows that MCP-L has a lower molecular weight than OS-L. Simultaneously, lignin may undergo acid-catalyzed repolymerization with formation of highly-crosslinked structures, which may be both responsible, together with
residual content of lignin-carbohydrate complexes, for the decrease in solubility of MCP-L in organic solvents.

To understand how the acid and the milling influence the lignin framework, the following experiment was designed. Beechwood OS-L was mixed with α-cellulose, 25wt% and 75wt% respectively, forming an ‘artificial wood’. The mixture was impregnated with an acid catalyst, H₂SO₄, was subjected to the mechanocatalytic process and then finally to saccharification. In addition, a blank without acid impregnation, was processed by milling to evaluate the action of the acid on the process. Fig. 4-1 shows the GPC analysis of the lignin fraction of the ‘artificial wood’ mechanically processed together with OS-L and MCP-L.

![Figure 4-1 GPC analysis of beechwood OS-L and lignin obtained by mechanocatalytic depolymerization of the ‘artificial wood’ with or without acid impregnation.](image)

When the artificial wood was milled with no additives, a product insoluble in water was obtained. The two components of the mixture (lignin and α-cellulose)
could be separated by solubilization of lignin (OS-L Milled) in acetone and filtration. Figure 4-1 shows that the molecular weight (Mw) distribution of the recovered lignin (OS-L Milled, grayish curve) is similar to that of OS-L, with a small increase in the population of polymers of Mw between 15.7 to 66 kDa.

In turn, milling of an acid-impregnated sample composed of OS-L (25 wt%) and $\alpha$-cellulose (75 wt%) led to a water-soluble product. Separation of the two components was possible by saccharification of the carbohydrates with the precipitation of lignin. The resultant lignin (OS-L Acid-Milled) was slightly soluble in organic solvents, yet sufficiently soluble for be analyzed by Gel Permeation Chromatography (GPC) and HSQC NMR. In the presence of an acid catalyst the lignin recovered after milling and saccharification (OS-L Acid-Milled) has a lower molecular weight distribution than the starting material (OS-L), and similar to MCP-L. This result demonstrates the ability of the acid catalyst to promote the lignin depolymerization.

The lower molecular weight of the acid-impregnated OS-L from ‘artificial wood’ shows that, during the mechanocatalytic process, the depolymerization of OS-L occurs to a larger extent from that of repolymerization. To shed light on which linkages in the lignin structure have been cleaved by mechanocatalytic processing, the processed materials were analyzed by 2-D HSQC NMR, a powerful technique which distinguishes the interunit linkages of lignin. Fig. 4-2 shows the HSQC NMR spectra of regular OS-L and the lignin obtained by acid impregnation and mechanocatalytic depolymerization of the ‘artificial wood’.
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Figure 4-2 Partial HSQC spectra showing the C₃ side-chain region of the lignin units.

a) OS-L; b) Lignin from impregnated and milled “artificial wood” together with the most common kind of linkages in the organosolv lignin.

Analysis of the OS-L (Fig. 4-2a) reveals that β-O-4 (A) β-5 (B) and β-β (C) ether linkages are still present in the organosolv lignin. In the NMR spectrum of the lignin obtained by acid impregnation and mechanocatalytic depolymerization (Figure 4-2b) the signal representing the β-O-4 linkage (A) disappeared. Other varieties of linkages, for example β-5 (B) and β-β (C), are still present after the mechanocatalytic depolymerization. Acid-catalyzed depolymerization of lignin model compounds has been already reported in literature. Moreover, Samuel et al. report a reduction of the β-O-4 linkage quantitatively in the Switchgrass ball-milled lignin after dilute acid pretreatment. We can conclude that the mechanocatalytic process is able to cleave the glycosidic bond of the carbohydrates together with the cleavage of the ether linkage in the lignin structure leading to lower molecular weight structures.
4.3 Acid catalyzed saccharification of WSL in a biphasic system.

The last section demonstrates that the mechanocatalytic process is able to depolymerize lignin via the hydrolysis of the lignins β-ether linkages. However, condensation of lignin oligomers may be responsible for a further repolymerization of lignin into a highly-crosslinked structure. To avoid the condensation, and thus increase the solubility of the lignin stream in mixed organic-aqueous solvents, the acid-catalyzed saccharification of WSL was performed in a biphasic system composed of water and 2-MeTHF. Figure 4-3 shows the conversion of beechwood into WSL that is soluble in the biphasic system (H₂O/2-MeTHF 50/50 v/v), and subsequently the saccharification step that leads to sugar monomers and soluble lignin.

![Figure 4-3](image)

**Figure 4-3** Conversion of beechwood into sugar monomers and soluble lignin via a mechanocatalytic-saccharification process performed in a biphasic system.

In native form, lignocellulosic biomass (wood) is not soluble in water or in the majority of conventional solvents. Acid-impregnation and solid-state depolymerization, employing ball mill, render wood soluble in a biphasic system composed of water and 2-MeTHF. When WSL is added to the solvent mixture, a stable phase is obtained in which water and 2-MeTHF do not separate. Subsequently, the solution is heated to 145 °C for one hour. At this temperature, hydrolysis of the saccharides is achieved, whilst the lignin oligomers are primary extracted from the aqueous phase into the organic phase (70%).

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The aqueous phase was analyzed by HPLC to ascertain the quantities of sugars produced. The results indicate that the glucose yields exceeding 50% relative to the glucan fraction and the remains glucans are arranged in small cello-oligomers. It has previously been demonstrated that the holocellulosic fraction of WSL is hydrolyzed in water, affording glucose yields of up to 90% at 145 °C after one hour. Therefore in our experiments, it was observed that the saccharification of WSL in a biphasic system composed of water and 2-MeTHF is in fact slower that the saccharification in pure water, most likely because of acid partition to the organic phase.

4.4 Characterization of the extracted lignin

The lignin stream extracted in 2-MeTHF is soluble in acetone and THF. GPC and HSQC NMR analyses were performed on the sample to determine the molecular weight distribution and the abundance of various types of linkage, respectively. GPC analysis of E-L, together with the chromatogram of OS-L and MCP-L for comparison, is shown in Figure 4-4. The reported data are obtained with an ELSD detector which gives quantitatively information about the molecular weight distribution.
Compared to OS-L, E-L exhibits a lower molecular weight distribution. Moreover, compared to MCP-L, E-L incorporates a higher population of compounds of $M_w$ between 1,250 to 200 Da, and the two sample present similar distribution for compounds of Mw between 66000 to 1250 (although analysis on MCP-L refers only to the part of sample that is soluble in THF). The mechanocatalytic depolymerization of wood to WSL followed by the saccharification in the biphasic system resulted in fractionation and repolymerization of lignin. Both mechanisms are acid-catalyzed. The acid is able to hydrolyze most of the ether bonds of lignin, as described in Chapter 3 and in the experiment of the ‘artificial wood’. However, increasing of the molecular weight of lignin occurs during acidolysis. When the saccharification of sugars is performed in an aqueous/2-MeTHF system, lignin is extracted into the organic layer, thereby preventing a long term contact of lignin with the acid (which will likely remain in the aqueous phase).

The HSQC NMR spectra of E-L and OS-L in the region of the ether bonds are shown in Figure 4-5.
Figure 4-5 Partial HSQC spectra showing the C₃ side-chain region of the lignin units. OS-L (left) and E-L (right) HSQC spectra are displayed, and the most common varieties of linkage (in Organosolv Lignin) are shown.

OS-L clearly exhibits β-O-4 (A), β-5 (B) and β-β (C) linkages. Conversely, for E-L, the signals characterizing the presence of β-O-4 (A) and β-5 (B) linkages are absence in the HSQC spectrum, while the signal for β-β (C) linkage (more resistant to acid depolymerization) is still seen. The HSQC spectra clearly demonstrate that the lower molecular weight of the E-L, compared to the OS-L, is primarily due to cleavage of the ether bonds. Moreover, as it has been previously discussed in Chapter 3, a lignin precipitate (MCP-L) is obtained when hydrolysis of the WSL is performed in pure water. The last results suggest that when lignin is not extracted into 2-MeTHF, repolymerization will occurs to a greater extent, leading to the formation of a highly crosslinked structure with decreased solubility. Extraction of lignin in 2-MeTHF is therefore an effective strategy for preventing the repolymerization of lignin oligomers without the need of protecting groups.
4.5 Thioacidolysis of E-L, OS-L and MCP-L

Analysis of the monophenolic products obtained by thioacidolysis of lignin enables estimation of the impact of a fractionation process on the extent of repolymerization.\textsuperscript{148} Thioacidolysis is able to quantify units linked by β-ether linkages, which are generally denoted ‘uncondensed units’.\textsuperscript{149} The GC×GC-FID chromatogram of trimethylsilylated derivatives from beechwood E-L following thioacidolysis is shown in Figure 4-6. Identification of the products was performed with a mass spectrometer in Selected-ion Monitoring (SIM) mode for \(m/z\) 239, 269 and 299.\textsuperscript{150}

\textbf{Figure 4-6} GC×GC-FID chromatograms of TMS derivatives of beechwood E-L after thioacidolysis. Compounds X1 and X2 are not derived from lignin.

The trimethylsilylated sample (after thioacidolysis) of lignin is composed of a complex mixture of products, as detected by the extreme sensitivity of the GC×GC-FID technique. Only certain products were identified. Compounds 6 and 7 derive from the uncondensed guaiacyl and syringyl units, respectively. Compounds 1 and 3 are C6C1 products, benzaldehyde end groups of the guaiacyl and syringyl units, respectively. These are the primary products originated from thioacidolysis of lignin.
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lignin. Compounds 2 and 4 are C6C2 products of the guaiacyl and syringil units, respectively. These products derived from vinyl ether structures originating from a minor pathway. Products X1 and X2 are not related to lignin but to other impurities (e.g. xylans). Scheme 4-1 shows the structures of compounds 1, 2, 3, 4, 6, 7 and 8. Figures 4-7 and 4-8 highlight the GC×GC-FID chromatogram of the TMS derivates for beechwood OS-L and MCP-L, respectively, after thioacidolysis.

\[
\begin{align*}
1: & \quad R=H; \quad R'=\text{-OMe} \\
2: & \quad R=H; \quad R'=\text{-OMe} \\
3: & \quad R=\text{OMe}; \quad R'=\text{OMe} \\
4: & \quad R=\text{OMe}; \quad R'=\text{OMe} \\
5: & \quad R=\text{H; } R'=\text{OMe} \\
6: & \quad R=\text{H; } R'=\text{OMe} \\
7: & \quad R=\text{OMe; } R'=\text{OMe} \\
8: & \quad R=\text{H; } R'=\text{H}
\end{align*}
\]

Scheme 4-1 Primary products obtained from thioacidolysis of beechwood lignin (E-L, MCP-L and OS-L).

![Retention time over 1st column / min](image)

**Figure 4-7** GC×GC-FID chromatogram of TMS derivatives of beechwood OS-L after thioacidolysis. Compounds X1 and X2 are not derived from lignin.
Figure 4-8 GC×GC-FID chromatogram of TMS derivatives of beechwood MCP-L after thioacidolysis. Compounds X1 and X2 are not derived from lignin.

The beechwood lignin was found to be primarily composed of guaicyl and syringyl units, whilst p-hydroxyphenyl unit, compound 8, was detected only in low concentrations by thioacidolysis of beechwood samples.

GC×GC-FID is able to quantify the volatiles products obtained by thioacidolysis of lignin. The ratios of S- and G-units calculated by thioacidolysis and HSQC NMR are shown in Table 4-1.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>E-L</th>
<th>OS-L</th>
<th>MCP-L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thioacidolysis</td>
<td>2.20</td>
<td>3.42</td>
<td>2.25</td>
</tr>
<tr>
<td>HSQC NMR</td>
<td>1.63</td>
<td>1.84</td>
<td>1.56</td>
</tr>
</tbody>
</table>

For beechwood E-L, the ratio of S- and G-units calculated by integration of the HSQC NMR spectra (S/G ratio 1.63) is lower to that measured from the thioacidolysis assay of the same sample (S/G ratio 2.20). Similarly, the S/G ratio for OS-L is higher.
when calculated by the thioacidolysis assay than by using HSQC NMR spectroscopy, 3.42 and 1.84, respectively. The value of the ratio S/G for MCP-L calculated by the thioacidolysis assay is higher again than the data obtained by HSQC NMR, 2.25 and 1.56, respectively. Overall, the ratio of S- and G-units is always lower when calculated by integration of HSQC NMR spectra than by the thioacidolysis assay. Notably, the volatile products evolving from thioacidolysis treatment represent only to the uncondensed units linked by β-O-4 motif (or other weak ether bonds). In lignin, the G-units may be linked by interunit linkages connected through the Cs position on the aromatic ring. These types include phenylcoumaran (β-5), biphenyl (5-5), and biphenyl ether (4-O-5) linkages. Phenylpropane units which incorporate these linkages are generally denoted ‘condensed’ units . Condensed units are invisible to the thioacidolysis assay and, therefore, not all the G-units can be quantified by thioacidolysis. This finding highlights that the G-units are more condensed than the S-units, which are instead linked mostly via uncondensed units.

The ratio of the lignin-derived products isolated by thioacidolysis of E-L, OS-L and MCP-L are shown in Table 4-2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>E-L/OS-L</th>
<th>E-L/MCP-L</th>
<th>OS-L/MCP-L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.90</td>
<td>8.05</td>
<td>10.37</td>
</tr>
<tr>
<td>2</td>
<td>7.68</td>
<td>4.58</td>
<td>0.71</td>
</tr>
<tr>
<td>3</td>
<td>0.68</td>
<td>8.23</td>
<td>13.45</td>
</tr>
<tr>
<td>4</td>
<td>2.97</td>
<td>4.17</td>
<td>1.37</td>
</tr>
<tr>
<td>6</td>
<td>0.36</td>
<td>0.80</td>
<td>2.24</td>
</tr>
<tr>
<td>7</td>
<td>0.23</td>
<td>0.80</td>
<td>3.41</td>
</tr>
<tr>
<td>Σ (1-7)</td>
<td>0.42</td>
<td>1.30</td>
<td>3.3</td>
</tr>
</tbody>
</table>

E-L exhibits 2-4 times fewer uncondensed units (which are units linked only by ether linkages, e.g. β-O-4) compared to OS-L, as indicated by ratio of the sum of
the major products (Σ 1-7) from thioacidolysis. This data is in agreement with the information collected in the NMR section. Figure 4-3 demonstrates that the β-O-4 ether linkage is unstable during mechanocatalytic depolymerization and subsequently saccharification step whilst a fraction of this variety of structure is preserved during an organosolv process. The ratio of the sum (Σ 1-7) of the major products obtained from thioacidolysis assay for E-L and MCP-L corresponds to 1.30. Hence, there is a significant difference in the quantity of uncondensed units when the saccharification step is performed in a single phase or biphasic system (i.e. with or without 2-MeTHF).

Compounds 1 and 3 (benzaldehyde ends groups) are ca. 8 times more abundant in the E-L material than in MCP-L (in the uncondensed units). Similar to the thioacidolysis process, benzaldehyde-like products derived from the lignin stream can be formed via the saccharification of the water-soluble product (Scheme 4-2). However, in the saccharification step, the aldehyde products may undergo repolymerization to afford higher-molecular-weight structures that may decrease the solubility of lignin. It is thus clear from the thioacidolysis results that extraction of lignin into the organic phase preserves the parent structures (those which are prone to thioacidolysis, releasing aldehydes) rendering a less condensed lignin. Noteworthy, the ratio E-L/OS-L of compounds 1 and 3 is close to one, highlighting that the aldehyde functionalities in 2-MeTHF during the saccharification step of the mechanocatalytic process are as stable as in an organosolv process, despite the more acidic conditions.
Scheme 4-2 demonstrates the acid-catalyzed depolymerization of lignin β-O-4 linkages into products 2 and 4.

**Scheme 4-2** Acid-catalyzed conversion of lignin uncondensed units into C₆C₂ products.

The quantities of compounds 2 and 4 are ca. 8 and 3 times larger in E-L than in OS-L, respectively (Table 4-1). The formation of vinyl ether structures (14) from lignin’s β-ether may be catalyzed by strong acid. Therefore, these products are mostly observed in acid-pretreated lignins. Hence, mechanocatalytic process and the subsequent hydrolytic step likely depolymerize the β-O-4 linkages into vinyl ether end groups (14) and, eventually, into aldehydes (2 and 4). The smaller fragments of lignin, originating via acid-catalyzed depolymerization, are extracted into the organic layer (2-MeTHF) preventing further polymerization. Compounds 2 and 4 are most likely obtained also in MCP-L, however, condensation of these units (a similar situation occurs in the Kraft lignin) could justify the lower quantity compared to E-L.
4.6 Hydrogenolysis of E-L

As described in Chapter 3, hydrogenolysis performed with Raney Ni is an effective strategy for depolymerization of lignin into ortho-methoxyphenol monomers. When performed on OS-L and MCP-L, hydrogenolysis leads to aromatic compounds as the primary products. Nevertheless, ortho-methoxyphenols are converted into phenols, by removal of the methoxy functionalities. Subsequently, phenols are converted, to some degree, into cyclohexanols via hydrogenation of the aromatic ring. Scheme 4-3 shows the proposed reaction pathways for the conversion of ortho-methoxyphenols. Overall, four moles of hydrogen-equivalent are required to convert a guaiacyl unit into the corresponding cyclohexanol plus methanol.

![Scheme 4-3 Proposed hydrogenolysis-hydrogenation pathway for conversion of methoxyphenols into cyclohexanols.](image)

Raney Ni has been utilized as the hydrogenation catalyst, and the reaction was carried out in 2-PrOH in an autoclave for 8 hours, at 200 °C and under a 70 bar pressure of H\textsubscript{2}. After reaction, a proportion of the lignin was rendered soluble in 2-PrOH and was separated from the remaining solid residue (SR) by filtration. After evaporation of the solvent, the liquid product (LP) of reaction was characterized. Figure 4-9 shows the weight yields percentages of LP and SR (as a proportion of starting material) for MCP-L, OS-L and E-L.
Extraction of lignin in a biphasic system and its downstream processing

**Figure 4-9** Weight yields of liquid product (soluble in the reaction solvent at room temperature) and solid residue after reaction. Reaction conditions: Substrate: 430 mg, Raney-Ni: 125 mg, 2-PrOH (13 mL, solvent), H₂: 70 bars (at room temperature), 200 °C, 8 hours.

It is high likely that the low conversion of the MCP-L into liquid products is primarily attributable to low solubility of this substrate in the reaction solvent (2-PrOH). However, many factors such as carbohydrate content, molecular weight distribution and different content of C-O bonds may be responsible for the lower conversion of MCP-L compared to E-L.153,154 Less than a half of the MCP-L starting material was converted into liquid products. By contrast, E-L and OS-L showed similar productivity of liquid products under the reaction conditions described above. The higher conversion is most likely attributed to high solubility in conjunction with the low molecular weight distribution of this substrate in addition to the absence of polysaccharides in the lignin stream (owing to the biphasic extraction of lignin from the aqueous phase).

Subsequently, elemental composition of the lignin samples was determined and compared. The van Krevelen’s diagram of MCP-L, OS-L and E-L is shown in Figure 4-10 (for starting materials and LPs after reaction).
The MCP-L exhibited a higher O/C ratio than OS-L, whilst E-L exhibited an intermediate value between them. However, E-L exhibited the highest H/C ratio, while MCP-L and OS-L shows similar H/C ratio. LPs were all found to have a lower O/C ratio and higher H/C ratio compared to the corresponding starting material. This aspect highlights that the substrates have undergone hydrogenation. The change in H/C ratio is higher for MCP-L compared to the other two analogous. Therefore, hydrogenation has occurred to a larger extent for MCP-L than the other lignin varieties. However, E-L was more prone to undergo deoxygenation reactions leading to a lower O/C ratio, compared to the other two lignins stream. Notably, traces of sulfur are detected for E-L (0.08 wt%) whilst OS-L and MCP-L were found to be completely sulfur free.
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The GC×GC-FID chromatogram of beechwood E-L LP is shown in Figure 4-11.

