Acid-assisted catalytic fractionation of lignocellulosic biomass

Hendriks, B.M.S.

Award date:
2017

Link to publication
Acid-Assisted Catalytic Fractionation of Lignocellulosic Biomass

Bart M.S. Hendriks

Graduation supervisor:
prof.dr.ir. Emiel J.M. Hensen

Project supervisor:
dr. Xiaoming Huang

Committee members:
dr. Evgeny A. Pidko
dr. M. Fernanda Neira d'Angelo
dr. Michael D. Boot
# Table of contents

## Title
Acid-Assisted Catalytic Fractionation of Lignocellulosic Biomass

### Abstract
5

1 Introduction 6

1.1 Lignocellulosic biomass 7

1.1.1 Carbohydrates: Cellulose and Hemicellulose 8

1.1.2 Lignin 8

1.1.3 Carbohydrate-lignin interlinkages 9

1.2 Biorefinery 9

1.2.1 Lignin isolation 11

1.2.1.1 Kraft pulping 12

1.2.1.2 Sulfite pulping 12

1.2.1.3 Soda pulping 12

1.2.1.4 Organosolv pulping 12

1.3 Lignin valorization 13

1.3.1 Valorization of isolated (technical) lignins 13

1.3.1.1 Acid-catalyzed/Base-catalyzed depolymerization 13

1.3.2 Reductive depolymerization/hydroprocessing 14

1.4 Acid-assisted reductive fractionation 16

1.5 Scope 18

1.6 References 19

2 Formic Acid as Co-Catalyst and Hydrogen Donor 22

2.1 Experimental 23

2.1.1 Chemicals and materials 23

2.1.2 Feedstock pretreatment 24

2.1.3 Catalytic reactions 24

2.1.4 Work-up procedure 24

2.1.5 Product analysis 25

2.1.5.1 GC-MS/GC-FID 25

2.1.5.2 $^1$H-$^{13}$C HSQC NMR 25

2.2 Results and discussion 26

2.2.1 Formic acid-assisted reductive fractionation of oak sawdust 26

2.2.1.1 Influence of the formic acid concentration 27

2.2.1.2 Influence of atmosphere and pressure 28

2.2.1.3 Influence of side-reactions 29

2.2.2 Catalytic cleavage of carbohydrate-lignin interlinkage models 30

2.2.3 Catalytic process 31

2.3 Conclusion 32

2.4 References 33
# Table of contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Comparing acid co-catalysts for the catalytic fractionation of oak sawdust</td>
<td>34</td>
</tr>
<tr>
<td>3.1</td>
<td>Experimental</td>
<td>35</td>
</tr>
<tr>
<td>3.1.1</td>
<td>Chemicals and materials</td>
<td>35</td>
</tr>
<tr>
<td>3.1.2</td>
<td>Feedstock pretreatment</td>
<td>35</td>
</tr>
<tr>
<td>3.1.3</td>
<td>Acid insoluble lignin (Klason lignin)</td>
<td>35</td>
</tr>
<tr>
<td>3.1.4</td>
<td>Catalytic reactions</td>
<td>36</td>
</tr>
<tr>
<td>3.1.5</td>
<td>Work-up procedure</td>
<td>36</td>
</tr>
<tr>
<td>3.1.6</td>
<td>Product analysis</td>
<td>36</td>
</tr>
<tr>
<td>3.1.6.1</td>
<td>GC-MS/GC-FID</td>
<td>36</td>
</tr>
<tr>
<td>3.1.6.2</td>
<td>$^1$H-$^{13}$C NMR analysis</td>
<td>37</td>
</tr>
<tr>
<td>3.1.6.3</td>
<td>GPC</td>
<td>37</td>
</tr>
<tr>
<td>3.1.6.4</td>
<td>XRD</td>
<td>37</td>
</tr>
<tr>
<td>3.1.6.5</td>
<td>SEM</td>
<td>38</td>
</tr>
<tr>
<td>3.2</td>
<td>Results and discussion</td>
<td>38</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Acid-assisted catalytic cleavage of model compounds</td>
<td>38</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Acid-assisted catalytic fractionation of oak sawdust</td>
<td>40</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Residue quality</td>
<td>45</td>
</tr>
<tr>
<td>3.2.4</td>
<td>Catalytic process</td>
<td>47</td>
</tr>
<tr>
<td>3.3</td>
<td>Conclusion</td>
<td>48</td>
</tr>
<tr>
<td>3.4</td>
<td>References</td>
<td>48</td>
</tr>
<tr>
<td>4</td>
<td>Stability of the tandem catalytic system: Investigating the fate of Pd/C and Lewis acid co-catalysts</td>