**Figure 4-11** GC×GC-FID chromatograms of beechwood E-L liquid product (LP).

Evaluating the GC×GC-FID chromatogram (Fig. 4-11), hydrogenolysis brings about selective conversion of the lignin extracted in 2-MeTHF into ortho-methoxy and dimethoxyphenols. 4-(3-hydroxypropyl)-2,6-dimethoxyphenol, which is obtained via depolymerization of the S-units, is the most abundant product, as already observed for the hydrogenolysis of OS-L and MCP-L (Chapter 3). Conversely, 4-(3-hydroxypropyl)-2-methoxyphenol was obtained via depolymerization of the G-Unit or via demethoxylation of 4-(3-hydroxypropyl)-2,6-dimethoxyphenol. Cleavage of the p-hydroxypropyl chain brings about the formation of the p-methyl, p-ethyl and p-propyl-substituted methoxy- and dimethoxyphenols. Surprisingly, when E-L is used as a substrate for the hydrogenolysis reaction, the obtained methoxyphenols were not further converted to cyclohexanols via saturation of the aromatic ring.

Finally, to determine the content of S- and G-units in the LP obtained via hydrogenolysis of E-L, OS-L, and MCP-L, and the possible demethoxylation activity
of the catalyst, the ratios between the S-lignin units and the G-Lignin were determined and are reported in Table 4-3.

**Table 4-3** Ratio between S-lignin and the G-lignin units in E-L, OS-L and MCP-L LPs

<table>
<thead>
<tr>
<th>Compound</th>
<th>E-L LP</th>
<th>MCP-L LP</th>
<th>OS-L LP</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Chemical Structure" /></td>
<td>2.17</td>
<td>3.20</td>
<td>6.20</td>
</tr>
</tbody>
</table>

The ratios between S-lignin and the G-lignin monomers in the liquid product obtained from hydrogenolysis change considerably between E-L, MCP-L and OS-L samples. OS-L LP contains significantly higher quantities of volatile ortho-dimethoxyphenols compared to MCP-L and E-L. This finding highlights that the difference in concentration of monomeric ortho-monomethoxy- or ortho-dimethoxyphenols described in Table 4-2 may account for the lower oxygen/carbon ratio for the E-L LP (Figure 4-10) compared to the two other substrates. Raney Ni may be able to catalyze demethoxylation reactions, when E-L is employed as the substrate, to a higher extent then on MCP-L and OS-L, converting S-units into G-units. However, no fully demethoxylated products were isolated into the LPs, highlighting that there may not be demethoxylation activity of the catalyst. Conversely, the ratio between the S-lignin and the G-lignin units obtained after hydrogenolysis may be related to the content of S- and G-units as uncondensed unit
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in the corresponding starting material. E-L and E-L LP samples exhibit lower S/G ratios, 2.20 and 2.17 respectively, compared to their starting material and LPS analogues. OS-L and OS-L LP exhibit higher S/G ratios, 3.42 and 6.20 respectively, whilst MCP-L and MCP-L LP have intermediate value (2.25 and 3.2, respectively).

4.7 Conclusion

The lignin incorporated into the structure of beechwood undergo to substantial transformation during a fractionation process. However, part of the uncondensed units of the beechwood lignin (mostly the S-Unit, see Chapter 3) is preserved from hydrolysis during an organosolv process. Nevertheless, repolymerization of the phenolic units by C-C bonds formation leads to high-molecular weight structures that,\textsuperscript{111,155} despite the good solubility in a range of organic solvents, are poorly reactive in a heterogeneous catalytic system.

Conversely, the combination of a mechanocatalytic process and a subsequently hydrogenolysis step are able to depolymerize lignin among the ether linkages. Depolymerization determines decreasing the molecular weight, as highlighted in the experiment of the artificial wood. However, condensation and repolymerization occur, possibly on the carbonyl functionalities, which are incorporated into the structure of native lignin or formed upon fractionation process.\textsuperscript{81} Overall this process composed of mechanocatalytic treatment and saccharification step yields a solid polymer which is not easy to solubilize in organic solvents.

Conversely, where the saccharification step is performed in the presence of water and of 2-MeTHF, as extracting media, β-O-4 (A) and β-5 (B) linkages are distinctly about, obtaining a low-molecular-weight polymer. Moreover, extraction of lignin in the organic layer protects the carbonyl functionalities from repolymerization, and the obtained lignin (E-L) is readily soluble in a range of
organic solvent. The good solubility and the low-molecular-weight of this variety of lignin render this substrate highly reactive in a heterogeneous catalytic system.

Finally, hydrogenolysis of E-L was performed, which surprisingly brings about the conversion of the substrates selectively into ortho-methoxyphenol. Benzaldehydes and vinyl ether end groups are known to decrease the activity of Raney Ni. Benzaldehydes are converted to the corresponding benzylic alcohol, toluene and benzene, via hydrogen transfer reactions with 2-PrOH as a hydrogen donor at 80 °C. Even increasing the temperature to 120 °C, small proportions of the aromatic ring of the benzaldehyde are hydrogenated to saturated products. Dimethoxyphenol incorporating an unsaturated p-propyl chain, as 4-allyl-2,6-dimethoxyphenol, is converted to the corresponding p-alkyl derivate whilst the aromatic ring is mostly preserved. Therefore, the high quantities of benzaldehyde and vinyl ether ends groups in the E-L may be responsible, together with the presence of small quantities of sulfur, for inhibition of the hydrogenation activity of Raney Ni and the lower saturation rate of the ring during hydrogenolysis for this variety of lignin compared to OS-L and MCP-L. Therefore, hydrogenolysis of E-L selectively yields ortho-methoxyphenols without saturation of the ring.
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CHAPTER 5

Conversion of phenolic mixtures into arenes

In this chapter, a “tandem dehydroxylation” procedure will be applied to the depolymerized lignin oil in order to convert it into arenes. 4-(3-Hydroxypropyl)phenol was firstly selected as a model compound representing highly-depolymerized lignin oil. We demonstrate that the hydrogenation of this molecule with Raney Ni in the presence of molecular hydrogen (H₂) leads to saturation of the ring whilst deoxygenation also occurs via a hydrogen transfer reaction with 2-PrOH. The deoxygenation follows a dehydrogenation/decarbonylation route that is enhanced when the reaction is performed in a hydrogen acceptor solvent (e.g. acetone). Subsequently, 4-(3-hydroxypropyl)phenol and seven alternative phenolic compounds are converted via tandem deoxygenation reactions, with high selectivity, towards arenes. H-BEA-35, Amberlyst-70 and Nafion SAC-13 are compared as solid acid catalysts. Amberlyst-70 is identified as the most suitable acid catalyst for the reaction because it is able, in combination with Raney Ni, to convert even phenolic mixtures into high yields of arenes.
5.1 Introduction

Current interest on lignin as platform feedstock for the upgrading of chemicals is justified by its structure and elemental composition. Ether bonds occur between ortho methoxylated para-hydroxypropyl phenols that originate a complex polymer where the carbon-to-oxygen ratio is above 2, i.e. the energy density is higher compare to cellulose and hemicellulose (C/O = 1). Moreover, lignin constitutes the main potential source of renewable aromatics. The depolymerization of lignin into methoxyphenols is possible where the ether β-O-4 bond is selective cleaved. New acid- or base-catalyzed strategies for depolymerization, as well in hydrothermal or oxidative conditions have been presented. However, the depleting of fossils resources increases the attention on the valuation of biomass as feedstock for the production of fuels. For the production of fuels from lignin, other kinds of challenges have to be tacked (i.e. decreasing the oxygen content for improve the combustion properties). Promising strategy for the reduction of the oxygen content of lignin are metal-catalyzed hydrogenation and metal-catalyzed decarbonylation and decarboxylation. In Chapter 3 and 4, we demonstrate that Raney Ni catalyzed reductive processes performed on lignin constitute method promising route for increasing the H/O ratio while decreasing the O/C ratio to a level of 0.24-0.28.

Hydrodeoxygenation (HDO) is capable of converting phenols into target products such as alkanes or arenes. In both circumstances two catalysts are employed in ‘tandem’: a metal catalyst for hydrogenation in conjunction with an acid catalyst for dehydration. For conversion of phenols to alkanes a high input of gaseous hydrogen (H₂) is required, in order to bring about saturation of the aromatic ring and effect HDO. For instance, high selectivity towards alkanes under low severity conditions is possible by employing a noble metal supported on carbon as the hydrogenation catalyst, in cooperation with phosphoric acid as the acid catalyst.

We previously introduced a catalytic route for the tandem dehydroxylation of phenols to arenes performed over Raney Ni and a zeolite catalyst. This system is
advantageous because the necessary input of hydrogen (provided by 2-PrOH via a transfer hydrogenation reaction) is stoichiometric and not in excess. Moreover, no external hydrogen pressure is required. Alternative catalytic techniques for the selective conversion of phenols and methoxyphenols to arenes have emerged in the recent chemical literature. Huang et al.\(^{162}\) and Luo et al.\(^{163}\) reported that a ruthenium-supported catalysts can achieve high selectivity for conversion of phenols to arenes (ruthenium was selected due to its reduced tendency to saturate benzene, in comparison with other noble metals). A MoO\(_3\) catalyst was also used for the selective conversion of phenols into arenes without saturation of the ring.\(^{164}\) Despite high observed selectivities, high temperatures (>220 °C) were required, and the system was nevertheless sensitive to the pressure of H\(_2\).

Recently, Ferrini and Rinaldi introduced a method for the Catalytic Upstream Biorefining (CUB) of lignocellulose rendering the fraction of biomass into holocellulose and depolymerized lignin oil.\(^{78}\) In this process, woood is is subjected to Raney Ni dispersed in a mixture of water and 2-PrOH (70/30 %v) at temperatures between 160- and 220 °C. Raney Ni is able to catalyze the hydrogenolysis of lignin’s ether bonds by transfer hydrogenation.\(^{66}\) GPC and GC×GC-MS analyses revealed that the resultant lignin oil is primarily composed of phenolic monomers, accompanied by minor quantities of cyclohexanol products. Furthermore, in comparison to analogous bio-oils (e.g. pyrolytic oils), the evolved lignin oil exhibits high long-term stability. Notably, the two most abundant products were the phenol monomers 4-(3-hydroxypropyl)-2-methoxyphenol and 4-(3-hydroxypropyl)-2,6-dimethoxyphenol.

In order to better understand the subsequent reactivity of the depolymerized lignin oil obtained from Catalytic Upstream Biorefining (CUB) using Raney Ni as a catalyst an 2-PrOH as a H-donor, in this investigation 4-(3-hydroxypropyl)phenol was initially selected as a lignin model compound, because it incorporates the 3-hydroxypropyl chain at the para-position of the phenol ring present in the two major components of the depolymerized lignin oil (described above). Hydrogenation
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employing hydrogen gas (H₂) and with 2-propanol (2-PrOH) as a hydrogen source were compared.

Next, a selection of phenols/methoxyphenols were employed as model compounds representing the depolymerized lignin oil, and were evaluated in the described tandem dehydroxylation process using Raney Ni and an acid catalyst. Zhao et al. highlighted that acid-catalyzed dehydration of cyclohexanol is the rate-limiting step for the conversion of phenol into saturated hydrocarbons via HDO. Therefore in our investigation, the catalytic performances of three solid acid catalysts were screened in conjunction with Raney Ni, in the new process.

Finally, in order to demonstrate that our novel and robust tandem dehydroxylation procedure is applicable beyond trivial phenol model compounds, the optimized low-severity process (<200 °C) was applied towards the reaction of 4-(3-hydroxypropyl)-2-methoxyphenol (isolated from a sample of crude lignin oil), and in addition to two true crude lignin oil streams obtained from native lignocellulosic biomass sources (beechwood and sprucewood). The reaction selectively rendered arenes in good yields.

5.2 Hydrogenation of 4-(3-hydroxypropyl)phenol

Due to the complex structure of lignin, numerous studies on lignin model compounds have been published in the last few years. Phenols and ortho-methoxyphenols have been used as models for the monomeric units. Diphenyl ether and benzylic ethers were previously utilized as models of the lignin’s ether linkages. Recently, the synthesis of molecules that represent the β-O-4 and α-O-4 linkages helped to get in-depth inside into the pathways of lignin depolymerization. The lignin bio-oil obtained from the catalytic upstream biorefining of wood is mostly composed of 4-(3-hydroxypropyl)-2-methoxyphenol (1) and 4-(3-hydroxypropyl)-2,6-dimethoxyphenol (2). Figure 5-1 shows the structure of the two most abundant phenolic monomers obtained from wood.
Three oxygenated functional groups are present in the structure: the phenolic –OH, the methoxyl unit in ortho position to the phenolic –OH, and a primary alcohol. Conversion of the first two functional groups have been focused in many studies,\textsuperscript{167,168} whilst the presence of the primary alcohol unit has been to a large extent overlooked. Our previous study reveals that the catalytic activity of Raney Ni, one of the most used catalysts for industrial hydrogenation,\textsuperscript{169} is inhibited by primary alcohols. The hydrogenolysis of diphenyl ether with $\text{H}_2$ occurs faster in presence of 2-PrOH as a solvent comparing to methanol or ethanol.\textsuperscript{66} In order to better understand the reactivity of the lignin bio-oil hydrogenation of 4-(3-hydroxypropyl)phenol was performed.

As mentioned above, hydrogenation of phenols is a possible strategy for increasing the H/C ratio and decreasing the O/C. Hydrogenation of 4-(3-hydroxypropyl)phenol (3) in the presence of Raney Ni may, in principle, occur \textit{via} two parallel reactions pathways: (a) saturation/hydrogenation of the aromatic ring, and (b) elimination of the primary alcohol (Scheme 5-1).
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Scheme 5-1 Proposed reaction pathways for the hydrogenation of 3.

Pathway (a) generates 4-(3-hydroxypropyl)cyclohexanol (4), whereas pathway (b) yields both 4-propylphenol (5) and 4-ethylphenol (6). The product distributions for hydrogenation of 3, with both gaseous H₂ and 2-PrOH as a hydrogen source, are shown in Figures 5-2 and 5-3, respectively.

Figure 5-2 Hydrogenation of 4-(3-hydroxypropyl)phenol (3) with H₂ gas. Reaction conditions: 4-(3-hydroxypropyl)phenol (3 mmol); Raney Ni (100 mg); 50 bar H₂; 2-PrOH (15 mL); 90 °C; 300 rpm; 2.5 h.
Figure 5-3 Hydrogenation of 4-(3-hydroxypropyl)phenol with 2-PrOH. Reaction conditions: 4-(3-hydroxypropyl)phenol (2 mmol); Raney Ni (1 g); 2-PrOH (7 ml); 80 °C; 800 rpm; 3 h.

Experiments performed in the presence of molecular H₂ leads predominantly to saturation of the aromatic ring, whilst the deoxygenation pathway is inhibited (Fig. 5-2). Surprisingly, when 2-PrOH is used as the sole hydrogen source (under an Argon atmosphere), the saturated compounds are not the main product, whilst the deoxygenation pathway becomes predominant (Fig. 5-3). This observation starkly contrasts to our previous results, demonstrating that 4-propylphenol completely converts into 4-propylcyclohexanol at 120 °C after three hours. Therefore, the current results highlights that when reacted in a system composed of 2-PrOH/Raney Ni, the 3-hydroxypropyl substituent of 3 inhibits the activity of Raney Ni and competes with the aromatic ring for reaction at the nickel surface.

The high selectivity towards either the saturation of the ring or the deoxygenation of the 3-hydroxypropyl side chain suggests that 3 is in contact with the surface of the Ni catalyst via both the alcohol and the phenolic moieties. Once the ring is saturated, the catalyst is no longer effective for further conversion of 4. Therefore, it appears that aromaticity is one of the factors accounting for the strong catalytic activity with Raney Ni. Moreover, if deoxygenation takes place, pathway
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(b), no further saturation towards formation of cyclohexanols occurs after three hours of reaction at 80 °C. For the investigated conditions, the overall conversion of 3 into products is significantly greater with 2-PrOH as the hydrogen source (ca. 80% conversion, Figure 5-2) rather than with gaseous H₂ (ca. 25% conversion, Figure 5-1). In order to achieve higher conversion in the experiment of hydrogen transfer with 2-PrOH, a higher amount of Raney Ni (1 g) was used compared to the experiment where H₂ (0.1 g) is used as hydrogen source. When the experiment of 2-PrOH/Raney Ni was repeated with a lower quantity of catalyst (0.1 g), identical selectivity was achieved; however the conversion was reduced from 78% to 5%. These results are summarized in Table 5-1.

Table 5-1 Reaction of model compound 3 performed with different quantity of catalyst.

<table>
<thead>
<tr>
<th>Raney Ni (g)</th>
<th>Conversion (%)</th>
<th>4-(3-hydroxypropyl)cyclohexan-1-ol (4)</th>
<th>4-propylphenol (5)</th>
<th>4-ethylphenol (6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>78</td>
<td>56%</td>
<td>32%</td>
<td>9%</td>
</tr>
<tr>
<td>0.1</td>
<td>5</td>
<td>58%</td>
<td>35%</td>
<td>7%</td>
</tr>
</tbody>
</table>

Reaction conditions: 4-(3-hydroxypropyl)phenol (2 mmol); Raney Ni (1 or 0.1 g); solvent (7 ml); 80 °C; 800 rpm; 3h.

Subsequently, in order to better understand the reactivity of the primary -OH moiety an alternate model compound, 3-phenylpropan-1-ol, was investigated with respect to transfer hydrogenation. The overall conversion and the distribution of products are shown in graphical form in Figure 5-4, below.
Hydrogenation of 3-phenylpropan-1-ol with 2-PrOH. Reaction conditions: 3-phenylpropan-1-ol (2 mmol); Raney Ni (1 g); 2-PrOH (7 ml); 80 °C; 800 rpm; 3 h.

Under equivalent conditions, a lower overall conversion (ca. 70%) was observed for 3-phenylpropan-1-ol relative to model compound 3. Previous investigations have demonstrated that aromatic hydrocarbons are far less reactive than phenols with respect to saturation of the phenyl ring, in transfer hydrogenation. However, when the phenolic –OH is removed the proportional yield of deoxygenated products is increased; in particular, propylbenzene accounts for approximately 70% of the product mixture. Hence, if the tendency towards hydrogenation of the aromatic ring is decreased, the rate of the deoxygenation of the propyl chain is increased. The deoxygenation occurs with formation of a high yield of propylbenzene and a lower quantity of ethylbenzene.

Hydrogenation of hydrocinnamaldehyde under the same reaction conditions was subsequently performed. The results are shown in graphical form in Figure 5-5.
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**Figure 5-5** Hydrogenation of hydrocinnamaldehyde with 2-PrOH. Reaction conditions: hydrocinnamaldehyde (2 mmol); Raney Ni (1 g); 2-PrOH (7 ml); 80 °C; 800 rpm; 3 h.

High conversion (ca. 90%) is achieved. The primary products are 3-phenylpropan-1-ol (ca. 43%) and ethylbenzene (ca. 20%). Notably, the mass balance is not close. Only ca. 65% of the starting carbon could be accounted in the products of reaction. In the presence of various catalysts and in the appropriate condition of reaction, aldehydes react with olefins and phenols. These reactions have been reviewed in the chemical literature. Condensation reactions may account as the reason because part of the products obtained could not be identify by GC-MS. Hydrogenation and deoxygenation pathways preceded in parallel, yet hydrogenation of the carbonyl group is favored whilst the hydrogenation of the ring is inhibited. Surprisingly, selectivity towards propylbenzene is relatively low (ca. 2%). This result clearly demonstrates that the formation of ethyl-substituted cyclic compounds from 3-arylpropan-1-ol substrates occurs via dehydrogenation of the primary –OH, forming an aldehyde, followed by decarbonylation of the aldehyde, resulting in the loss of one carbon atom from the propyl chain. Further oxidation of the aldehyde to the corresponding carboxylic acid and subsequently decarboxylation of the carboxylic acid may also lead to the ethyl-substituted cyclic compounds.
Subsequently, the reaction of model compound 3 in the presence of Raney Ni and an alternative solvent to 2-PrOH was investigated. The deoxygenative pathway (Scheme 5-1) yields 5 and 6, via loss of water and CO respectively. It was found that when 3 was reacted in the presence of a hydrogen acceptor solvent (e.g. acetone), the yield of 5 increases (Table 5-2).

**Table 5-2** Reaction of model compound 3 performed in different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conversion (%)</th>
<th>4-(3-hydroxypropyl)cyclohexan-1-ol (4)</th>
<th>4-propylphenol (5)</th>
<th>4-ethylphenol (6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-PrOH</td>
<td>78</td>
<td>56%</td>
<td>32%</td>
<td>9%</td>
</tr>
<tr>
<td>Acetone</td>
<td>30</td>
<td>0%</td>
<td>12%</td>
<td>85%</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>60</td>
<td>0%</td>
<td>28%</td>
<td>72%</td>
</tr>
<tr>
<td>1-Octene</td>
<td>72</td>
<td>0%</td>
<td>22%</td>
<td>78%</td>
</tr>
</tbody>
</table>

Reaction conditions: 4-(3-hydroxypropyl)phenol (2 mmol); Raney Ni (1 g); solvent (7 ml); 80 °C; 800 rpm; 3h.

The proposed mechanistic pathway for formation of 5 and 6 is shown in Scheme 5-2, below.

**Scheme 5-2** Proposed reaction pathway for the deoxygenation of model compound 4-(3-hydroxypropyl)phenol, 3.

The formation of 6 initially proceeds via dehydrogenation of the primary hydroxyl group, yielding aldehyde 7. In the second step, the decarbonylation of 7
Conversion of phenolic mixtures into arenes

yields 6. The formation of 5 instead may proceeds via dehydration of 3, catalyzed by the Brønsted acid sites of the Raney Ni, to yield alkene 8. Subsequent hydrogenation of the double bond yields product 5. It is possible that a hydrogen acceptor solvent promotes dehydrogenation of 3, shifting equilibrium ‘a’ to the right, whilst a hydrogen donor solvent enhances the reaction to form 5 (‘b’) because hydrogen is required for the hydrogenation. Higher conversion of 3 occurs in cyclohexene and 1-octene than in acetone because Raney Ni is more active in non-polar solvents.66

Aldehydes are known to undergo decarbonylation in the presence of a metal catalyst,172,173 and recently Raney Ni was also investigated for this type of reaction.174 Keresszegi et al. explored the oxidation of trans-cinnamyl alcohol catalyzed by palladium and platinum-supported catalysts.175 They proposed that the loss of activity of the catalyst, during the oxidation reaction, is due to the (in situ formed) aldehyde decarbonylation and strong adsorption of CO. However, analysis of the gas phase of reaction, by FT-IR, performed on 4-(3-hydroxypropyl) as a substrate in the presence of 2-PrOH as the solvent and hydrogen donor revealed that no gas are release in the gas phase upon reaction. Therefore, the shortening of the alkyl side chain may happening through the elimination of formaldehyde, which may be trapped by the phenolic substrate bringing about oligomers or polymeric species that are not detectable by GC techniques. This hypothesis is verified by the observation of loss in the mass balance when the reaction is performed on 7.

5.3 Tandem dehydroxylation of lignin model compounds

We previously demonstrated that the conversion of phenol into benzene is possible in a one-pot process, when a sub-stoichiometric quantity of 2-PrOH is employed.54 The reactions occurring in this process are highlighted in Scheme 5-3. Raney Ni catalyzes the transfer hydrogenation of phenol to cyclohexanol. Subsequently, the intermediate cyclohexanol is dehydrated over a solid acid catalyst (H-BEA-35) yielding cyclohexene, which is then converted into benzene via aromatization of the ring (transfer dehydrogenation). Hence, cyclohexene is employed as an internal
hydrogen donor (i.e. in-situ formed), allowing for continued hydrogenation of phenol. This procedure renders a 90% yield of benzene at 160 °C in 4 hours.

![Scheme 5-3](image)

**Scheme 5-3** One-pot tandem dehydroxylation of phenol to benzene based on the reaction sequence 1) transfer hydrogenation, 2) dehydration, and 3) transfer dehydrogenation. Adapted from literature. 54

In the present work, to exploit the potential of tandem dehydration of phenols present in the lignin oil obtained from CUB, the process was performed on 4-(3-hydroxypropyl)phenol as a model compound. The conversion and selectivity for the Raney Ni- and H-BEA-35 solid acid-catalyzed reaction of 4-(3-hydroxypropyl)phenol is shown in Figure 5-6.

![Figure 5-6](image)

**Figure 5-6** Products of tandem dehydroxylation of 4-(3-hydroxypropyl)phenol. Reaction conditions: 4-(3-hydroxypropyl)phenol (1 mmol); Raney Ni (0.60 g); H-BEA (80 mg); methylcyclohexane (3 mL); 2-PrOH (1.5 mmol); 190 °C; 800 rpm; 4 h.

Almost full conversion was also achieved, leading to arenes (84%) as the primary products. Ethylcyclohexane and propylcyclohexane accounted for the remaining 16%. Partial cleavage of the aliphatic chain was observed, yielding
Conversion of phenolic mixtures into arenes

ethylbenzene and toluene. The reaction was subsequently also performed in the absence of 2-PrOH; these results obtained without a hydrogen donor are shown in graphical form in Figure 5-7.

![Conversion and selectivity graph](image)

**Figure 5-7** Products of tandem dehydroxylation of 4-(3-hydroxypropyl)phenol without 2-PrOH. Reaction conditions: 4-(3-hydroxypropyl)phenol (1 mmol); Raney Ni (0.60 g); H-BEA (80 mg); methylcyclohexane (3 mL); 190 °C; 800 rpm; 4 h.

As for experiments with added 2-PrOH, arenes are the primary products when 2-PrOH is absent. However, the proportion of arenes in the product mixture is reduced by approximately 10% (to 73%). Cyclohexanol and cyclohexanone species amount to the majority of the remaining mass, whilst aliphatic compounds (e.g. propylcyclohexane) are present in minor quantities (ca. 2%). Since no hydrogen donor is present, apparently, part of the hydrogen that it is stored in the structure of the Raney Ni was used for the tandem dehydroxylation. Also, the absence of a hydrogen donor solvent shifts the selectivity towards 4-ethylphenol (6) with a corresponding reduction in the quantity of 4-propylphenol (5). As discussed in the previous section (Scheme 5-2), formation of ethyl-substituted compounds is likely to occur via decarbonylation route or formaldehyde loss. Hydrogen produced by this pathway could also be utilized for the tandem dehydroxylation process; 1 mole of phenol requires a net addition of only one mole of H₂ to form 1 mole of benzene (Scheme 5-3). Therefore, tandem dehydroxylation of 3 has the potential to be self-
sufficient in terms of hydrogen demand for the overall reaction: \(4-(3\text{-hydroxypropyl})\text{phenol (3)}\rightarrow\text{ethylbenzene.}\)

Subsequently alternate solid acid catalysts besides H-BEA-35 were investigated. The selected solid acid catalysts were Amberlyst-70 (a macroporous polymer) and Nafion SAC-13. Results obtained for tandem dehydroxylation with the two additional solid catalysts are shown in Table 5-3. Using Amberlyst-70, 76% arenes were obtained and full conversion was achieved; far low quantities of arenes were formed with Nafion SAC-13 (ca. 52%).

**Table 5-3** Products of tandem dehydroxylation of \(4-(3\text{-hydroxypropyl})\text{phenol. Reaction conditions: 4-(3-hydroxypropyl)phenol (1 mmol); Raney Ni (0.60 g); Amberlyst-70 or Nafion SAC-13 (10 mg); methylcyclohexane (3 mL); 2-PrOH (1.5 mmol); 190 °C; 800 rpm; 4 h.}

<table>
<thead>
<tr>
<th>Raney Ni Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-PrOH/substrate = 1.5 methylcyclohexane (Solvent), 463 K, 4 h</td>
<td></td>
</tr>
<tr>
<td><strong>Amberlyst-70</strong></td>
<td>100</td>
</tr>
<tr>
<td><strong>Nafion SAC-13</strong></td>
<td>100</td>
</tr>
</tbody>
</table>

Subsequently, in order to examine recyclability/stability of the three solid acid catalysts (H-BEA-35, Amberlyst-70 and Nafion SAC-13) employed in conjunction with Raney Ni, experiments were performed using diphenyl ether as a lignin model compound. With the experiment performed on this model compound, the stability of
Conversion of phenolic mixtures into arenes

both Raney Ni and a solid acid catalyst can readily be assessed. On the one hand, through the hydrogenolysis of diphenyl ether and sequential hydrogenation of phenol to cyclohexanol, the hydrogenation performance of Raney Ni can be evaluated. On the other hand, through the levels of cyclohexanol, the stability of the solid acid catalyst can be examined. Overall, the accumulation of phenol in the reaction medium is associated with the deactivation of Raney Ni, while the accumulation of cyclohexanol is related to the deactivation of the solid acid catalyst. In the recycling experiments, the catalyst mixture was recycled for six successive cycles/runs. The conversion and selectivity results are summarized in Table 5-4.

Table 5-4 Recycling of the catalysts.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>100</td>
<td>92 6 0 0 0</td>
</tr>
<tr>
<td>2nd</td>
<td>55</td>
<td>82 11 7 0 0</td>
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<tr>
<td>3rd</td>
<td>57</td>
<td>86 9 5 0 0</td>
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<tr>
<td>4th</td>
<td>71</td>
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<td>85 7 2 3 2</td>
</tr>
<tr>
<td>6th</td>
<td>81</td>
<td>82 6 2 5 4</td>
</tr>
</tbody>
</table>

Reaction conditions: a) H-BEA-35 (80 mg); diphenyl ether (1 mmol); Raney Ni (0.60 g); methylcyclohexane (3 mL); 2-PrOH (4 mmol); 190 °C; 800 rpm; 4 h.
Table 4b. Recycling of the catalysts.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
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<td>6</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>17</td>
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</tbody>
</table>

Reaction conditions: a) Nafion SAC-13 (10 mg); diphenyl ether (1 mmol); Raney Ni (0.60 g); methylcyclohexane (3 mL); 2-PrOH (4 mmol); 190 °C; 800 rpm; 4 h.

Table 4c. Recycling of the catalysts.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
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<tr>
<td></td>
<td>7</td>
<td>8</td>
</tr>
</tbody>
</table>

Reaction conditions: a) Amberlyst-70 (10 mg); diphenyl ether (1 mmol); Raney Ni (0.60 g); methylcyclohexane (3 mL); 2-PrOH (4 mmol); 190 °C; 800 rpm; 4 h.
Conversion of phenolic mixtures into arenes

In the first cycle for the three catalytic systems, full conversion of diphenyl ether was achieved. Additionally, the selectivity towards arenes was between 87 and 94%. Therefore, no major differences in the conversion or the selectivity were observed between the three catalysts in the first cycle.

By contrast, a lower conversion is achieved in the second cycle, most notably for H-BEA-35 and Amberlyst-70. Nevertheless, selectivities toward arene products remain high. Although the overall conversion is significantly diminished in the second cycle with H-BEA-35, quantities of oxygenated products (e.g. phenol, cyclohexanol, cyclohexanone) are low or zero; the absence of cyclohexanol/cyclohexanone is indicative of the strength and stability of the solid acid catalyst for the dehydration reaction. Interestingly, from the second up to the sixth cycles with H-BEA-35, the activity of Raney Ni appears to be partially regenerated and the conversion increases from 55 to 81%. The selectivity towards arenes, however, does not change (Table 5-4a). In turn, for the experiments employing Amberlyst-70 low conversions are achieved between the second and sixth cycles (suggesting instability of Raney Ni), although the high selectivity towards arenes remains (Table 5-4c).

By contrast, whilst the overall conversion is consistently high using Nafion SAC-13 as the solid acid catalyst, the selectivity for the arene products drops substantially after the first cycle (from 94 to 64%) and is thereafter consistently at 57-62% for the third through sixth cycles (Table 5-3b). Therefore in this latter case, the rate-limiting step in the tandem dehydrogenation process appears to be dehydration of the cyclohexanol derivative to the cyclohexene. Raney Ni is evidently more tolerant in the reaction incorporating Nafion SAC-13 than in reactions with the other acid catalysts, for tandem dehydroxylation of diphenyl ether.

The encouraging selectivities of Amberlyst-70 and H-BEA-35 solid acid catalysts towards the production of arenes led us to further explore the tandem
dehydroxylation for other phenolic substrates. Seven further phenolic model compounds were selected for tandem dehydroxylation with Raney Ni and Amberlyst-70/H-BEA-35. Conversion and selectivity results for these experiments are listed in Table 5-4.

The catalytic system consisting of Raney Ni and Amberlyst-70 performed well with all non-alkylated and three of the alkylated phenol model compounds (entries 1-5 and 7, Table 5-5); full conversion and good yields to arenes where obtained.
**Conversion of phenolic mixtures into arenes**

**Table 5-5** Tandem dehydroxylation of several model compounds with Raney Ni and H-BEA-35 or Amberlyst-70

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sub.</th>
<th>Con. (%)</th>
<th>Other</th>
<th>Other</th>
<th>Other</th>
<th>Other</th>
<th>Other</th>
<th>Other</th>
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<td>0 0 0</td>
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</tr>
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<td>0 0 0</td>
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<tr>
<td>3</td>
<td>H-BEA</td>
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<td>0 0 9</td>
<td>0 0 0</td>
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</tr>
</tbody>
</table>

**Reaction conditions:** Substrate (1 mmol); Raney Ni (0.60 g); H-BEA-35 or Amberlyst-70 (10 mg); methylcyclohexane (3 mL); 2-PrOH (1.5 mmol); 190 °C; 800 rpm; 4 h.
Generally, the full conversion of the substrates to arenes is prevented by the formation of cyclohexane species, occurring \textit{via} saturation of cyclohexene intermediate (internal H-donor). The relative propensity to form a cyclohexane increases with the number of methoxy substituents: phenol (entry 1) < guaiacol (entry 2) < 2,6-dimethoxyphenol (entry 3). Therefore, the substitution of the phenolic ring with methoxy group on the ortho-positions decreases the overall arene yield. Likewise, the presence of a propyl chain in the para-position to the phenolic –OH of the guaiacol unit further decreases the yield of arenes (entry 4, Table 5-5). Interestingly, the replacement of the methyl group of 4-propylguaiacol with a –OH moiety (entry 5, Table 5-5) or the presence an hydroxyl group on the propyl chain (entry 7, Table 5-5) increase the selectivity towards arenes up to 76%. Primary –OH moiety are present in the lignin oil and the occurrence of this functionality is here proved to increase the yields of arenes in the tandem dehydroxylation of methoxyphenols. Low yields of arenes were obtained for 4-allyl-2,6-dimethoxyphenol (entries 6, Table 5-5). Raney Ni is known to catalyze the hydrogenation of cyclic ketones and phenols in good yield, yet lower conversions are achieved for olefins (especially trans olefins).\textsuperscript{176} This may explain the low yield of arenes for 4-allyl-2,6-dimethoxyphenol (entry 6, Table 5-5).

Full conversion of all seven phenol substrates was also observed when H-BEA-35 was employed as a solid acid catalyst (Table 5-5). For phenol itself and the simple ortho-methoxyphenols (entries 1-3), selectivities are comparable to the experiments performed with Amberlyst-70 and arenes were produced in high yields. 4-Propylguaiacol (entry 4) is converted into arene products in lower yield than unsubstituted guaiacol. Interestingly, the yield of arenes increases when the para-propyl chain is substituted with a terminal hydroxyl group (entry 7), accompanied by a decrease in the phenol yield, as already observed for the experiments with Amberlyst-70. Higher quantities of arene products were produced from 4-allyl-2,6-dimethoxyphenol using H-BEA-35 rather than Amberlyst-70, although the primary
Conversion of phenolic mixtures into arenes

Product of the reaction is still 2,6-dimethoxy-4-propylphenol incorporating a saturated alkyl side chain (entry 6). No arene products were formed from reaction of the homovanillin alcohol model compound (entry 5).

Subsequent to the investigation of tandem dehydroxylation of the seven individual phenolic model compounds (Table 5-5), mixtures of phenol model compounds (3 with guaiacol, and 3 with 2,6-dimethoxyphenol) were studied with Raney Ni in conjunction with either Amberlyst-70 or H-BEA-35. The experimental details and the conversion and selectivity data for experiments performed with these two solid acid catalysts are listed in Tables 5-6. Reactions were performed under optimized conditions as determined in previous experiments.

Table 5-6 Products obtained from tandem dehydroxylation of a mixture of phenol species with Raney Ni and Solid acid-catalyst (Amberlyst-70 or H-BEA-35)

<table>
<thead>
<tr>
<th></th>
<th>Conversion (%)</th>
<th>Selectivity %</th>
</tr>
</thead>
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<td><strong>Amberlyst-70</strong></td>
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</tr>
<tr>
<td>Arenes</td>
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<td>H-BEA-35</td>
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<td><strong>Amberlyst-70</strong></td>
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<td></td>
</tr>
<tr>
<td>Cyclohexanes</td>
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<td>8</td>
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<tr>
<td><strong>Amberlyst-70</strong></td>
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<td></td>
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</tr>
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<td>75</td>
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</table>

Reaction conditions: a) 4-(3-hydroxypropyl)phenol (0.5 mmol), guaiacol (0.5 mmol); b) 4-(3-hydroxypropyl)phenol (0.5 mmol), 2,6-dimethoxyphenol (0.5 mmol); Raney Ni (0.60 g); H-BEA (80 mg) or Amberlyst-70 (10 mg); methylcyclohexane (3 mL); 2-PrOH (1.5 mmol); 190 °C; 800 rpm; 4 h.
It was observed that it is equally possible to convert mixtures of phenolic species into arenes, as for the individual model compounds. For the experiments performed with Amberlyst-70, full conversion of both of the components of the mixture was observed (Table 5-6). In addition, high yields (≥71% from each phenol starting compound) of arene products were obtained. There is no apparent reduction in reactivity of any component in the mixtures, in the presence of a second model compound; rather, the yield of arene products derived from 2,6-dimethoxyphenol are higher as a result of the inclusion of 4-(3-hydroxypropyl)phenol, 3.

Full conversion of 3 and ortho-methoxyphenols was observed in both experiments incorporating H-BEA-35 as a solid acid catalyst (Table 5-6). However, the ortho-methoxyphenol component was only partly converted to arene in each instance, following four hours of reaction. This demonstrates the lower catalytic reactivity of H-BEA-35 in comparison to Amberlyst-70 for the tandem dehydroxylation of a phenol model compound mixture. Similarly, yields of arene products were modest or low; in particular, compound 3 was predominantly converted into phenols in both mixtures (Table 5-6), and the yield of arenes derived from the ortho-methoxyphenol component did not exceed 55%.