<td>50</td>
</tr>
<tr>
<td>4.1</td>
<td>Experimental</td>
<td>51</td>
</tr>
<tr>
<td>4.1.1</td>
<td>Chemicals and materials</td>
<td>51</td>
</tr>
<tr>
<td>4.1.2</td>
<td>Acid treatment of catalyst</td>
<td>51</td>
</tr>
<tr>
<td>4.1.3</td>
<td>Spent catalyst characterization</td>
<td>51</td>
</tr>
<tr>
<td>4.1.3.1</td>
<td>ICP-AES</td>
<td>51</td>
</tr>
<tr>
<td>4.1.3.2</td>
<td>TEM</td>
<td>52</td>
</tr>
<tr>
<td>4.1.3.3</td>
<td>XPS</td>
<td>52</td>
</tr>
<tr>
<td>4.1.4</td>
<td>Feedstock pretreatment</td>
<td>52</td>
</tr>
<tr>
<td>4.1.5</td>
<td>Catalytic reactions</td>
<td>52</td>
</tr>
<tr>
<td>4.1.6</td>
<td>Work-up procedure</td>
<td>53</td>
</tr>
<tr>
<td>4.1.7</td>
<td>Product analysis</td>
<td>53</td>
</tr>
<tr>
<td>4.1.7.1</td>
<td>GC-MS/GC-FID</td>
<td>53</td>
</tr>
<tr>
<td>4.2</td>
<td>Results and discussion</td>
<td>53</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Stability of Pd/C</td>
<td>53</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Lewis acid co-catalyzed reductive fractionation</td>
<td>56</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Lewis acid stability</td>
<td>58</td>
</tr>
<tr>
<td>4.3</td>
<td>Conclusion</td>
<td>59</td>
</tr>
</tbody>
</table>
# Table of contents

## Title
Acid-Assisted Catalytic Fractionation of Lignocellulosic Biomass

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4 References</td>
<td>59</td>
</tr>
<tr>
<td>5 p-Toluenesulfonic acid co-catalyzed reductive fractionation of birch wood chips</td>
<td>60</td>
</tr>
<tr>
<td>5.1 Experimental</td>
<td>61</td>
</tr>
<tr>
<td>5.1.1 Chemicals and materials</td>
<td>61</td>
</tr>
<tr>
<td>5.1.2 Feedstock pretreatment</td>
<td>61</td>
</tr>
<tr>
<td>5.1.3 Catalytic reactions</td>
<td>61</td>
</tr>
<tr>
<td>5.1.4 Work-up procedure</td>
<td>62</td>
</tr>
<tr>
<td>5.1.5 Product analysis</td>
<td>62</td>
</tr>
<tr>
<td>5.1.5.1 GC-MS/GC-FID</td>
<td>62</td>
</tr>
<tr>
<td>5.2 Results and discussion</td>
<td>63</td>
</tr>
<tr>
<td>5.2.1 p-TsOH co-catalyzed reductive fractionation of oak sawdust</td>
<td>63</td>
</tr>
<tr>
<td>5.2.2 Al(OTf)₃ co-catalyzed reductive fractionation of birch chips</td>
<td>64</td>
</tr>
<tr>
<td>5.3 Conclusion</td>
<td>65</td>
</tr>
<tr>
<td>5.4 References</td>
<td>65</td>
</tr>
</tbody>
</table>

Conclusion and outlook                                                  67

Acknowledgments                                                         69
Abstract

Current biorefinery schemes are highly focused on the upgrading of the carbohydrate fraction of lignocellulose. During pretreatment, lignin, constituting up to 30 wt% of the feedstock, is isolated from the carbohydrate fraction. This isolated lignin is often considered to be waste and burned for (internal) energy supply. With regard to the viability of the biorefinery, further valorization of this propylphenolic biopolymer is highly desired. Therefore, depolymerizing lignin into high value aromatic building blocks is an interesting option. However, during lignin isolation, the lignin structure is disruptively modified. Intralignin ether bonds, accounting for approximately 65% of the linkages between the propylphenols, are cleaved. These bonds are replaced by carbon-carbon bonds (i.e. recondensation), resulting in a recalcitrant polymer. Hence, depolymerization of isolated lignin is very challenging and requires harsh conditions.