5.4 Tandem dehydroxylation of lignin oil

The optimized tandem dehydroxylation process (with Raney Ni and Amberlyst-70 catalysts) was applied to the treatment of true depolymerized lignin oil derived from native biomass feedstocks. Volatile compounds from the reaction of Beechwood lignin oil tandem dehydroxylation are shown in graphical form in Figure 5-8.
Conversion of phenolic mixtures into arenes

Figure 5-8 GC×GC-MS spectra of the Beech wood lignin oil stream before (a), and after (b) tandem dehydroxylation. Reaction conditions: Raney- Ni (0.6 g), Amberlyst-70 (0.010 g), substrate (0.05 g), 2-PrOH (0.110 g), methylcyclohexane (3 mL) processed at 190 °C for 4 h.

Interestingly, considering reaction of beechwood, 4-(3-hydroxypropyl)-2-methoxyphenol and 4-(3-hydroxypropyl)-2,6-dimethoxyphenol (the main components of depolymerized lignin oil) were fully absent. The volatile fraction was primarily composed of dimethoxyphenols (37 wt%) and arenes (29 wt%). Cyclohexanol and cyclohexanone products accounted for 14 and 11 wt% of the volatile fraction, respectively. Highly-reactive phenol and guaiacol species were mostly absent.
Therefore for treatment of beechwood lignin oil, tandem dehydroxylation can be employed to selectively yield primarily arenes and dimethoxyphenols, under low severity conditions. The syringyl units are therefore only partially demethoxylated, whilst guaiacyl units are more reactive, demonstrated by the relative absence of guaiacol-derived compounds in the product volatile fraction. The composition of the volatile fraction of the lignin oil stream from sprucewood, prior to tandem dehydroxylation, is shown in graphical form in Figure 5-9a.

**Figure 5-9** GC×GC-MS spectra of the Spruce wood lignin oil stream before (a), and after (b) tandem dehydroxylation. Reaction conditions: Raney Ni (0.6 g), Amberlyst-70 (0.010 g), substrate (0.05 g), 2-PrOH (0.110 g), methylcyclohexane (3 mL) processed at 190 °C for 4 h.
The major component was 4-(3-hydroxypropyl)-2-methoxyphenol (guaicyl units); the quantity of syringyl units present in this softwood biomass feedstock is negligible. Methoxylated compounds were almost completely absent from the volatile components of the product after the tandem dehydroxylation reaction (Fig. 5-9b). Furthermore, arene products accounted for a greater proportion of the volatile products (59 wt%) than with beechwood (29 wt%); arene species are therefore the primary products of the tandem dehydroxylation of the Spruce wood feedstock. By contrast, aliphatic compounds were present in negligible quantities. Cyclohexanol and cyclohexanone products accounted for 29 and 19 wt% of the volatile fraction, respectively. Phenol and guaiacol species were detected in minor yields.

Therefore the tandem dehydroxylation of depolymerized lignin oil from both hardwood and softwood feedstocks leads to a relatively narrow distribution of products, whereby desirable arenes account for a major fraction of the resultant mixture; a high proportion of the oxygen-containing functional groups are removed by the deoxygenative process. Decarbonylation also occurs to a significant extent. The volatile fraction of the product oil contains 60 wt% of C2-alkylated aromatics (alongside C1 and C3-alkylated analogues) products with a high value as naturally-derived commodity chemicals. For example, ethylbenzene is predominantly used as a precursor of the styrene monomer for the production of polystyrene. This method may be efficient for providing a green lignin derived platform molecule to integrate into the existing petrochemical refinery.

5.5 Conclusion

Our results demonstrate that Raney Ni is an effective catalyst for the reduction of the O/C ratio, achieved by transfer hydrogenation, and for increase the H/C ratio. Formation of 4-ethylphenol by decarbonylation or elimination of formaldehyde from 4-(3-hydroxypropyl)phenol is important for the production of fuels from lignocellulosic biomass. This method substantially reduces oxygen content without
the consumption of added hydrogen. Moreover, the removal of reactive aldehyde groups inhibits undesirable repolymerization of the depolymerized lignin oil.\textsuperscript{81}

Regarding the tandem dehydroxylation of phenolic substrates, the system incorporating Amberlyst-70 is significantly more effective for the conversion of phenol mixtures into arene products than the analogous H-BEA-35 zeolite system. Systems incorporating two or more phenolic lignin model compounds are a closer representation of the true depolymerized lignin oil stream than a system incorporating just one model compound. Therefore, the results evolving from the mixture investigations offer valuable insights into the reactivity of the intended lignin oil feedstock.

Moreover, a catalytic system comprising both Raney Ni and a solid acid (Amberlyst-70), and 2-PrOH acting as a hydrogen donor, is capable of converting depolymerized lignin oil derived from either a hardwood or a softwood feedstock into a mixture with a significant fraction of value-added C\textsubscript{n}-alkylated arenes (n = 1-3). The low required temperature and the sub-stoichiometric demand for hydrogen arise from the transfer hydrogenation of 2-PrOH, enabling high selectivities and avoiding the formation of hydrocarbons. Therefore, the procedure benefits from improved hydrogen economy, and may be regarded as an environmentally-benign technique for the targeted upgrading of lignin-derived bio-oil into arenes.
Conversion of phenolic mixtures into arenes
CHAPTER 6

Selective Raney-Ni-catalyzed Hydrodeoxygenation of Phenol to Benzene

6.1 Introduction

Hydrogen transfer reactions of phenol proceed via initial dehydrogenation of a hydrogen donor species, followed by addition of the hydrogen atom to phenol. For conventional HDO processes on phenolic compounds (e.g. processes performed under H₂ pressure) several pathways have been proposed. Saturation of the aryl ring (pathway ‘a’, Scheme 6-1)⁵² competes with the hydrogenolysis of the C-O bond (pathway ‘b’)¹⁶² and the partial hydrogenation (pathway ‘c’).¹⁷⁷ Scheme 6-1.
Scheme 6-1 Reaction pathways for the hydrogenation and deoxygenation of phenol.

When pathway ‘a’ is followed, saturation of the ring occurs with the formation of cyclohexanone and, eventually, reduction of the C=O bond leads to cyclohexanol. By contrast, hydrogenolysis of the phenolic –OH substituent converts phenol into benzene and water. However, the C-O bond in phenol is strong, with a standard dissociation enthalpy of 465 kJmol$^{-1}$. Direct cleavage of this bond is possible only at relatively high temperatures.\textsuperscript{162,163,179} When partial hydrogenation of the ring occurs, phenol is converted into cyclohexa-2,4-dien-1-ol, which in the presence of an acid may be dehydrated into benzene.\textsuperscript{177}

Benzene may also be obtained from cyclohexanol via dehydration to cyclohexene, followed by dehydrogenation to yield benzene.\textsuperscript{13} A further saturation step to the formation of cyclohexane is thermodynamically very favorable, and therefore, very likely under high H$_2$ pressure.\textsuperscript{51,52} Considering the H$_2$ economy, four equivalents of molecular hydrogen (H$_2$) are required for the conversion of phenol into cyclohexane whilst only equimolar H$_2$ is required for completion of the reaction to form benzene.

Raney Ni is an established catalyst for the hydrogenation of phenols when molecular hydrogen (H$_2$) or a hydrogen donor compound is selected as the hydrogen
Raney Ni is also able to catalyze dehydrogenation of cyclic alkanes. In a previous study, when methylcyclohexane (0.5 ml) was reacted in the presence of a high quantity of Raney Ni (8 g), at temperatures between 180 to 300 °C, hydrogen and methane were generated in the gas phase whilst the residual liquid phase was composed of methylcyclohexane (MCH), benzene, and toluene. The highest conversion of MCH was observed at 250 °C, whilst at lower temperatures, the equilibrium rate for the dehydrogenation was lower. At temperatures higher than 250 °C, the residence time of the reactant on the surface of the catalyst will be reduced, thereby decreasing the dehydrogenation rate.

In this chapter, hydrodeoxygenation of lignin model compounds and depolymerized lignin stream is investigated in the presence of liquid hydrogen carriers (e.g. MCH, 2-PrOH) as both the solvent and source of hydrogen. It was observed that Raney Ni selectively converts phenol into benzene when hydrocarbons (e.g. MCH) are used as the solvent media. Subsequently, this strategy was successfully applied for the deoxygenation of lignin-derived phenols into arenes.

6.2 Transfer hydrogenation of phenols in the presence of Raney Ni and MCH as a reaction media

The conversion and selectivities for the hydrogen transfer reaction on phenol, catalyzed by Raney Ni at 220 °C in MCH or 2-PrOH solvents are shown in Figures 6-1 and 6-2, respectively. Experimental conditions are listed in Figure captions.

Figure 6-1 Hydrogenation of phenol with MCH. Reaction conditions: phenol (1 mmol); Raney-Ni (0.6 g); MCH (3 ml); 220 °C; 800 rpm; 4 h.
Selective Raney-Ni-catalyzed Hydrodeoxygenation of Phenol to Benzene

![Diagram of reaction](image)

**Figure 6-2** Hydrogenation of phenol with 2-PrOH. Reaction conditions: phenol (1 mmol); Raney-Ni (0.6 g); 2-PrOH (3 ml); 220 °C; 800 rpm; 4 h.

In the liquid-phase transfer hydrogenation reaction performed on phenol, the nature of the solvent determined the predominant reaction pathway. When cyclic alkanes (*e.g.* MCH) were employed as solvent, deoxygenation was exclusively observed, leading to the selective formation of arenes, primarily benzene (58%) and, interestingly, biphenyl (6%) and traces of *m*-terphenyl; no cyclohexane (*via* saturation of the phenolic ring) was observed. Dehydrogenation of MCH occurs and 0.13 mmols of toluene are formed. The amount of abstracted H-atoms from MCH was quantified from the quantity of toluene present in the product mixture. Hence, the H-balance could be calculated using Eqn (1).

\[
\text{H-balance} = \frac{\text{H-atoms added into the substrate}}{\text{H-atoms abstracted from the H-donor}} \tag{1}
\]

The reaction has an H-balance of 1.5 considering the full conversion of phenol into benzene and the dehydrogenation of MCH into toluene. Therefore, dehydrogenation of MCH may be one but not the only source of hydrogen of the reaction. Notably, Raney Ni has in its structure a large amount of hydrogen stored (*ca.* 2 mmol/g), which may be utilized for the HDO of phenol into benzene. A substantial quantity of the carbon of starting material (*ca.* 30%) could not be accounted in the evolved products of the reaction performed in MCH (Figure 6-1), indicating possible coke formation throughout the process.
Phenol reacts with 2-PrOH (as a solvent) at 80 °C, in the presence of Raney Ni as a hydrogenation catalyst, affording cyclohexanol in 99.9% yield (whilst benzene is obtained in trace quantity).\textsuperscript{52} If 2-PrOH is employed as the hydrogen donor and solvent at 220 °C, pathway ‘a’ (Scheme 6-1) still dominates. Cyclohexanol (60%) and cyclohexanone (20%) are obtained as the main products, against just 5% of benzene. Small quantities of cyclohexane (4%) and o-cresol (2%) were also formed upon reaction.

Subsequently, dehydrogenation of MCH was performed under the same conditions of the experiment described above (Figure 6-1), without the presence of phenol. The reaction yielded toluene and cyclohexane, 1.12 and 0.68 mmols respectively, according to chemical literature.\textsuperscript{184} Raney Ni, therefore, in the absence of phenol catalyzes dehydrogenation and demethylation of MCH simultaneously, whilst cyclohexane is not dehydrogenated into benzene. Raney Ni may act as a bifunctional catalyst for the conversion of MCH into cyclohexane and toluene, according to chemical literature.\textsuperscript{185} Ni sites may promote dehydrogenation of the ring and, simultaneously, acidic sites may catalyze demethylation of MCH. Therefore, these results lend insight into important characteristics: (i) - Raney Ni promotes selective HDO of phenol into benzene in the presence of MCH as a solvent; (ii) – Raney Ni may acts as a bifunctional catalyst in the conversion of phenol into benzene in the presence of MCH (Raney Ni is able to perform as a hydrogenation and an acid catalyst); (iii) - the presence of phenol fully suppresses the demethylation reaction of MCH, whilst dehydrogenation of MCH still occurs to a minor extent.

6.3 Catalyst stability and the influence of alcohols in the Hydrodeoxygenation of Phenol into Arenes

In order to evaluate the stability of the Raney Ni catalyst in the conversion of phenol in the presence of MCH, spent Raney Ni was recovered and recycled for five successive cycles/runs. The conversion of phenol, the composition of the product
Selective Raney-Ni-catalyzed Hydrodeoxygenation of Phenol to Benzene

stream and the quantities of toluene formed for the five runs are showed in Figure 6-3. Figure 6-4 shows the C-balance % and the H-balance for the five runs.

**Figure 6-3** Recycling of the catalyst. Reaction conditions: phenol (1 mmol); Raney-Ni (0.6 g); MCH (3 ml); 220 °C; 800 rpm; 4 h.

**Figure 6-4** Recycling of the catalyst. C-balance % and H-balance for the five runs.
Linear catalyst decay is observed during the five runs, with a decrease in conversion and selectivity for the reaction of phenol into benzene. HDO of phenol to benzene occurs together with methylation of the aromatic ring of phenol from the second run; mostly o-cresol is formed, together with small quantities of other products. This finding may highlight that other kinds of active sites are incorporated onto the surface of the catalyst upon reaction after recycling. It is noteworthy that the ortho position (to the phenolic –OH) is more reactive that the para position regarding alkylation. At the same time, decreasing of the rate of dehydrogenation of MCH to toluene occurs. Ni supported catalysts have been intensively studied in the dehydrogenation of cyclic alkanes, and it is generally accepted that the reaction proceeds as the reverse of benzene hydrogenation.\textsuperscript{186} Therefore, cyclohexane is firstly dehydrogenated into cyclohexene, then into cyclohexadiene, and finally into benzene.\textsuperscript{187-189} Dehydrogenation reactions of cyclic alkanes on catalysts at high temperatures are regularly accompanied by the deposition of coke onto the catalyst surface.\textsuperscript{185} In a previous report by Corma et al.,\textsuperscript{190} fouling of the catalyst was found to be six times higher when methylcyclohexene was used as substrate compared to MCH, related to the presence and decomposition of partially dehydrogenated species of the surface of the catalyst that are responsible for coke formation.\textsuperscript{188,191} Therefore, coke formation on the surface of the catalyst is likely one explanation for catalyst fouling in this investigation.

As described above (Figure 6-4), during the first run, the C-balance is not close. Only the 70% of the starting carbon is recovered in the products of the reaction. The polymerization of phenol into poly-aromatic products (this pathway may also be responsible for the formation of biphenyl and m-triphenyl) may deposit high-molecular-weight compounds on the surface of the catalyst and decrease the activity of the catalyst. The C-balance increases progressively during the five runs.

During the first run, the H-balance is equal to 1.5. Moreover, the H-balance value increases even more from the first to the fifth run. This finding highlights that
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MCH is not the only H-donors used by RANEY Ni in the reaction. Indeed, part of the hydrogen stored in the structure of Raney Ni may be employed for convert phenol into benzene. However, this amount would not suffice to maintain the conversion of phenols into arenes. Considering that, when using MCH as an H-donor, the formation of carbon species on the catalyst is observed (as shown by EDX analysis in the next section), it is apparent that a portion of the H-content transferred into the initial phenolic stream arises from the formation of coke. The latter hypothesis seems to be the most plausible. This is because coke remains on the catalyst surface. Therefore, the apparent H-lack to account for the conversion of phenol is justified, as the equivalent amount of spent H-donor can be thus not found in the reaction mixture, but it is adsorbed on the catalyst surface.

Transmission Electron Microscopy (TEM) analysis of the spent Raney Ni after one cycle transfer hydrogenation with MCH is shown in Figure 6-5. In order to quantify carbon on the surface of the catalyst, Energy-Dispersive X-ray spectroscopy (EDX) was also performed on the fresh and spent catalyst. The commercial Raney Ni after reaction has a spongelike morphology and is mostly composed of distinct nickel domains (Region A, Figure 6-5) and aluminum species (Region B, Figure 6-5), in agreement with previous reports.\textsuperscript{192} The nickel domains are responsible for the hydrogenation activity of Raney Ni whilst the aluminum species may be accounted as the acidic species, which are responsible for dehydration and trans-alkylation reactions. Notably, cobalt and iron were also found in trace quantities. Accordingly to chemical literature, these elements may favor the deoxygenation activity of the catalyst via hydrogenolysis of the C-O bond.\textsuperscript{193,194} Elemental analysis by EDX generally leads to an over estimation of quantities of carbon and oxygen. Nevertheless, higher quantities of carbon were found in the spent catalyst, compared to the fresh catalyst before reaction (Appendix, Fig. 9-1 and Fig. 9-2). Conversely, the quantities of aluminum, cobalt, and iron remain identical before and after reaction.
Therefore, after reaction, a thin layer of carbon may be present on the surface of Raney Ni, which may be responsible for deactivation of the catalyst.

![TEM analysis of the Raney Ni after reaction of phenol with MCH.](image)

**Figure 6-5** TEM analysis of the Raney Ni after reaction of phenol with MCH.

The dehydrogenation ability of Raney Ni, when MCH is used as H-donor, decreases over time. This observation seems to be related to the formation of coke, which generate the hydrogen equivalents necessary for the formation of arenes from phenols. Therefore, the presence of other H-donor in the medium could conducive for a sustained hydrogenation activity of the catalyst. It is well-known that Raney Ni can easily use 2-PrOH as a hydrogen donor. Therefore, in order to decrease the likelihood of formation of coke, the HDO of phenol in the presence of sub-stoichiometric quantities of 2-PrOH (1, 2, and 4 mmol) was performed. The influence of MeOH on the reaction was also evaluated and the results of the reaction of phenol with Raney Ni/MCH in the presence methanol and 2-PrOH are shown in Figure 6-6.
As described above, phenol yields ca. 65% of arenes (benzene and biphenyl) when reacted in the presence of Raney Ni and MCH, and no other volatile products are detected. Where 1 mmol of phenol was reacted with Raney Ni/MCH in the presence of 1 mmol of methanol, a primary alcohol, the yield of arenes increased from 65 to 75%, although ca. 5% of cyclohexane was also obtained. However, when higher quantities of methanol were utilized, far greater quantities of cyclohexane were formed. Moreover, dehydrogenation of MCH into toluene also increased when methanol was added to the solution. The positive effect may be related to the competitive adsorption of phenol and the alcohol on Raney Ni, which may increase both the rate of adsorption of MCH on the catalyst surface and consequent dehydrogenation of the cyclic alkane. Methanol was not detected at the end of the reaction. Since cyclohexanol is deoxygenated into cyclohexane, it is correspondingly possible that methanol is deoxygenated into methane. This finding highlights, that the conversion of lignin into arenes in the presence of Raney Ni/MCH may also benefit from the presence of methoxy functionalities ortho to the phenolic –OH functional group.