To circumvent this challenge, an approach is proposed that reductively fractionates native wood and depolymerizes lignin, simultaneously. Because lignin is not isolated first, the intralignin ether linkages are still present. By this so-called lignin-first approach, lignin fragments are released from the lignocellulose matrix by solvolytic delignification. Subsequently, a reduction catalyst (e.g. Ru, Pd, Ni) can cleave the relatively weak ether bonds by hydrogenolysis, while limiting recondensation. As delignification by solvolysis is relatively slow, an acid is added to promote delignification. Both Lewis and Brønsted acids have been applied before, but the required nature of this acid is not elucidated yet. Therefore, several acids have been screened in this work, for catalyzing reductive fractionation of oak sawdust in combination with Pd/C in a H$_2$ atmosphere.

First of all, the addition of the weak carboxylic acid formic acid is attempted. This acid acts as a hydrogen donor, which could make the hydrogen atmosphere redundant. Upon addition of 75 g/L formic acid, a significant promotive effect is observed, as the aromatic monomer yield increased from 14 wt% for the Pd/C catalyzed neutral reaction (30 bar H$_2$) to 28 wt% for the acid assisted reaction (10 bar N$_2$). Although a high acid concentration is used, the delignification is rather low. Based on model compound studies on lignin-carbohydrate interlinkages, formic acid is not effective in cleavage of the phenyl glycoside bonds. Moreover, formylation reactions can take place that convert formic acid.

Although the formic acid co-catalyst gave rise a yield enhancement, more acids are compared via a more systematic approach. Based on this study, the strong Brønsted acids HCl and H$_2$SO$_4$ and the Lewis acid Al(OTf)$_3$ perform best as acid co-catalysts. These acids show high delignification yields and monomer yields of 44 wt%, 35 wt% and 46 wt% can be obtained, respectively, based on the Klason lignin content of the oak sawdust. In comparison with weak acids H$_3$PO$_4$ and CH$_3$COOH, relatively low concentrations are required for efficient delignification of the oak feedstock. In contrast to the other acids, HCl causes significant catalyst leaching and autoclave corrosion. Therefore, this acid does not seem the most suitable co-catalyst. Alternatives such as p-toluenesulfonic acid, AlCl$_3$ and FeCl$_3$ have also been revealed as promising acid co-catalysts.

In addition to aromatics, a high-quality cellulose residue is produced by this reaction, which is not separable from the solid catalyst used. As this residue requires further upgrading, separation of the solids is an essential step in the future biorefinery. Hence, the reaction feedstock is changed to birch chips in a size range from 0.5 to 5 mm. Promising monomer yields are obtained. After particle-size based separation of the catalyst from the wood residue, the yield drop is less than 20%. Further optimization is required to assess the full potential.
1 Introduction

The oldest archeological evidence for the controlled use of fire brings us back to prehistorical mankind, living on our planet one million years ago. Although the exact historical starting point for mankind using fire is not clear, the fuel that was used ages ago is obvious: plant biomass. Until the 19th century, energy required for domestic use (i.e. for cooking, heating or illumination) was predominantly obtained from wood, charcoal and plant oil. In fact, in the first decades of the 20th century, plant material was still an important industrial feedstock for the production of fibers, solvents and dyes.

Since the industrial revolution, coal, natural gas and oil have turned out to be brilliant substitutes for many bioresources, powering a technological and societal revolution in the 19th and 20th century. The reliable, abundant and affordable energy supply has been a major contributor to the enhanced prosperity in the world and the exceptional population growth.4 Electricity networks, combustion engines and fossil-based fuels and materials have emerged whose existences entirely rely on the availability of fossil resources and that strongly influence our everyday lives.

Now, after years of increasing production and consumption of fossil-based energy, fuels and chemicals, the downside of this fossil dependence is becoming evident. First of all, the supply of fossil raw materials is finite, as these are not renewable within an appropriate time span. In 2009, an evaluation on dwindling fossil reserves estimated the reserves to be sufficient for 107, 37 and 35 years for coal, gas and oil, respectively. As a matter of fact these estimates have changed over and over; in the 1960s oil was said to be depleted in the early 21st century.