Where 1 mmol of phenol was reacted in a system composed of Raney Ni/MCH in the presence of 1 mmol of 2-PrOH, a secondary alcohol, the yield of
arenes increased again to 75%, although interestingly no cyclohexane was formed. Notably, 85% of arenes were obtained from phenol when 2 mmols of 2-PrOH were added to the mixture of reaction, whilst the yield of arenes fell to 70%, and 15% of cyclohexane was formed, when 4 mmol of 2-PrOH were added. 2-PrOH was both dehydrogenated and deoxygenated into acetone and propane, respectively. The formation of toluene, via dehydrogenation of MCH, increased proportionally to the quantities of 2-PrOH added to the solution. Simultaneously, the selectivity in the conversion of phenol into benzene decreased when the polarity of the system was increased, whilst the formation of cyclohexane rose. This finding confirms that the presence of basic compounds likely decreases the predominance of HDO of phenol into benzene, most likely because of inhibition of the Lewis acid sites of the catalyst. Supposedly, as methanol is more polar than 2-PrOH, a lower amount of methanol than 2-PrOH is required to inhibit these acidic sites.

The C-balance % and the H-balance in the hydrogenation of phenol in the presence of 1, 2 and 4 mmol of 2-PrOH are shown in Table 6-1.

<table>
<thead>
<tr>
<th>mmol of 2-PrOH</th>
<th>1</th>
<th>2</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-balance %</td>
<td>85</td>
<td>94</td>
<td>94</td>
</tr>
<tr>
<td>H-balance</td>
<td>1.15</td>
<td>1.07</td>
<td>0.27</td>
</tr>
</tbody>
</table>

The presence of 2-PrOH as hydrogen donor increases the C-balance % proportionally to the quantities of alcohol introduced into the system. When 1 mmol of 2-PrOH is employed, the H-balance is higher than 1. Therefore, the system is not self-sufficient in the conversion of phenol into benzene. Hence, a part of the hydrogen necessary to complete the reaction may derive from the hydrogen stored.
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on the surface of the catalyst or the hydrogen arises from the formation of coke. Conversely, when 2 or 4 mmol of 2-PrOH are employed, the production of H₂ from is sufficient to complete the reaction. Notably, the H-balance is very close to one when 2 mmol of 2-PrOH are employed. When 4 mmol of alcohol are utilized, much higher amounts of H₂ than required are produced.

The influence of alcohols, on the selectivity of conversion of phenol into biphenyl, is shown in Figure 6-7.

![Figure 6-7](image)

**Figure 6-7** Influence of alcohols (methanol and 2-PrOH) on the Raney Ni-catalyzed formation of biphenyl.

The selectivity of phenol to biphenyl is indirectly proportional to the mmol of alcohols added. Moreover, the negative slope in the formation of biphenyl is more pronounced with 2-PrOH compared to MeOH, which is understandable on the basis that Raney Ni can utilize more easily 2-PrOH than MeOH as hydrogen donor. The formation of biphenyl and other polycyclic product (e.g. m-terphenyl) via coupling reaction may be responsible for the formation of coke, which may cover the active sites of the catalyst and decrease the activity of Raney Ni. Hence, the concomitant use of small quantities of alcohols during the reaction has a positive effect on the
reaction. Indeed, inhibition of a polymerization pathway decreases the formation of high molecular weight aromatic compounds, which cannot be detected by GC.

If high quantities of methanol are employed, the formation % of cyclohexane increases. Conversely, for small quantities of methanol and for 2-PrOH, the selectivities to benzene are improved. The spent catalyst after reaction of phenol with 1 mmol of methanol was reused for 4 more runs in order to evaluate the stability of the catalyst. An identical procedure was undertaken for the experiments performed in the presence of 1, 2 and 4 mmols of 2-PrOH. The results are shown in Figure 6-8.

Figure 6-8 Recycling of Raney Ni in the presence of MeOH and 2-PrOH: a) 1 mmol methanol; b) 1 mmol 2-PrOH; c) 2 mmol 2-PrOH; d) 4 mmol 2-PrOH

With the incorporation of 1 mmol MeOH, a slight decay in catalyst activity was observed. The ratio between benzene and other saturated products (i.e.
cyclohexanol and cyclohexanone) diminished during the five runs, however, high yields of benzene were still obtained. Where the catalyst was recycled, phenol was partially alkylated at the aromatic ring affording 2-cresol, which may be further deoxygenated into toluene.

In the presence of 2-ProH, the activity of the catalyst could also be preserved. Almost full conversion was obtained in the five sequential runs when 2 or 4 mmols of 2-ProH were employed. Notably, cyclohexane was not detected when the catalyst was reused. The ratio between benzene and other saturated products increased where higher quantities of 2-ProH were employed, encouragingly high selectivities to benzene when 4 mmols 2-ProH was incorporated. Full formation of benzene was hampered by the formation of saturated oxygenated compounds and by the alkylation of phenol into o-cresol, which may be subsequently deoxygenated into toluene or else further alkylated into 2,6-dimethylphenol. Over longer reaction time than 4 hours, full dehydroxylation of o-cresol into toluene may possibly be achieved. From the second run of reaction, a decrease of the activity of the acidic sites occurs when alcohols are utilized in the reaction, and cyclohexanol and cyclohexanone are also obtained as products. The activity of the catalyst towards dehydrogenation of MCH into toluene fell when the catalyst was reused. Conversely, 2-ProH was dehydrogenated quantitatively into acetone during all the runs, providing hydrogen to the system for the hydrodeoxygenation of phenol.

To evaluate the influence of temperature on the experiments with added alcohols, phenol was reacted with MCH/Raney Ni in the presence of 4 mmol 2-ProH at 120, 190 and 220 °C. The conversion and the distribution of the products are shown in Figure 6-9.
Figure 6-9 Effect of the temperature in the hydrogenation of phenol. Reaction condition: Raney-Ni (0.6 g); MCH (3 ml); 2-PrOH (3 mmol); 800 rpm; 4 h.

Notably, at relatively low temperature (e.g. 120 °C), hydrogenation of the aromatic ring is favored and minimal deoxygenation of the reactant is achieved. Cyclohexanol and cyclohexanone were obtained as main products, whilst benzene accounted only for 3% of the product mixture. Increasing the temperature to 190 °C, hydrogenation of the aromatic ring was still observed to be the primary pathway of reaction. In Chapter 5, it was demonstrated that in a system composed of Raney Ni/MCH and in the presence of stoichiometric quantities of 2-PrOH, phenol is fully converted at 190 °C, affording really good yields of benzene (ca. 89%) when a solid acid catalyst (e.g. H-BEA-35, Amberlyst-70) is incorporated into the system. This finding highlights that at such temperature (190 °C), Raney Ni presents high hydrogenation ability whilst poor activity as an acid catalyst. Conversely, a far higher quantity of benzene was obtained at a higher temperature when Raney Ni was utilized as the sole catalyst. Indeed, at 220 °C, benzene was the primary product of the reaction and full deoxygenation of the reactant occurred. Therefore, the activity of the acidic sites of Raney Ni may be raised when the temperature increases.
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Hence phenol can be converted into benzene when MCH or 2-PrOH are utilized as hydrogen donor. Scheme 6-2 and 6-3 show the thermodynamic data of the conversion of phenol into benzene or cyclohexanol, using MCH or 2-PrOH as the hydrogen donor at 220 °C.

**Scheme 6-2** Hydrogenation of phenols in the presence of MCH, alongside ΔS, ΔH and ΔG values of reactions at 220 °C.

**Scheme 6-3** Hydrogenation of phenols with 2-PrOH and entropy (S), ΔH, ΔG of reaction at 220 °C.

At 220 °C, the formation of benzene and dehydrogenation of the MCH is highly exergonic (ΔG= -183.7KJ mol⁻¹). Conversely, the saturation of the ring of phenol into cyclohexanol with dehydrogenation of MCH is a slightly endergonic reaction at 220 °C (ΔG= +3.8 KJ mol⁻¹). Where 2-PrOH is employed as hydrogen donor at 220 °C both reactions are exergonic, at ca. -25 and -50 KJ mol⁻¹, respectively (Scheme 6-3). These results highlight that at 220 °C both when MCH or 2-PrOH are utilized as a hydrogen donor, deoxygenation of phenols is more favored than the saturation of the ring. However, quantitatively yields of benzene are obtained only
when MCH is utilized as a solvent (with or without sub-stoichiometric quantities of 2-PrOH). Conversely, when 2-PrOH is utilized as solvent (Figure 6-2) phenol is mostly hydrogenated into saturated products. Notably, the surface acidity of a catalyst is easily inhibited where oxygenated solvents are utilized,\textsuperscript{195,196} hence, 2-PrOH could inhibit the Lewis acidic sites of Raney Ni, which are required for the formation of benzene and cyclohexane.

Notably, thermodynamically, the conversion of phenol into deoxygenated products, through an elimination of water, is a highly entropically-favored process (Scheme 6-2 and 6-3). Therefore, shifting the temperature to higher value it is possible to favor entropic process. Therefore, temperature is an important parameter (though not exclusive) for enhancing the yields of aromatic products in the conversion of phenol. The polarity of the system also plays a primary role, because reaction of phenol in pure 2-PrOH at high temperature, up to 220 °C, yielded primarily saturated products (Figure 6-2). To summarize, selective conversion of phenol to benzene in the presence of Raney Ni occurs if: a) relatively high temperatures are employed; b) the reaction is performed in a non-polar solvent which may increase the strength of the acidic sites of the catalyst; c) MCH or 2-PrOH are employed as hydrogen sources. However, if MCH is used as the sole hydrogen donor the activity of the catalyst decrease upon the time due to the limited ability of Raney Ni to catalyze the dehydrogenation of cyclic alkanes. Conversely, employing sub-stoichiometric quantities of 2-PrOH the activity of the catalyst remains high for at least 5 runs.

6.4 Evaluation of the mechanism of reaction

This section of the chapter will describe a variety of experiments, which have been carried out aiming the in-depth understanding of the selective Raney-Ni-catalyzed hydrodeoxygenation of phenol to benzene. Initially, alternative solvents to MCH and 2-PrOH were employed in the reaction of Raney Ni and phenols. 4-Propyl-2-methoxyphenol was selected as the model compound for these studies because it
Selecting Raney-Ni-catalyzed Hydrodeoxygenation of Phenol to Benzene

incorporates a methoxy functional group in the ortho position and a propyl chain in the para position relative to the phenolic –OH, a typical feature of lignin products. The reactions of 4-propyl-2-methoxyphenol in the presence of Raney Ni and n-heptane or tetralin (tetrahydronaphthalene) are shown in Table 6-2. 2-MeTHF and Hex-F-2-PrOH (1,1,1,3,3,3-hexafluoropropanol) were also investigated in order to evaluate the reactivity of the substrate in non-hydrocarbon solvents.

**Table 6-2** Hydrogenation of 4-propyl-2-methoxyphenol in different solvents. Reaction conditions: 4-propyl-2-methoxyphenol (1 mmol); Raney-Ni (0.6 g); Solvent (3 ml); 220 °C; 800 rpm; 4 h.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Arenes</th>
<th>Phenols</th>
<th>Others</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Heptane</td>
<td>46%</td>
<td>10%</td>
<td>0%</td>
<td>100%</td>
</tr>
<tr>
<td>Tetralin</td>
<td>12%</td>
<td>0%</td>
<td>0%</td>
<td>100%</td>
</tr>
<tr>
<td>2-MeTHF</td>
<td>3%</td>
<td>80%</td>
<td>10%</td>
<td>97%</td>
</tr>
<tr>
<td>Hex-F-2-PrOH</td>
<td>30%</td>
<td>39%</td>
<td>20%</td>
<td>100%</td>
</tr>
</tbody>
</table>

Full conversion of 4-propyl-2-methoxyphenol was achieved in all experiments performed in hydrocarbon solvents.

Where n-heptane was selected as the solvent and hydrogen source, cyclization and aromatization of the n-alkane occurred in the presence of the catalyst, accordingly to previous chemical literature.197,198 MCH (0.08 mmols), ethylcyclopentane (0.02 mmols) and toluene (0.09 mmols) were formed from n-heptane. Accordingly to chemical literature, reforming of n-heptane occurs via dehydrogenation of the alkane, followed by acid-catalyzed cyclization into MCH via formation of an intermediate carbocation.199 Subsequently, Ni-catalyzed aromatization of the ring occurs.185 4-Propyl-2-methoxyphenol is completely converted, affording yields up to ca. 10 % of phenols and ca. 46 % of arenes. Where the reaction was performed in tetralin, the only product obtained from 4-propyl-2-
methoxyphenol was propylbenzene, albeit in very low yield. During the reaction, part of the tetralin was converted into naphthalene, and small quantities into decalin.

The reaction performed in 2-MeTHF achieved 97% conversion of the starting material, whilst low yields of arenes (3%) were obtained. Because 2-MeTHF is not a hydrogen donor the catalyst may use the hydrogen stored in its structure to complete the reaction. However, hydrogen is differently added to the substrate when the reaction was performed in the presence of alkanes or in 2-MeTHF. In the presence of 2-MeTHF, demethoxylation of the substrate primarily occurs with the formation of propylphenol as the primary product together with other methylated phenols (at the aromatic ring). Hex-F-2-PrOH exhibits unique characteristics among all the investigated solvents. Hex-F-2-PrOH is a polar protic solvent with an acceptor number higher than 2-MeTHF and low nucleophilicity with a donor number of zero, similar to alkanes.⁶⁶ In the presence of Hex-F-2-PrOH, 4-propyl-2-methoxyphenol is fully converted, yielding arenes, phenols and cyclohexanones (propylbenzene is the primary product). Partial hydrogenation of the phenolic ring also occurred with the formation of 4-propylcyclohexanone (19 %), yet without formation of 4-propylcyclohexanol.

Subsequently, in order to evaluate the ability of MCH to act as a hydrogen donor for other phenolic and non-phenolic substrates, 2,6-dimethoxyphenol, 4-propyl-2-methoxyphenol, cyclohexanol, cyclohexene, cyclohexanone and hydroxymethylfurfural (HMF) were selected with respect to transfer hydrogenation. Table 6-3 summarizes the transfer hydrogenation results of these substrates in the presence of MCH, and Raney Ni as a hydrogenation catalyst.
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Table 6-3 Hydrogenation of phenols with MCH. Reaction conditions: substrate (1 mmol); Raney-Ni (0.6 g); MCH (3 ml); 220 °C; 800 rpm; 4 h. a) A portion of cyclohexane could be also obtained via demethylation of MCH. b) 10 minutes of reaction. c) Deoxygenation of HMF leads to furfuryl alcohol and 2,5-dimethylfuran.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Arenes</th>
<th>Alkanes</th>
<th>Toluene (mmol)</th>
<th>Conversion (%)</th>
<th>H-balance</th>
<th>C-Balance %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,6-dimethoxyphenol</td>
<td>74%</td>
<td>0%</td>
<td>0.30</td>
<td>100%</td>
<td>2.5</td>
<td>80</td>
</tr>
<tr>
<td>4-propyl-2-methoxyphenol</td>
<td>70%</td>
<td>0%</td>
<td>0.25</td>
<td>100%</td>
<td>2</td>
<td>70</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>3%</td>
<td>95%a</td>
<td>1.3</td>
<td>100%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>20%</td>
<td>50%a</td>
<td>1.5</td>
<td>100%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>40%</td>
<td>24%a</td>
<td>1.0</td>
<td>100%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HMFb</td>
<td>18%c</td>
<td>0%</td>
<td>traces</td>
<td>100%</td>
<td>-</td>
<td>15</td>
</tr>
</tbody>
</table>

Complete conversion was achieved for all substrates. A selectivity of up to 71% of benzene was achieved when 2,6-dimethoxyphenol was employed, whilst 3% selectivity to biphenyl was observed. The H-balance has a value of 2. Therefore, part of the hydrogen stored in the structure of Raney Ni or hydrogen equivalent from coke formation was utilized. The latter hypothesis is verified by the lack in C-carbon balance, indicating that part of the substrate may be converted into coke. In the experiment where 4-propyl-2-methoxyphenol was employed as the substrate, ca. 70% arenes were formed. n-Propylbenzene was recovered as the primary product and indane was also formed as a consequence of cyclization of propylbenzene. Biphenyl was not detected as product of reaction. This finding highlights that biphenyl is most likely obtained via deoxygenation of phenol than from MCH (which is utilized as solvent). 4-Propylphenol and small quantities of methylated phenols were also detected as products. For 4-propyl-2-methoxyphenol the H-balance is higher than one and the C-balance was below one hundred, as already observed for
phenol and 2,6-dimethoxyphenol were utilized. In summary, the system composed of Raney Ni and MCH is also effective for the hydrogenolysis of the methoxy functional group.

Subsequently, cyclohexanol, cyclohexanone, cyclohexene and HMF were selected as non-phenolic substrates for the reaction. Where cyclohexanol was employed, cyclohexane was recovered as the primary product in up to 95% (0.84 mmols) yield, whilst low quantities of benzene (ca. 3%) were formed. The mass balance appeared to be almost fully accountable when cyclohexanol was chosen as the substrate, however, it must be taken into account that a portion of observed cyclohexane could arise via demethylation of MCH (with 4-methylcyclohexanol 0.37 mmols of cyclohexane are also formed). Dehydrogenation of MCH is limited by the presence of phenols, whilst cyclohexanol may not inhibit the dehydrogenation ability of Raney Ni.

Conversely, cyclohexene was selectively dehydrogenated into benzene (40%) when reacted in the presence of Raney Ni and MCH, which is dehydrogenated into toluene and demethylated into cyclohexane. The C- and H-balance are not close when cyclohexanol, cyclohexanone, and cyclohexene are utilized as the substrate. However, it is not possible to identify if the products (e.g. cyclohexane) are obtained from the substrates or from the solvents, therefore, a value for the H- and C-balance cannot be calculated.

Notably, cyclohexanone yields considerably higher quantities of benzene (ca. 20%) when reacted in the presence of Raney Ni and MCH compared to cyclohexanol. Cyclohexane (0.52 mmols) and toluene (1.45 mmols) are also formed during the reaction as a consequence of demethylation and dehydrogenation of MCH, respectively. However, part of cyclohexane may be also formed from cyclohexanone.

The kinetics underpinning conversion of phenol, and the selectivity of the products, in the presence of MCH and Raney Ni, is shown in Figure 6-10. The
formation of bicyclic compounds is omitted from the plot, and will be described later in this chapter. From the very beginning of the reaction, phenol is then primarily converted into cyclohexanone, which is partially hydrogenated into cyclohexanol (pathway ‘a’, Scheme 6-1). Increasing the reaction time, cyclohexanone and cyclohexanol are depleted from the mixture of reaction, and they may be is converted into benzene. In the first minutes, during which time the autoclave is being heated and has not yet equilibrated, hydrogen may be added to the substrate producing saturated products (cyclohexanol and cyclohexanone). In the previous section, it was shown that when phenol is reacted in a system composed of Raney Ni/MCH with stoichiometric quantities of 2-PrOH, at relatively low temperature (e.g. 120 °C) saturation of the ring mostly occurs whilst at a higher temperature (e.g. 220 °C) mostly benzene is obtained. Indeed, hydrogenation of phenol into cyclohexanol in the presence of Raney Ni requires low temperature (80 °C). When the reaction temperature is stable at 220 °C, the acidic sites of the catalyst (e.g. aluminum species) may become effective and deoxygenated products, mostly benzene, are obtained.