A second concern associated to the current fossil-based economy is the reducing energy security. Political instability in regions where fossil resources are located as well as rising prices are main contributors to this. Moreover, from a global point of view, the concept of fossil energy security is only locally applicable due to unequal development of regions. Approximately 40% of the world population still depends on the preindustrial types of bioenergy, despite the superior properties of their fossil substitutes.

Although these issues might seem alarming, the most severe threat caused by our dependence on fossil resources is probably climate change. In the most recent report by the Intergovernmental Panel on Climate Change (IPCC), it is concluded that the concentrations of carbon dioxide, methane and nitrous oxide in the earth’s atmosphere have increased since the 1750s. Rising atmosphere and ocean temperatures, melting snow and ice and rising sea levels are observed, for which fossil carbon dioxide emissions are assigned as the primary cause. Therefore, the report states that it is “extremely likely” that the anthropogenic contribution plays dominant role in climate change. If anthropogenic greenhouse gas emissions are continued, further harmful changes in the climate are predicted by models.

These three adverse consequences of our fossil-based economy have urged national governments and intergovernmental organizations to design policies to mitigate our dependence on fossil resources. One of the most recent efforts is the Paris Agreement, a deal established at the United Nations Climate Change Conference 2015 in Paris (COP21). This agreement focusses on climate change and legally limits the global average temperature rise to well below 2.0 °C relative to the preindustrial temperature. Whilst the ambition of the Paris Agreement is explicitly stated, the practical interpretation and implementation is not part of the agreement itself. More specific roadmaps to accomplish the targets have been developed and will be developed at (inter)governmental level. The EU, for example, has published energy strategies for 2020, 2030 and 2050, defining key steps, both in technology and legislation. Similarly, the U.S.
Department of Energy has a strategic plan for the period 2014-2018 and moreover, the Office of Energy Efficiency and Renewable Energy expanded this work into a plan for the period 2016-2020.\textsuperscript{16,17}

To meet the growing demand for energy, alternative, reliable resources for the production of energy, fuels and materials are explored.\textsuperscript{18} In response to this exploration, a shale gas revolution has been going on in the U.S. for the last few years. Whereas shale gas is cheap and abundant, environmental concerns are growing, because again, a fossil, non-sustainable feedstock is arising.\textsuperscript{9}

At the same time, the desired transition to renewable alternatives is started, addressing the ambitions of the Paris Agreement and governmental strategic plans. Harvesting wind and solar energy is promising, for example, but for the production of materials and fuels, a carbon source is still required. As biomass is a renewable source of organic carbon, this preindustrial feedstock might become more attractive again.\textsuperscript{5,6} The shale gas revolution seems to oppose the biomass move, but, in fact, the small hydrocarbons (<C4) in shale gas are complementary to the larger hydrocarbons (>C5) obtained from biomass. Moreover, cheap shale gas can provide low-cost hydrogen, required for the upgrading of biomass.\textsuperscript{19}

1.1 Lignocellulosic biomass

The term biomass covers all plant material growing on earth. The total production rate of biomass is almost $10^{11}$ ton per year and only 3.5% of this total production is used nowadays. For satisfying the full human carbon demand, approximately one quarter is estimated to be sufficient.\textsuperscript{20}

Two major biomass types can be distinguished: first-generation and second-generation. First-generation biomass comprises edible plant materials that function predominantly as energy storage tissues in plants, such as sugar, starch and plant oil.\textsuperscript{21} The conversion of first-generation plant material is commercialized, but requires fertile land. Therefore, it competes with food production.\textsuperscript{22} The sugarcane-based ethanol industry in Brazil is a well-known success of the expanding supply of biobased products, resulting in up to 80% reduction of greenhouse gas emissions.\textsuperscript{6,23} However, the reduction by corn-based ethanol production is much lower.\textsuperscript{6}

The processing of second-generation lignocellulosic crops has not matured yet.\textsuperscript{6} Lignocellulose is the most abundant plant material, representing over 50% of the world biomass.\textsuperscript{24} It is found in the cell walls of vascular plants, which include woody plants (e.g. softwood and hardwood) and grasses.\textsuperscript{20} Therefore, lignocellulose conversion methods could offer the potential to utilize cheap, inedible energy crops and even agricultural, forestry, pulping industry or municipal wastes.\textsuperscript{6}