![Figure 6-10](image_url)

**Figure 6-10** Kinetics of conversion of phenol, and selectivities to the monocyclic products, in the presence of MCH and Raney Ni.
The reaction pathways for hydrogenolysis and hydrogenation of phenol into benzene, cyclohexanone and cyclohexanol are shown in Scheme 6-4. Red arrows represent reactions catalyzed by hydrogenation sites, whilst blue arrows represent reactions catalyzed by acidic functions. As described previously in this chapter, three possible mechanisms of reaction have been reported for the conversion of phenol into benzene. All of them require a hydrogenation catalyst in combination with an acidic catalyst. One possible mechanism involves the hydrogenation of phenol into cyclohexanol, in combination with an acidic species, which is able to catalyze the dehydration of cyclohexanol into cyclohexene. Dehydrogenation of cyclohexene, which is again catalyzed by the hydrogenation catalyst, yields benzene. High selectivity conversion of phenols into benzene has been carried out also via direct cleavage of the Csp2-O bond, although a high input of energy is required for this pathway. One successful approach to selectively hydrolyze the Csp2-O bond of phenol requires a high-valence metal with a Lewis acid that can chelate the oxygen. This strategy has been applied for a Ni-catalyzed reduction of aryl ethers in organic synthesis. Alternatively, selective hydrogenation of phenol into cyclohexa-2,4-dien-1-ol followed by dehydration may also lead to benzene. Therefore, Raney Ni acts a bifunctional catalyst in the selective conversion of phenol into benzene. According to chemical literature, Raney Ni incorporates nickel hydrogenating sites and Al3+ Lewis acid sites, which can be reduced upon pretreatment with LiOH. The Lewis acid sites in Raney Ni may promote both the dehydration (Scheme 6-1) reaction and the activation of the Csp2-O bond of phenol towards direct hydrogenolysis.
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Scheme 6-4 Proposed reaction pathways for conversion of phenol, in the presence of Raney Ni.

The Raney Ni-catalyzed HDO reaction of phenol is complex due to the synergic effect of acidic and metal sites in the catalyst. Remarkably, the previous results suggest that the highly-selective Raney Ni-catalyzed conversion of phenol to benzene in the presence of MCH does not involve the saturation of the aromatic ring to the formation of cyclohexanol (pathway ‘a’), which is instead observed in the presence of 2-PrOH as reactive media. Indeed, once cyclohexanol is formed from phenol it is not dehydrated into cyclohexene, which is instead dehydrogenated into benzene when reacted in the presence of Raney Ni and MCH.

Direct hydrodeoxygenation of phenol with cleavage of the C-O bond (pathway ‘b’) was found to be the most energetically and kinetically favorable route on Fe(110), however in another study, the same pathway has been found to be highly endothermic on the Ni(111) surface. Therefore, direct hydrogenolysis of the C-O bond catalyzed by Raney Ni is unlikely the mechanism of the reaction.

Conversely, partial hydrogenation of phenol into cyclohexa-2,4-dien-1-ol (pathway ‘c’) followed by dehydration into benzene may be a sensible mechanism
for this kind of reaction, although, in the absence of detectable intermediates one cannot distinguish between these mechanisms.

Compared to MCH, solvents with high nucleophilicity, similar to 2-PrOH, may in principle decrease the acid strength of the catalyst and favor full hydrogenation of the ring to the detriment of deoxygenation. It is well known in the chemical literature that Lewis acids promote activation of the phenolic ring towards hydrogenation, and suppress the conversion of cyclohexanone into cyclohexanol via coordination of the C=O double bond of cyclohexanone.\textsuperscript{204} Hex-F-2-PrOH has been used as a Lewis acid substitute for several classes of reaction.\textsuperscript{205} These findings highlight that the presence of a solvent with low basicity may be required to enhance the ability acidic sites of the catalyst towards dehydration, and that the H-donor solvent property may promote the selective conversion of phenol into cyclohexanone.

The reaction of phenol in the presence of MCH and Raney Ni yields 2-phenylphenol and biphenyl as primary bicyclic molecules whilst \textit{m}-terphenyl was identified as the sole tricyclic product (albeit in very low yield). 2-Phenylphenol and biphenyl were quantified, and the kinetics of formation of these compounds is shown in Figure 6-11. Since the beginning of the reaction, 2-phenylphenol was observed as a product. After 30 minutes, the formation of 2-phenylphenol began to decrease rapidly and was likely converted into biphenyl, which is produced as the primary bicyclic product after 4 hours. The reaction of 2-phenylphenol under Raney Ni yields biphenyl and dibenzofuran as the primary products when in the presence of MCH solvent. This finding further demonstrates that biphenyl is obtained from 2-phenylphenol.
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Figure 6-11 Kinetics for the selectivities of bicyclic products, in the presence of MCH and Raney Ni.

Raney Ni is an established catalyst for the desulfurization of thiophenol into benzene, in which the Csp2-S bond is readily cleaved via formation of radical intermediates.206-208 In a previous study, thiophenol yields 23% of biphenyl, a product of a radical reaction, when reacted at 220 °C in the presence of degassed Raney Ni (0.5 ml of H2 per gram).209 At the lower temperature of 140 °C, the same catalyst is responsible for incomplete removal of sulfur from thiophenol, and biphenyl was not formed. It has been suggested that the reaction of thiophenol into biphenyl is topochemical between nickel and the sulfur compound, occurring when low quantities of H2 are present.210 However, where a Raney Ni catalyst composed of higher quantities of hydrogen was used as the desulfurization agent, the greatest fraction of the sulfur compounds was desulfurized hydrogenolytically and the formation of biphenyl was observed after the hydrogen had been consumed.211 Therefore, the hydrogen participates in the splitting of the C-S bond.

A very interesting analogy to the phenomena described above occurs when phenol is reacted in the system Raney Ni/MCH. However, the Csp2-O bond of phenol is more stable than the Csp2-S bond of thiophenol, with BDE values of ca. 465 kJmol⁻¹.
Chapter 6

and ca. 370 kJmol⁻¹, respectively.¹⁷⁸,²¹² Therefore, a direct hydrogenolysis of the C₆H₅-O bond of phenol is most likely to not occur.

Several studies have suggested that the initial decomposition step of phenol on a Nickel surface is more likely to occur via O-H bond cleavage rather than via C-O bond cleavage.²⁰³ Hence, the formation of C-phenylated phenols may be obtained via an acid-catalyzed reaction.²¹³ For this kind of reactions, chelation of the phenolic oxygen to Lewis acid species may render the ring more electrophile. Reaction with a nucleophile such as benzene yields 2- and 4-phenylated phenols. Notably, 2-phenylphenol is formed exclusively as the product of reaction. 4-phenylphenol was not isolated as a product, showing that the acid-catalyzed reaction between the phenol and benzene may not happen in solution, yet on the surface of the catalyst, which may influence the path of reaction.

HMF is a promising renewable platform molecule that arises via dehydration of monosaccharides.²¹⁴ 2,5-dimethylfuran (DMF) (which is particularly attractive because of its nearly ideal boiling point, its high energy density, and high octane number) can be obtained via selective hydrogenation of HMF, using H₂ or formic acid as a hydrogen source.²¹⁵,²¹⁶ Where reacted in the presence of MCH, HMF is fully converted within 10 minutes at 220 °C. Toluene is detected only in trace quantities in the product mixture. The only detectable compounds are DMF, in low yield (8%), 2-methylfurfural (6%) and furfuryl alcohol (4%), as products of hydrodeoxygenation and decarboxylation of HMF. Therefore, the C-balance % has a really low value (ca. 15%). No saturation of the ring, to the formation of 2,5-dimethyltetrahydrofuran and 2-MeTHF, occurs. This finding further highlights the ability of the system composed of Raney Ni and MCH to deoxygenate aromatic compounds sparing the aromatic ring moieties.

In conclusion, due to the low basicity of such solvents, n-alkanes and cyclic hydrocarbons may be utilized as hydrogen donors for the selective conversion of
Selective Raney-Ni-catalyzed Hydrodeoxygenation of Phenol to Benzene

phenols into arenes. However, the dehydrogenation activity of Raney Ni for cyclic alkane decrease readily and an external source of hydrogen have to be provided (e.g. 2-PrOH). The conversion of phenol into benzene may involve the hydrogenating and the acidic sites of the catalyst, however, further studies (e.g. isotopic labeling) are required for further classification. Higher reactivity and selectivity to arenes in the conversion of phenols, where MCH is employed, renders this solvent the best candidate as a reaction media.

6.5 Deoxygenation of lignin-derived phenolic mixture

The promising results where MCH was used as reaction media (for the conversion of phenols) led to the hypothesis that the use of real lignin-derived feedstocks as a substrate for this reaction may be prove to be effective.

Depolymerized lignin oils are more reactive compared to other varieties of technical lignins obtained by other pulping processes (e.g. organosolv, Kraft process).

The GC×GC-FID chromatograms of a sprucewood depolymerized lignin oil, obtained from Catalytic Upstream Biorefining (CUB)\textsuperscript{14} with Raney Ni and 2-PrOH, is displayed in Figure 6-12.
Figure 6-12 GC×GC-FID chromatogram of the sprucewood lignin oil stream.

This lignin oil stream is mostly composed of monomeric alkyl-phenols originating from the depolymerization of lignin. However, hemicellulose is also partially depolymerized during the process and converted to soluble alcohols and polyols.

The 2D-HSQC NMR spectrum of the sprucewood lignin oil stream is shown in Figure 6-13.
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Figure 6-13 HSQC spectrum of the sprucewood lignin oil stream. Structures of common lignin linkages are shown below.

The HSQC spectrum is composed of three primary regions: the aromatic region, the area of alcohols and ethers, and the alkane region. In the aromatic region, it is possible to identify the guaiacyl units that compose the sprucewood lignin. In the area of alcohols and ethers, the signals of the β-O-4 (Aα and Aβ), β-5 (Bα) and β-β (Cγ and Cβ) linkages together with the other signals derived from the partially depolymerized hemicellulose are visible. The presence of polyols could decrease the activity of Raney Ni towards the conversion of the phenolic “bio-oil” into arenes, with the formation of cyclohexanes. Therefore, the ‘bio-oil’ was purified by liquid-liquid extraction with ethyl acetate (EtOAc) and water (50:50 v/v), in order to isolate the phenolic compounds. After separation of the two phases, a phenolic-rich organic phase, a water phase and a solid residue was obtained. The majority of the starting
material was recovered in the organic phase (62%\textsubscript{w}), 30%\textsubscript{w} of the starting material was recovered in the water phase, and the insoluble fraction represents only a small proportion (5%\textsubscript{w}).

The Van Krevelen’s diagram of the three aliquots isolated by extraction, together with the starting material, in which the mole ratio of carbon/hydrogen and oxygen/carbon are reported, is shown in Figure 6-14.

![Van Krevelen’s diagram of the sprucewood lignin oil stream, water extracted phase, solid precipitate, and organic extracted phase.](image)

The organic phase and the precipitate each exhibit a lower O/C and H/C ratio compared to the starting material (‘bio-oil’, Figure 6-14). Conversely, the water extracted phase exhibits a higher O/C and H/C ratio compared to the starting material. These results suggest that highly oxygenated products are extracted into the water layer, whilst lignin-derived aromatic products are extracted predominantly into the organic layer.

The GC×GC-FID chromatograms of the fractions of depolymerized lignin oil extracted in the water phase and the solid precipitate are shown in Figure 6-15. In the water extracted phase, no phenols or other cyclic compounds were detected. The volatile species were mostly composed of low boiling point alcohols and polyols.
The solid precipitate fraction is instead composed of residual quantities of phenols. The GC×GC-FID chromatogram of the fraction of depolymerized lignin oil extracted in the organic phase is shown in Figure 6-16.

**Figure 6-15** GC×GC-FID chromatograms of the water extracted layer (a), and the precipitate fraction (b), from the sprucewood lignin oil stream.

**Figure 6-16** GC×GC-FID chromatogram of the organic extracted fraction from the *sprucewood* lignin oil stream.
The chromatogram in Figure 6-16 demonstrates that most of the volatile phenols are extracted into the organic layer, whilst no alcohols or polyol species are incorporated into this fraction.

The HSQC spectra of the organic extracted fraction (a) from sprucewood lignin oil stream, the water extracted fraction (b), and the solid precipitate (c), are shown in Figure 6-17.

![HSQC spectra](image)

**Figure 6-17** HSQC spectra of the organic extracted fraction (a) from sprucewood lignin oil stream, the water extracted fraction (b), and the solid precipitate (c).

The spectra clearly revealed that the organic phase is mostly composed of aromatic lignin-derived products. Conversely, aromatic species are distinctly absent from the water extracted phase, highlighting that only residual quantities of phenols...
incorporate this fraction. The solid precipitate exhibits a similar HSQC spectrum to the organic phase. However, the intensity of the signals of the β-O-4 (Aα and Aβ) and the β-5 (Bα) linkages is much larger for this fraction that for the organic phase.

Subsequently, the organic extractive layer was reacted at 220 °C in the presence of MCH and Raney Ni. The GC×GC-FID chromatogram of the depolymerized lignin oil after transfer hydrogenation with MCH, and reaction condition, is shown in Figure 6-18.

![GC×GC-FID chromatogram of the sprucewood lignin oil stream, after reaction of the extracted organic layer. Reaction conditions: Raney Ni (0.6 g), substrate (0.05 g), MCH (3 mL), 220°C, 4 h. Proposed compounds are reported with the molecular weight of the molecular ion detected by MS.](image)

**Figure 6-18** GC×GC-FID chromatogram of the sprucewood lignin oil stream, after reaction of the extracted organic layer. Reaction conditions: Raney Ni (0.6 g), substrate (0.05 g), MCH (3 mL), 220°C, 4 h. Proposed compounds are reported with the molecular weight of the molecular ion detected by MS.

The most significant individual volatile product of the reaction was found to be toluene. MCH was dehydrogenated and the hydrogen may have been consumed for the deoxygenation of phenols, which were selective converted into alkylbenzenes; these are primarily ethylbenzene and propylbenzene, which form indane via
cyclization. Moreover, biphenyl and triphenyl-derived compounds were found to have formed upon reaction. Most likely, the formation of these products occurs via acid catalyzed reaction. Excluding toluene, which is the primary obtained from deoxygenation of MCH (however it could also be obtained in part from deoxygenation of lignin), from 50 mg of lignin bio-oil 8 mg of alkylarenes were formed. Overall, 35% of monocyclic arenes, 30% of bicyclic arenes and ca. 1% of tricyclic arenes were incorporated in the sample upon deoxygenation. Because of the complexity of the lignin bio-oil sample, the reaction of bio-oil was performed with a ratio bio-oil/catalyst higher than the ratio utilized when phenol had been reacted. Therefore, the ratio of surface of the catalyst/molecules also increases. The reactions responsible for the formation of bicyclic products take place most likely on the catalyst surface. This finding may explain why the ratio between bicyclic and monocyclic products is much higher when the reaction was performed on the actual lignin bio-oil, compared to the study on model compounds. Hydrogenolysis of the methoxyl functional groups and deoxygenation of phenols both occurs. Moreover, deoxygenation of the primary alcohol at the p-propyl chain of 4-(3-hydroxypropyl)methoxyphenol, the main component of the starting mixture, and in related compounds, demonstrates the indiscriminate ability of the system Raney Ni/MCH to act as deoxygenative reductive media.

The HSQC spectrum of the organic extracted fraction after reaction with Raney Ni and MCH is shown in Figure 6-19. After the reaction, the sample was concentrated under reduced pressure at 40 °C, to evaporate the solvent prior to HSQC analysis. Nevertheless, toluene and other compounds with a low boiling point could also have evaporated. Alternatively, an efficient separation of the aromatic products of reaction from the alkane solvent (MCH) may be accomplished by the sulfolane process, which employs sulfolane as extractive media in the extraction of aromatic hydrocarbons from hydrocarbon mixtures. Recently, several ionic liquids have been investigated as a green alternative to sulfolane.
Figure 6-19 HSQC spectra of sprucewood lignin oil stream after reaction and concentration under reduced pressure (by using a rotovapor).

The HSQC spectrum is consistent with the data obtained from GC×GC-FID. The products of the reaction are mostly composed of aromatic and aliphatic hydrocarbons. Full deoxygenation of the sample was achieved upon reaction with Raney Ni and MCH. Methoxy functional groups, as well as the ether linkages typical of the lignin structure, were not incorporated into the products of reaction.

The appearance of the NMR tube of the lignin oil stream upon solubilization of the samples in DMSO-d$_6$ is highlighted in Figure 6-20. The appearance of the sample upon extraction and deoxygenation is also reported.
The lignin stream oil stream has a brownish color. Upon extraction, the solid residue gives a dark brownish coloration in solution, indicating a more polymerized structure compared to the organic phase, which exhibits a pale brownish color. Conversely, the water extracted fraction exhibits a pale yellow color. A colorless product is obtained upon reaction of lignin with Raney Ni. This finding further highlight that the full depolymerization and deoxygenation of the initial lignin sample is successfully achieved.

6.6 Conclusions

Overall, it has been demonstrated that Raney Ni is a suitable catalyst for the selective HDO of phenols into arenes, at relatively low temperature (220 °C) and without any external pressure. It appears that the enhanced activity of Raney Ni in the presence of
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non-polar solvents (e.g. alkanes) and at a temperature as higher as 220 °C may allow the Lewis acid sites of the catalyst to catalyze dehydration reactions. Hence, the process leads to deoxygenation as the preferential pathway over saturation of the ring.

The catalyst is prone to deactivation after the first cycle of reaction, most likely because of the formation of coke, which may derive from an acid-catalyzed polymerization of phenol products or from the dehydrogenation of MCH. However, the incorporation of a small quantity of an alcohol (e.g. 2-PrOH) helps the catalyst to maintain its activity without losing selectivity. The ability of alkanes to serve as reagent media (and in a small extent as hydrogen donor) for the selective conversion of the lignin-derived phenolic mixture into arenes, opens a new route for the conversion of biomass into liquid fuels.
CHAPTER 7

General Conclusions & Final Remarks

In this thesis, the catalytic conversion of lignin (obtained via different fractionation processes) into monomeric and low-boiling-point chemicals was investigated in detail. New processes were explored and established processes were evaluated and optimized. The goal of this project was to insert lignin-derived products into the existing refinery scheme. The employed strategy was based on the conversion of lignin via hydrogenation and hydrodeoxygenation. H₂ and 2-PrOH were used as sources of hydrogen, and mayor attention was devoted to the influence of the molecular structure and composition of lignin on hydrogenation and deoxygenation activity by the selected catalyst (Raney Ni). To achieve this result, several studies were performed on lignin model compounds. Subsequently, the obtained information was applied to an investigation of the behavior of actual lignin or lignin-derived samples.

Lignin is a promising source of aromatic compounds and energy. However, due to the complex structure and the presence of a broad variety of complex linkages between the monomers, the conversion of lignin into value-added products is rendered difficult. The quality of the products obtained upon fractionation is highly
influenced by: (1) the process utilized for the fractionation of lignin from cellulose and hemicellulose, and; (2) the native structure of lignin. As described in Chapter 3, the use of a strong acid in the mecanocatalytic process (and the subsequent hydrolysis stage) is responsible for the depolymerization of carbohydrates into monomers and precipitation of lignin as a poorly water-soluble material. Condensation reactions between the aromatic units (leading to a ‘recalcitrant’ material) and the decrease in concentration of uncondensed phenolic units lead to a poorly-reactive material.

Inspired by existing literature regarding biomass fractionation and current knowledge of the chemistry of lignin, Chapter 4 introduced a rational and successful approach for the extraction of low-molecular-weight lignin into an organic phase during the hydrogenolysis step performed on a depolymerized wood sample. The obtained lignin exhibited good solubility in a variety of conventional organic solvents, and promising reactivity in the presence of Raney Ni and molecular hydrogen. Moreover, the obtained lignin was selectively converted into phenols and methoxyphenols and no saturation of the ring was observed. As a consequence, the H-economy of the reaction was improved, rendering this process highly attractive.