Lignocellulose is a complex network of three biopolymers, cellulose, hemi-cellulose and lignin, complemented by small amounts of salts and minerals, waxes, fatty acids, pectins and proteins (Figure 1.1).\textsuperscript{5} Secondary cell walls, deposited in perennials (e.g. plants that live for multiple years) after cell growth has stopped, are the main source of lignocellulosic tissues. After this secondary wall is constructed by a cell, the cell dies, but the wall still provides mechanical strength and rigidity to plant cells. Moreover, these secondary cell walls enable water transport throughout the plant and they function as chemical barrier, offering resistance against organisms and pathogens.\textsuperscript{5,25,26}
1.1.1 Carbohydrates: Cellulose and Hemicellulose

Cellulose is the major component of lignocellulose, constituting 35-50 wt%. It is a linear polymer consisting of glucose units linked by β-1-4 glycosidic bonds. In native wood, the degree of polymerization of cellulose is commonly about 10,000.\(^6\) By both intermolecular and intramolecular hydrogen bonding, these polymers are bundled into crystalline microfibrils with a diameter of 10-25 nanometer. These microfibrils can coil around each other, to form macrofibrils providing additional strength to the cell wall.\(^27,28\)

Hemicellulose is a family of branched, amorphous polysaccharides which consist of pentose and hexose sugars, like xylose, arabinose, glucose and mannose. Moreover, functional groups (e.g. acetyl and methyl groups) are connected to the hemicellulose polymer, particularly important for interconnecting the various wood constituents.\(^6,26\) Constituting about 25 wt% of the lignocellulose, hemicellulose forms the cell wall framework in which the cellulose fibers are embedded.\(^6,28\) The degree of polymerization of hemicellulose is 100 to 200, much lower than that of cellulose.\(^6\)

Due to the differences in degree of polymerization and morphology, cellulose and hemicellulose show distinct solubility and reactivity behavior. Both polysaccharides do not dissolve in water at low temperatures, but dilute acids are already sufficient for solubilizing hemicellulose at slightly elevated temperatures. Cellulose is not solubilized at these relatively mild conditions due to the crystalline nature. To dissolve cellulose, higher temperatures or concentrated acids are required. However, in these conditions, the cellulose polymer is hydrolyzed and thus, degraded.\(^26\)

1.1.2 Lignin

Lignin is the third main constituent of lignocellulose, mainly found in the secondary cell walls of plants. This three-dimensional amorphous polymer network is made up of three phenylpropane building blocks, called monolignols (Figure 1.2a). \(p\)-Coumaryl alcohol forms the \(p\)-phenyl or hydroxyphenyl (H) unit, coniferyl alcohol is found in lignin as the guaiacyl (G) unit and sinapyl alcohol is the syringyl (S) unit.\(^29\) The amount of lignin present in the cell wall matrix and the composition of lignin depend on the plant type.
Technische Universiteit Eindhoven University of Technology

Figure 1.2a) Monolignols p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol; b) common lignin-carbohydrate interlinkages include the γ-ester, the phenyl glycoside and the benzyl ether.

and plant part. In grasses, lignin constitutes 16-21 wt% and consists of all three monolignols. Only coniferyl and sinapyl alcohol units are found in hardwood, while lignin covers 16-24 wt% of this wood type. Lignin in softwood, accounting for 25-31 wt%, consists mostly of coniferyl alcohol.

Further complexity of the lignin polymer is derived from the variety in linkages between the building blocks. In Figure 1.3, typical intralignin linkages and important characteristics of these linkages are displayed. In hardwood as well as in softwood and grasses, the β-O-4 bond has the highest occurrence. Important to note is the relatively high prevalence of high dissociation energy biphenyl and dibenzodioxocin bonds in softwoods. This particular feature is caused by the presence of less methoxy groups compared to hardwood, which also leads to a more branched polymer.

1.1.3 Carbohydrate-lignin interlinkages

For several decades, characterization of the interlinkages between polysaccharides and lignin has remained a challenge, as advanced techniques are required for identification and quantification of these structural elements. Cellulose and hemicellulose are not bound to each other by covalent bonds, but by physical hydrogen bonds. Lignin is, however, covalently linked to the carbohydrates. The main lignin-carbohydrate bonds present in native wood are proposed to be benzyl ester (e.g. γ-ester), phenyl glycoside and benzyl ether linkages (Figure 1.2b).