The emergence of ‘Early-stage Catalytic Conversion of Lignin’ process has turned attention to use of the partially depolymerized lignin oil stream as an alternative to technical (e.g. kraft) lignin. Partially depolymerized lignin oil streams are highly reactive in heterogeneous catalytic systems because of the comparatively low molecular weight (and lack of recalcitrant C-C bonding motif). Therefore, mild reaction conditions can be employed, leading to improved quality of the products. In Chapter 5, a low-temperature (190 °C) hydrogen transfer process was applied to phenols in order to convert them into arenes. The reaction conditions were optimized and finally applied to a true lignin feedstock. In particular, activities and the stabilities of systems composed of Raney Ni (the hydrogenation catalyst) with
different solid acid catalyst (for dehydrogenation) were evaluated. For this type of reaction, Amberlyst-70 was selected as the most effective acid catalyst.

Finally, in Chapter 6, it was demonstrated that Raney Ni, as the sole catalyst, can effectively catalyze the deoxygenation of a lignin oil stream into a mixture of arenes when the reaction is performed in a solvent of low polarity (e.g. methylcyclohexane, heptane). When employed in such solvent, Raney Ni is highly active towards the hydrogenolysis of diphenyl ether, whilst oxygenated solvents decrease the ability of Raney Ni to convert diphenyl ether into saturated and deoxygenated products. The hydrogen necessary to complete the reaction phenol→benzene may arise from the dehydrogenation of MCH, which is partially converted into toluene, or from the catalyst itself. However, dehydrogenation of MCH occurs only to a small extent. Once the hydrogen in the reaction system is exhausted, the conversion of phenol diminished. A higher quantity of carbon was detected on the spent catalyst compared to the fresh catalyst (prior to reaction). Therefore, fouling of the catalyst may be related to the formation of coke on the surface of Raney Ni. In order to supply the required hydrogen to the catalytic system, sub-stoichiometric quantities of 2-PrOH were added, increasing both the deoxygenation of phenol and the dehydration of MCH, and rendering the system sustainable over (at least) 5 cycles of reaction.

In conclusion, new processes were developed for the selective conversion of lignin and lignin oil streams into methoxyphenol and arene species. Hence, lignin is converted into a tailored mixture of volatile monomers, which still incorporate the aromaticity characteristic of the lignin feedstock. This aspect is particularly interesting for lowering the consumption of hydrogen necessary for the conversion of biomass feedstock into commodities. However, considering a future application, a more comprehensive study regarding the cost efficiency of each stage of this process is required, in order to evaluate the competitiveness of a biomass-to-crude-oil strategy for the existing chemical market.
Experimental

8.1 Chapter 3

8.1.1 Chemicals

Pellets from beechwood, pinewood and sugarcane were comminuted with a blender. The sawdust was sieved. Powders with a particle size smaller than 250 μm were collected and used for the mechanocatalytic experiments. Sulfuric acid (95–97%, J. T. Baker), α-cellulose (76% glucans, 16% xylans, 6% humidity, 0.1% ash, an 1.9% others, Aldrich), Diethyl ether (99%, Aldrich), Tetrahydrofuran (Aldrich, 99.9%); 1,4-dioxane (Aldrich, 99.8%); Ethanthiol (Aldrich, 97%); N,O-Bis(trimethylsilyl)trifluoroacetamide (Aldrich, 99%); Boron trifluoride diethyl etherate (Aldrich, for synthesis); Pyridine (Aldrich 99.8%); Dichloromethane (aldrich, 99%), 2-PrOH (Aldrich, 99.8%), RANEY®Ni 2800 (aldrich), Dibutyl ether (Aldrich, ≥99%) and Ethyl acetate (Aldrich, 99%) were used as received.

8.1.2 Wet impregnation with an H₂SO₄ solution in diethyl ether

Beechwood, pinewood or sugarcane were suspended in a diluted H₂SO₄ solution in diethyl ether (150 mL). Note: To avoid degradation of the substrates upon the
Experimental

prolonged contact with the acidic solution, we chose to use a 0.065 mol L⁻¹ H₂SO₄ solution for the acid impregnation. The suspension was shaken for 1 h (IKA shaker, KS 130 control, 350 rpm). The organic solvent was removed under reduced pressure at 40 °C. A fine powder with loose particles was obtained. This procedure led to an acid-loading of 0.8 ± 0.1 mmol H₂SO₄ per gram of substrate. The powder was immediately processed in a ball mill or stored in a closed vial and kept in a freezer (−10 °C) to prevent substrate decomposition that would normally occur to form grayish to black powder after several days of storage at room temperature.

8.1.3 Determination of acid loading

Typically, 1 g of the acid impregnated substrate was suspended in 40 mL water. Subsequently, titration with a 0.0100 mol L⁻¹ NaOH solution was performed on a Metrohm Titrino Plus 848 automated titrator.

8.1.4 Mechanocatalytic depolymerisation

The mechanocatalytic depolymerization of lignocellulose was performed in a stainless steel vial (12 mL; 5 stainless steel balls of 4 g each) using a planetary ball mill (Fritsch, Pulverisette P7). The acid-impregnated substrate (1 g) was processed at 800 rpm. Full conversion of beechwood, pinewood and sugarcane was achieved at a milling duration of 2 h. The mill was switched off every 0.5 h for 10 min to avoid overheating and thermal decomposition of the sample. The product was then collected and kept in an air-tight vial at −10 °C prior to analysis or saccharification experiments.

8.1.5 Extraction of lignin from beechwood, pinewood and sugarcane (Organosolv lignin)

Beechwood, pinewood or sugarcane (16–17 g) was suspended in a 140 mL solution of ethanol–water (1:1, v/v) in a 250 mL autoclave equipped with a mechanical stirrer. The suspension was processed at 180 °C for 3 h. In sequence, the mixture was left to
cool down to room temperature. A reddish-brown solution was obtained after filtering off the lignocellulose fibers (pulp). Ethanol was partially evaporated at 60 °C using a rotoevaporator. This procedure leads to lignin precipitation. The solid was collected by filtration and, in sequence, resuspended in hot water in order to remove hemicellulose sugars. Next, the suspension was filtered and the solid washed several times with hot water. Finally, the organosolv beechwood lignin was dried in oven at 40 °C for 1 day.

8.1.6 Saccharification of ‘water-soluble’ beechwood, pinewood and sugarcane

Depolymerized samples (H₂SO₄-impregnated samples milled for 2 h) were solubilized in water forming a 10% solution with a pH value of 1. In a closed glass vial, the beechwood solution (10 mL) was heated at 145 °C for 1 h. Upon heating, a solid residue was formed, which was isolated from the sugar solution by centrifugation. The precipitate was washed with 20 mL water six times. The aqueous solutions were combined and set aside for HPLC analysis. In turn, the solid residue was dried in an oven at 60 °C for 24 h. The solid residue was weighed and stored at −10 °C.

8.1.7 FTIR analysis

The FTIR spectra were collected on a Bruker Vertex 70 spectrometer using a Zn–Se ATR probe. For each spectrum, 128 scans were recorded at 4 cm⁻¹ resolution.

8.1.8 Thermogravimetric analysis

The weight loss profile of the indicated samples was measured on a Mettler Toledo TGA/DSC 1 Star System operating from 25 to 1000 °C at 5 °C min⁻¹ under argon.

8.1.9 Elemental analysis

The CHNS/O elemental analysis was performed on triplicates for each sample (2 mg) on a Vario Micro cube elemental analyser.
8.1.10 Gel filtration chromatography

To analyze the apparent molecular weight distribution, all the samples (2 to 4mg) were dissolved in THF (2 mL) and filtered prior to injection. The GPC analyses were performed at 60 °C on a Perkin–Elmer HPLC 200 equipped with 4 columns (2×TSKgel Super HZ1000, TSKgel Super HZ2000 and TSKgel Super HZ3000, 4.6 mm × ID 15.0 cm, Tosoh Bioscience), and using inhibitor-free THF as eluent (0.4 mL min⁻¹, S4 Aldrich). For detection, a diode-array detector was used. The reported results show the chromatogram at 216 nm. The DAD response was normalized to 1. The apparent molecular weight is given relative to poly styrene standards (200 to 60,000 Da, Aldrich), and thus is only for a relative assessment of the overall changes in the apparent molecular weight distributions.

8.1.11 Solution NMR experiments

All spectra were acquired at 25 °C with a Bruker AV spectrometer (400 or 500 MHz 1H frequency) equipped with a BBFO probe head with z-gradient. Spectral widths of 20 ppm were used for the 1D ¹H spectrum. The relaxation delay for the 1D ¹H spectrum was 5.0 s following a 30-degree excitation pulse. For the 1D inverse-gated ¹³C spectrum, the relaxation delay was set to 1.0 s following a 30-degree excitation pulse. ¹H-decoupling with the Waltz-16 sequence was applied during acquisition. The number of collected points was 64k for ¹H and for ¹³C. The 1D ¹H spectra were processed using an exponential weighting function (lb 0.2 Hz) prior to Fourier transform. The 2D HSQC NMR (Bruker standard pulse sequence “hsqcetgpsi” with delay optimized for ¹JC of 145 Hz) were set up with spectral widths of 20 ppm and 180 ppm for ¹H- and ¹³C-dimensions, respectively. The number of collected complex points was 2048 for ¹H-dimension with a recycle delay of 3.13 s (3.0 s relaxation delay and 0.13 s acquisition time). The number of transients for the HSQC spectra was between 12 and 24, and 512 time increments were recorded in ¹³C-dimension resulting in an overall experiment time of 6 to 12 h. For HSQC experiments, a
squared cosine-bell apodization function was applied in both dimensions, followed by zero-filling to 1024 points in the $^{13}$C-dimension prior to Fourier transform. The 1D $^1$H NMR and 2D HSQC NMR spectra were processed using MestReNova 8.1.1 software. Noteworthy, HSQC spectrum data must be interpreted with caution, since the $^1$J$_{CH}$ dependence of polarization transfer in HSQC experiments is not suppressed in regular HSQC pulse sequences. As a result, the absolute intensity of cross peaks is not fully quantitative in the entire spectral range. Regular HSQC NMR experiments still offer extremely valuable (direct) semiquantitative information for characterization and comparison of lignins as well as whole plant cell compositions. Semiquantitative determination of volume integral ratios is possible for $^1$H–$^{13}$C pairs in a similar chemical environment (e.g. Cα–Hα signals for the side-chain of lignin units or the C2–H2 and C6–H6 signals for lignin aromatic units), due to the fact that the $^1$J$_{CH}$ values for the specific entities are reasonably similar. Accordingly, for the different regions of the HSQC spectra, semiquantitative analysis was performed separately by integration of $^1$H–$^{13}$C pairs of interest.

8.1.12 Thioacidolysis lignin samples

The thioacidolysis reagent is prepared immediately before use; 2.5 ml of BF₃ etherate and 10 ml of ethanethiol are successively introduced into a 100-ml volumetric flask containing 20 ml of dioxane and the final volume is adjusted to 100 ml with dioxane. To the lignin samples (10 mg) 10 ml of thioacidolysis reagent are added in a tube fitted with a Teflon-lined screwcap under an atmosphere of argon. The thioacidolysis is all owed to proceed at 100°C (in an oil bath) for 4 h with occasional shaking. The reaction tube is cooled in an ice-bath and the reaction mixture, together with a few ml of water to rinse the tube (3 x 5 ml), are poured over CH₂Cl₂ (analytical grade) to which the gas chromatography (GC) internal standard (hexadecane, 4 mg) has been added. The pH of the aqueous (upper) phase is adjusted to 3–4 as indicated by pH-indicator paper by the addition of aqueous 0.4 M NaHCO₃ and the two phases are together extracted with CH₂Cl₂ (3 x 50 ml). The combined organic extracts are dried
over anhydrous Na₂SO₄, and then evaporated under reduced pressure at 40°C. The oily residue is carefully redissolved in 0.5-1 ml of CH₂Cl₂ to recover a solution appropriately diluted for the following silylation and GC steps. 10 μl of this dried organic solution is trimethylsilylated (TMS) at room temperature with 50 μl of N,O bis (trimethylsilyl) trifluoroacetamide (BSTFA) and 5 μl of GC-grade pyridine in a 200-μl reaction vial fitted with a Teflon-lined screwcap before GC analysis.

8.1.13 Hydrogenation of OS-L and MCP-L

OS-L or MCP-L (0.5 g), Raney Ni (dry 0.15 g) and 2-PrOH (15 mL) were charged in an autoclave equipped with mechanical stirrer, under atmosphere of Argon. After purging the reaction vessel with H₂, the reactor was loaded with 70 bar H₂ (25 °C). The autoclave was heated to 200 or 300 °C. After 8 h at 200 or 300 °C, the autoclave was quenched in an ice-bath. The suspension was filtered on a Teflon filter previously weighted. The filtrate (LP) was collected and the solvent evaporated with rotatory evaporator at 40 °C. Raney Ni was digested with a 5-mol L⁻¹ hydrochloric acid (HCl) solution, thus enabling the determination of the amount of unconverted solid lignin (SR).

8.1.14 GC×GC-MS/FID Analysis

Lignin sample after hydrogenation and thiacidolysis were analyzed using 2D GC×GC-MS/FID (first column: ZB-1HT 30 m, 0.25 mm ID, df 0.25 μm; second column: BPX50, 1 m, 0.15 mm ID, df 0.15 μm) in a GC-MS 2010 Plus (Shimadzu) equipped with a ZX1 thermal modulation system (Zoex). The injector temperature was 280 °C. The temperature program started with an isothermal step at 40 °C for 5 min. Next, the temperature was increased from 40 to 300 °C by 5.2 °C min⁻¹. The program finished with an isothermal step at 300 °C for 5 min. The modulation applied for the comprehensive GC×GC analysis was a hot jet pulse (400 ms) every 9000 ms. 2D chromatograms were processed with GC Image software (Zoex). The products were identified by a search of the MS spectrum with the MS libraries NIST.
08, NIST 08s, and Wiley 9. In some cases, the structure was proposed by the analysis of the EI-fragmentation pattern and by comparison of retention times with other samples. The semi-quantification of the products was performed using the GC×GC-FID images.

8.1.15 Solid-state 13C CP-MAS NMR experiments

The 13C CP-MAS NMR spectra were measured on a Bruker Avance 500WB spectrometer with a double-bearing standard MAS probe (DVT BL4) at a resonance frequency of 125.8 MHz using 4 mm MAS probe spinning at 10 kHz. The experimental conditions were 2s recycle delay, between 8000 and 28 000 scans, 1 ms contact time, and 4.3 μs 1H π/2 pulse.

8.2 Chapter 4

8.2.1 Chemicals

Pellets from beechwood were comminuted with a blender. The sawdust was sieved. Powders with a particle size smaller than 250 μm were collected and used for the mechanocatalytic experiments. Sulfuric acid (95–97%, J. T. Baker), α-cellulose (76% glucans, 16% xylans, 6% humidity, 0.1% ash, an 1.9% others, Aldrich), Diethyl ether (99%, Aldrich), Tetrahydrofuran (Aldrich, 99.9%); 1,4-dioxane (Aldrich, 99.8%); Ethanthiol (Aldrich, 97%); N,O-Bis(trimethylsilyl)trifluoroacetamide (Aldrich, 99%); Boron trifluoride diethyl etherate (Aldrich, for synthesis); Pyridine (Aldrich 99.8%); Dichloromethane (aldrich, 99%), 2-PrOH (Aldrich, 99.8%), RANEY®Ni 2800 (aldrich), Dibutyl ether (Aldrich, ≥99%), 2-Methyltetrahydrofuran (Aldrich, ≥99%, Inhibitor-free) and Ethyl acetate (Aldrich, 99%) were used as received.

8.2.2 Wet impregnation with an H2SO4 solution in diethyl ether

Beechwood was suspended in a diluted H2SO4 solution in diethyl ether (150 mL). Note: To avoid degradation of the substrates upon the prolonged contact with the acidic solution, we chose to use a 0.065 mol L⁻¹ H2SO4 solution for the acid
impregnation. The suspension was shaken for 1 h (IKA shaker, KS 130 control, 350 rpm). The organic solvent was removed under reduced pressure at 40 °C. A fine powder with loose particles was obtained. This procedure led to an acid-loading of 0.8 ± 0.1 mmol H₂SO₄ per gram of substrate. The powder was immediately processed in a ball mill or stored in a closed vial and kept in a freezer (−10 °C) to prevent substrate decomposition that would normally occur to form grayish to black powder after several days of storage at room temperature.

8.2.3 Determination of acid loading

Typically, 1 g of the acid impregnated substrate was suspended in 40 mL water. Subsequently, titration with a 0.0100 mol L⁻¹ NaOH solution was performed on a Metrohm Titrino Plus 848 automated titrator.

8.3.4 Mechanocatalytic depolymerisation

The mechanocatalytic depolymerization of lignocellulose was performed in a stainless steel vial (12 mL; 5 stainless steel balls of 4 g each) using a planetary ball mill (Fritsch, Pulverisette P7). The acid-impregnated substrate (1 g) was processed at 800 rpm. Full conversion of beechwood, pinewood and sugarcane was achieved at a milling duration of 2 h. The mill was switched off every 0.5 h for 10 min to avoid overheating and thermal decomposition of the sample. The product was then collected and kept in an air-tight vial at −10 °C prior to analysis or saccharification experiments.

8.2.5 Extraction of lignin from beechwood, pinewood and sugarcane (OrganoSolv lignin)

Beechwood (16–17 g) was suspended in a 140 mL solution of ethanol–water (1 : 1, v/v) in a 250 mL autoclave equipped with a mechanical stirrer. The suspension was processed at 180 °C for 3 h. In sequence, the mixture was left to cool down to room temperature. A reddish-brown solution was obtained after filtering off the
lignocellulose fibers (pulp). Ethanol was partially evaporated at 60 °C using a rotoevaporator. This procedure leads to lignin precipitation. The solid was collected by filtration and, in sequence, resuspended in hot water in order to remove hemicellulose sugars. Next, the suspension was filtered and the solid washed several times with hot water. Finally, the organosolv beechwood lignin was dried in oven at 40 °C for 1 day.

8.2.6 Saccharification of ‘water-soluble’ beechwood in a biphasic system

1 g of depolymerized samples (H₂SO₄-impregnated samples milled for 2 h) were solubilized in 10 ml solution H₂O/2-MeTHF (50/50 v/v). In a closed glass vial, the beechwood solution (10 mL) was heated at 145 °C for 1 h. Upon heating, separation of the solvents occurs. The organic layer was separated from the water layer and washed tree times with water. Subsequently, 2-MeTHF was evaporated under reduced pressure at 50 °C. The aqueous solutions were combined and set aside for HPLC analysis.

8.2.7 Preparation of the ‘artificial wood’

0.500 g of organosolv beechwood lignin and 1.500 g α-cellulose were suspended in a 40 ml of diethyl ether. Drop to drop H₂SO₄ were added to the mixture. The organic solvent (diethyl ether) was removed under reduced pressure at 40 °C. A fine powder with loose particles was obtained. This procedure led to an acid-loading of 0.8 ± 0.1 mmol H₂SO₄ per gram of substrate. The acid-impregnated substrate (1 g) was processed to ball mill at 800 rpm. The depolymerized samples (H₂SO₄-impregnated samples milled for 2 h) were solubilized in water forming a 10% solution with a pH value of 1. In a closed glass vial, the beechwood solution (10 mL) was heated at 145 °C for 1 h. Upon heating, a solid residue was formed, which was isolated from the sugar solution by centrifugation. The precipitate was washed with 20 mL of water six times.
8.3 Chapter 5

8.3.1 Chemicals

2-PrOH (Aldrich, 99.8%), 4-(3-hydroxypropyl)phenol (Aldrich, 99%), Hexadecane (Aldrich, 99%), RANEY®Ni 2800, 3-phenylpropan-1-ol (Aldrich, 98%), Acetone (Aldrich, 99.8%), Cyclohexene (Aldrich, 99%), 1-octene (Aldrich, 98%), diphenyl ether (Aldrich, ≥99%), Phenol (aldrich, ≥99.5%), Guaicol (Aldrich, ≥98%), 2,6-dimethoxyphenol (Aldrich, 99%), Homovanillyn alcohol (Aldrich, 99%), 4-propyl-guaicol (Aldrich, ≥97%), 4-allyl-2,6-dimethoxyphenol (Aldrich, ≥90%), Ethyl acetate (Aldrich, 99%), Methylcyclohexane (Aldrich, ≥98%), Nafion SAC-13 (Aldrich) were used as received. Amberlyst-70 (Room and Haas) was dry before use. Na-BEA-35 was calcinated at 500 °C for 4 hours before use in order to obtain the proton form.

8.3.2 Hydrogenation of 4-(3-hydroxypropyl)phenol with H₂

4-(3-hydroxypropyl)phenol (2.9 mmol), hexadecane (internal standard - ISTD, 0.78 mmol), Raney Ni 2800 (dry 100 mg, pre-dried in vacuum), and 2-PrOH as solvent (15 mL) were placed in a batch reactor (30 mL) under argon atmosphere (glove box). After purging the reactor with H₂, the reaction vessel was loaded with 50 bar H₂ (25 °C). The reaction was performed at 90 °C for 2.5 h (RT to 90 °C: 10 min) using overhead mechanical stirring (300 rpm).

8.3.3 Hydrogen transfer reaction of 4-(3-hydroxypropyl)phenol, 3-phenylpropan-1-ol and hydrocinnamaldehyde with 2-PrOH

4-(3-hydroxypropyl)phenol, 3-phenylpropan-1-ol or hydrocinnamaldehyde (2.1 mmol), hexadecane (internal standard, ISTD, 0.8 mmol), RANEY Ni 2800 (1 g, wet), solvent (7 mL) and a magnetic stirrer bar were placed in a glass vial (20 mL). The vial was flushed with Argon and then tightly closed. The experiment was performed at 80 °C under magnetic stirring (800 rpm) in a stainless steel heating block for 3 h. The reactions were performed in 2-PrOH, acetone, cyclohexene and 2-octene as solvent.
8.3.4 FT-IR analysis of the gas phase

An aliquot of the gas phase was injected into an Avatar 370 FT-IR from Thermo Nicolet, in transmission mode. A background was collected under a flow of nitrogen which was then replaced with a mixture of the gas collected from the reaction and the nitrogen flow.

8.3.5 Dehydroxylation of phenols

Substrate (1 mmol), Raney Ni 2800 (0.6 g wet), solid acid (H-BEA-35:80 mg, Nafion SAC-13: 10 mg, Amberlyst-70: 10 mg), H-donor (2-propanol, 1.5 mmol), hexadecane (INST 20 mg) methylcyclohexane (MCH, 3 mL) and a magnet bar were placed in a stainless steel vial (20 mL). The vial was flushed with argon and then tightly closed. The experiment was performed at 190 °C under magnetic stirring (800 rpm) in a stainless steel heating block for 4 h. Ethyl acetate (10 mL, to produce a homogeneous mixture) was added into the reaction mixture (at 298 K) after the completion of the experiment. The reaction was performed on phenol, 4-(3-hydroxypropyl)phenol, guaiacol, 2,6-dimethoxyphenol, 4-propylguaiacol, homovanillyl alcohol, 4-allyl-2,6-dimethoxy-phenol, 4-(3-hydroxypropyl)-2-methoxyphenol.

8.3.6 Recycling of the catalyst

A solution of diphenyl ether (3 mmol), 2-PrOH (12 mmol), hexadecane (INST 60 mg) in MCH (9 ml) was prepared. 3 ml of this solution, Raney Ni 2800 (0.6 g wet), solid acid (H-BEA-35:80 mg, or Nafion SAC-13: 10 mg, or Amberlyst-70: 10 mg) and a magnet bar were added in a stainless steel vial (20 mL). The vial was flushed with argon and then tightly closed. The experiment was performed at 190 °C under magnetic stirring (800 rpm) in a stainless steel heating block for 4 h. Ethyl acetate (10 mL, to produce a homogeneous mixture) was added into the reaction mixture (at 298 K) after the completion of the experiment. The catalyst was washed with three aliquots of EtOAc and subsequently with 3 three aliquots of MCH previous reutilization.
Experimental

8.3.7 Dehydroxylation of phenolic mixture

4-(3-hydroxypropyl)phenol (0.5 mmol), guaiacol or 2,6-dimethoxyphenol (0.5 mmol), Raney Ni 2800 (0.6 g wet), solid acid (H-BEA-35:80 mg, or Amberlyst-70: 10 mg), H-donor (2-propanol, 1.5 mmol), hexadecane (INST 20 mg) MCH (3 mL) and a magnet bar were placed in a stainless steel vial (20 mL). The vial was flushed with argon and then tightly closed. The experiments were performed at 190 °C under magnetic stirring (800 rpm) in a stainless steel heating block for 4 h. Ethyl acetate (10 mL, to produce a homogeneous mixture) was added into the reaction mixture (at 298 K) after the completion of the experiment.

8.3.8 Catalytic biorefining method

Wood (16-17 g), Raney Ni (10 g wet) and solvent (140 mL; 2-PrOH:water 7:3 v/v) were placed in a 250 mL autoclave and heated to 180 °C within 1 h under mechanical stirring. The reaction proceeded under autogenous pressure for 3 h. In sequence, the mixture was left to cool down to room temperature. The liquor was separated from the solids (Raney Ni plus pulp) by filtration through a glass fiber filter (GF6, Ø 90 mm, Whatman). Very important: as Raney Ni is a pyrophoric material in its dried form, the wet solids (catalyst plus pulp) were immediately poured into a round-flask (250 mL) containing 2-PrOH (100 mL). In sequence, under overhead mechanical stirring, the solids were resuspended in 2-PrOH. Raney Ni was attracted to the flask bottom by a magnet externally placed on the bottom of the round flask. This procedure was repeated another four times in order to remove the entire catalyst content from the pulp fibers. The spent catalyst was washed and stored in 2-PrOH. The pulp remained in suspension, and was recovered by filtration. The liquor and the filtrates (from the catalyst separation procedure) were combined. The non-pyrolytic lignin bio-oil was isolated by removing the solvent at 60 °C under vacuum with a rotoevaporator.
8.3.9 Isolation of the 4-(3-hydroxypropyl)-2-methoxyphenol from the lignin oil stream from sprucewood.

The non-pyrolytic lignin bio-oil was purified by a fractionated distillation under reduced pressure. Three fractions were collected from this Kugelrohr distillation (100 °C - 30 min, 125 °C – 30 min and 180 °C – 60 min) at 0.1 mbar. The last fraction was further purified by flash column chromatography (SiO2, MTBE:Dichloromethane, 1:3) in order to isolate the 4-(3-hydroxypropyl)-2-methoxyphenol from the lignin oil stream such as yellowish oil.

8.3.10 Dehydroxylation of lignin stream oil

50 mg of lignin stream oil (beechwood or sprucewood), Raney Ni 2800 (0.6 g wet), solid acid (Amberlyst-70: 10 mg), H-donor (2-propanol, 1.5 mmol), hexadecane (INST 20 mg) MCH (3 mL) and a magnet bar were placed in a stainless steel vial (20 mL). The vial was flushed with argon and then tightly closed. The experiment was performed at 190 °C under magnetic stirring (800 rpm) in a stainless steel heating block for 4 h. Ethyl acetate (10 mL, to produce a homogeneous mixture) was added into the reaction mixture (at 298 K) after the completion of the experiment.

8.3.10 GC analysis

The samples were analyzed by GC using a Shimadzu QP2010 Plus gas chromatograph, equipped with a ZB-1HT Inferno column (30 m, 0.25 mm ID, df 0.25 μm). The injector temperature was 300 °C. The temperature program started at 40 °C for one minute. Next, the temperature was increased at 8 °C min\(^{-1}\) to 140 °C, then increased at 20 °C min\(^{-1}\) to 180 °C and then again increased at 340 °C min\(^{-1}\) for an isothermal step at 340 °C for 5 min. The compounds were identified comparing the EI-MS spectrum with the MS libraries NIST 08, NIST 08s, and Wiley 9. The quantification was performed using the response of the FID.
8.4 Chapter 6

8.4.1 Chemicals

2-PrOH (Aldrich, 99.8%), Hexadecane (Aldrich, 99%), RANEY®Ni 2800, Acetone (Aldrich, 99.8%), Phenol (aldrich, ≥99.5%), 2,6-dimethoxyphenol (Aldrich, 99%), 4-propyl-guaiacol (Aldrich, ≥97%), Ethyl acetate (Aldrich, 99%), Methylcyclohexane (Aldrich, ≥98%), n-heptane (Aldrich, 99%), Tetralin (Aldrich, 99%), 2-Methyltetrahydrofuran (Aldrich, ≥99%, Inhibitor-free), 1,1,1,3,3,3-Hexafluoro-2-propanol (Aldrich, ≥99%), cyclohexanol (Aldrich, ≥99%), cyclohexanone (Aldrich, ≥99%) 5-Hydroxymethyl-2-furaldehyde (Aldrich, 99%), Methanol (aldrich, 99.8%), were used as received.

8.4.2 Hydrogenation of phenolic and non-phenolic substrates in different solvents

Substrate (1 mmol), hexadecane (internal standard - ISTD, 0.11 mmol), Raney Ni 2800 (0.6 g wet), solvent and a magnet bar were placed in a stainless steel vial (20 mL). The vial was flushed with argon and then tightly closed. The experiment was performed at 220 °C under magnetic stirring (800 rpm) in a stainless steel heating block for 4 h. Ethyl acetate (10 mL, to produce a homogeneous mixture) was added into the reaction mixture (at 298 K) after the completion of the experiment. Phenol, 4-propyl-2-methoxyphenol, 2,6-dimethoxyphenol, cyclohexanol, cyclohexanone, hydroxymethylfurfural (HMF) were employed as substrates. MCH, 2-PrOH, n-heptane, tetralin, 2-MeTHF and 1,1,1,3,3,3-Hexafluoro-2-propanol (Hex-F-2-PrOH) were employed as substrates.

8.4.3 Recycling of the catalyst

A solution of phenol (3 mmol) and hexadecane (INST 60 mg) in MCH (9 ml) was prepared. 3 ml of this solution, Raney Ni 2800 (0.6 g wet) and a magnet bar were added in a stainless steel vial (20 mL). The vial was flushed with argon and then tightly closed. The experiment was performed at 220 °C under magnetic stirring (800 rpm).
rpm) in a stainless steel heating block for 4 h. Ethyl acetate (10 mL, to produce a homogeneous mixture) was added into the reaction mixture (at 298 K) after the completion of the experiment. The catalyst was washed with three aliquots of EtOAc and subsequently with 3 three aliquots of MCH previous reutilization.

8.4.4 Analysis of the spent catalyst (TEM and EDX)

Transmission electron microscopy (TEM) and Energy-dispersive X-ray spectroscopy (EDX) analyses were carried out with Hitachi HF-2000 and Hitachi S3500N microscopes, respectively.

8.4.5 Dehydroxylation of lignin stream oil

50 mg of lignin stream oil (sprucewood), Raney Ni 2800 (0.6 g wet), hexadecane (INST 20 mg), MCH (3 mL) and a magnet bar were placed in a stainless steel vial (20 mL). The vial was flushed with argon and then tightly closed. The experiment was performed at 220 °C under magnetic stirring (800 rpm) in a stainless steel heating block for 4 h. Ethyl acetate (10 mL, to produce a homogeneous mixture) was added into the reaction mixture (at 298 K) after the completion of the experiment.

8.4.6 Hydrogenation of phenol in the presence of sub stoichiometric quantities of alcohols

Phenol (1 mmol), 1, 2, 3 or 4 mmol of an alcohol (methanol or 2-PrOH), hexadecane (internal standard - ISTD, 0.11 mmol), Raney Ni 2800 (0.6 g wet), MCH (3 mL), and a magnet bar were placed in a stainless steel vial (20 mL). The vial was flushed with argon and then tightly closed. The experiment was performed at 220 °C under magnetic stirring (800 rpm) in a stainless steel heating block for 4 h. Ethyl acetate (10 mL, to produce a homogeneous mixture) was added into the reaction mixture (at 298 K) after the completion of the experiment.
Experimental
CHAPTER 9

Appendix

<table>
<thead>
<tr>
<th>Element</th>
<th>Massen%</th>
<th>Massen%</th>
<th>Atom%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>4.00</td>
<td>0.34</td>
<td>12.03</td>
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<tr>
<td>O K</td>
<td>17.64</td>
<td>0.21</td>
<td>39.79</td>
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<tr>
<td>Fe K</td>
<td>0.15</td>
<td>0.03</td>
<td>0.10</td>
</tr>
<tr>
<td>Co K</td>
<td>0.72</td>
<td>0.06</td>
<td>0.44</td>
</tr>
<tr>
<td>Ni K</td>
<td>77.48</td>
<td>0.34</td>
<td>47.64</td>
</tr>
</tbody>
</table>

Insgesamt 100.00

**Figure 9-1** Elemental analysis of Raney Ni (fresh catalyst before reaction, Chapter 6).
### Appendix

![Spectrum 1](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Masses%</th>
<th>Masses%</th>
<th>Atom%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sigma</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C K</td>
<td>5.68</td>
<td>0.32</td>
<td>18.67</td>
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<tr>
<td>O K</td>
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<td>0.16</td>
<td>24.67</td>
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<tr>
<td>Fe K</td>
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<td>0.12</td>
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<tr>
<td>Co K</td>
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<td>0.05</td>
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<tr>
<td>Ni K</td>
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<td>56.14</td>
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<tr>
<td><strong>Sum</strong></td>
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<td></td>
</tr>
</tbody>
</table>

**Figure 9-2** Elemental analysis of Raney Ni after reaction with phenol in the presence of MCH at 220 °C (Chapter 6).
CHAPTER 10

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References
CHAPTER 11

Curriculum and Scientific Contribution
Curriculum and Scientific Contribution

Curriculum Vitae

Personal Information:
Name: Gaetano Calvaruso
Nationality: Italian
Date and place of birth: 14th Set 1987 | Alcamo, Italy
Phone / Mobile: +49 (0) 15170065887
Email: gaetano.calvaruso1987@gmail.com
LinkedIn: www.linkedin.com/in/gaetano-calvaruso-9529a510b?trk=hp-identity-name

Academic Education:

Jul 2013 to present  
PhD in Chemistry  
Max-Planck-Institut für Kohlenforschung, Department of Heterogeneous Catalysis, supervised by Dr. Roberto Rinaldi  
Thesis: Valorization of lignin and lignin bio-oil for the production of fuels and fine chemicals.

Main activities and developed skills:
- In-depth understanding of the State-of-the-Art about wood structure (natural polymer structure) and catalysis.
- Optimize catalytic processes for fractionation of wood into cellulose and lignin.
- Designing and performing heterogeneous processes for the selective conversion of lignin into arenes and phenols.
- Ability to work effectively with others, problem-solving skills, analyze and report data, time management.

Oct 2006 – Mar 2012  
MS in Pharmaceutical Chemistry and Technology  
University of Palermo (Unipa), Faculty of Pharmacy, supervised by Dr. Gianfranco Fontana  
Dissertation undergraduate research projects: Synthesis of new chiral organic salts.

Final grade: 110 cum laude (min 60/max 110)

Main activities and developed skills:
- Studies of disciplines which introduce into a career in a variety of industries, particularly the pharmaceutical and related industries.
- The program provided training in GMP, pharmacokinetics, drug Metabolism and drug synthesis.
- Master’s thesis in Organic Chemistry working on the synthesis of new chiral organic compounds useful as homogeneous phase transf catalysts.
- Ability to work independently, laboratory and equipment maintenance.
Awards and Grants:

**Sep 2013**  
‘Best Poster Award’ for preparing poster during “2nd International Congress on Catalysis for Bio-refineries” (CatBior2013)

**Jul 2013**  
PhD’s grant, from the Cluster of Excellence “Tailored Made Full fro Biomass” based in Aachen University (RWTH Aachen, Germany)

**Mar 2012**  
Inscription at the “Italian Chemical Society“ for the excellent results obtained during the Master’s Degree

Technical Skills:

| Chromatographic techniques | HPLC, LC-MS, flash chromatography, GC-MS |
| Chemical structure          | NMR, 2D-NMR, MS, ATR-FTIR, UV-Vis, MS, Elemental analysis |

Additional Skills:

| Languages | Italian (native)  
| English (speaking and writing fluent, daily working language)  
| German (A2) |
| IT | Microsoft Office (Excel/Word/PowerPoint), OriginLab, ChemDraw, SciFinder, MestReNova, Linux system |

Drive License | B, Active

Training:

**Jan 2016**  
Basic Scientific Presentation for Natural Sciences

**Apr 2015**  
Ruhr-Lehrverbung-Katalyse (A German course on catalysis)

**Apr 2014**  
Scanning Probe Microscopy

Other Activities:

**Mar 2012 – Jan 2013**  
Volunteer researcher at the Department of Organic Chemistry, Unipa

**Feb 2011 – Oct 2011**  
Pharmacist

**Aug 2010 - Dec 2010**  
Support for teaching in Organic Chemistry I and II, Unipa
Conferences with Scientific Contribution

**Oral Presentations (presenting author is underlined)**

G. Calvaruso, R. Rinaldi,


G. Calvaruso, R. Rinaldi,

“Hydrogenolysis of Lignin originated from the mechanocatalytic treatment of lignocellulosic biomass”, TMFB General Meeting 2015, Aachen (Germany), Nov. 11, 2015.

G. Calvaruso, R. Rinaldi,

“Mechanochemical hydrolysis of lignocellulose to water soluble products” TMFB IRF-A1 Meeting 2015, Aachen (Germany), Dec. 10, 2015.

Roberto Rinaldi, Xingyu Wang and Gaetano Calvaruso

“A novel catalytic route for the conversion of lignin and bio-oils into arenes”, 22nd European Biomass Conference and Exhibition, Hamburg (Germany), June. 26, 2014.

**Poster Presentations (presenting author is underlined)**

G. Calvaruso, R. Rinaldi,

“Downstream processing of lignin oil streams obtained from the catalytic upstream biorefining of lignocelluloses”, CATBIOR, Rio de Janeiro (Brazil), Sept. 30, 2015.

G. Calvaruso, R. Rinaldi,

G. Calvaruso, R. Rinaldi,


G. Calvaruso, R. Rinaldi,


M. D. Kaufman Rechulski, G. Calvaruso, R. Rinaldi,

“Downstream processing of lignin originated from the mechanocatalytic treatment of lignocellulosic biomass”, CATBIOR, Dalian (China), Sept., 25, 2013.

Publications (first author is underlined)

G. Calvaruso, M. Clough, M. D. Kaufman Rechulski, R. Rinaldi,

“Hydrogenolysis of lignin originated from the mechanocatalytic treatment of lignocellulosic biomass” (in preparation).

G. Calvaruso, M. D. Kaufman Rechulski, M. Clough, R. Rinaldi,

“Extraction of low molecular weight lignin from mechanocatalytically treated wood in a biphasic system and its down streaming process” (in preparation).

G. Calvaruso, M. Clough, R. Rinaldi,


G. Calvaruso, R. Rinaldi,

“Selective Raney-Ni-catalyzed Hydrodeoxygenation of Phenol to Benzene” (in preparation).