1.2 Biorefinery

The processes and equipment employed for the integrated conversion of biomass, are often referred to as the biorefinery, in analogy to the conventional petroleum refinery. In other words, instead of the crude oil feedstock of petroleum refineries, this facility makes use of a biomass feedstock for the production of fuels, bulk chemicals, fine chemicals and energy. Aiming for the highest value yield from biomass, refinery processing creates the opportunity to utilize and valorize all biomass components and thus, to produce a variety of products.

Although the aim is identical for both petroleum refineries and biorefineries, the well-known processes applied in the petroleum refinery cannot be directly translated into biorefinery counterparts. A first challenge is the presence of large quantities of oxygen in biomass. For the production of fuels, oxygen is undesirable, because it reduces the energy density. Moreover, the polarity oxygen causes blending difficulties with fossil fuels. On the other hand, commodity chemicals often contain oxygen and are currently produced by catalytic oxidation of hydrocarbons. As many biomass-derived intermediates are

9 Acid-Assisted Catalytic Fractionation of Lignocellulosic Biomass / Version Final
already functionalized by oxygen, it seems rather counterintuitive to customize them for the petrochemical production methods by complete deoxygenation, followed by an oxidation of the deoxygenated species. Therefore, the feedstock shift could result in major changes in platform chemicals.\textsuperscript{2,21}

Moreover, herbaceous and woody biomass are inherently different. Even variability in composition of a particular biomass type can occur due to growth conditions. Hence, the feedstock of the biorefinery is not uniform in carbohydrate and ash composition, bulk density, moisture content and particle size and shape. This non-uniformity is a constraint in the development of processes, because the demanded product quality could require a well-defined feedstock.\textsuperscript{32}

![Figure 1.3. Common lignin intralinkages and corresponding occurrences and binding energies. The Greek letters \(\alpha\), \(\beta\) and \(\gamma\) are assigned to the carbon atoms of the propyl side chain; numbers 1-6 correspond to the position of a carbon atom in the ring (Adapted from Rinaldi et al.).\textsuperscript{30}](image-url)
Despite the challenges expressed, several designs for biorefineries have already been proposed. Figure 1.4a summarizes the key steps of the biorefinery supply chain, in which the heterogeneous feedstock is converted into high-volume/low-value (HVLV) and low-volume/high-value (LVHV) products. Electricity and heat are produced and internally supplied to the processes applied in the biorefinery or sold, in case of excess energy.\textsuperscript{18} A selection and combination of processes ideally results in full utilization of the feedstock. However, since the 19\textsuperscript{th} century, carbohydrate valorization has been the focus of biomass processing, leaving lignin underexploited.\textsuperscript{20} In the pulp and paper industry, for example, which has been applying biorefinery concepts for centuries, 70 million tons of lignin are produced annually.\textsuperscript{33} Regarded as recalcitrant, complex waste, 98\% of this lignin is “valorized” as low-value fuel, providing energy for internal use and for recovery of chemicals applied in the pulping process.\textsuperscript{30,33}

1.2.1 Lignin isolation

As valorization methods of the carbohydrate fractions in the current (pulping industry) biorefineries are often based on a pure cellulose feedstock, lignocellulose is first separated into its three main biopolymers.\textsuperscript{35} Thus, prior to carbohydrate upgrading, lignin is removed from the harvested feedstock. This pretreatment is one of the most challenging and costly biorefinery processes, because this first step requires transformation of the complex, rigid and recalcitrant feedstock into useful delignified cellulose.\textsuperscript{20,26,29}

Several fractionation methods are applied for delignification, of which four main technologies are discussed in this section: Kraft pulping, sulfite pulping, soda pulping and organosolv pulping. These methods commonly not only result in removal of lignin from the wood matrix, but also significantly alter the chemical structure of lignin itself.\textsuperscript{30} Therefore, the selected isolation method has a profound impact on further upgrading by depolymerization.\textsuperscript{36}
1.2.1.1 Kraft pulping
In the Kraft pulping process, lignocellulose is fractionated by an aqueous mixture of the two inorganic salts sodium sulfide (Na$_2$S) and sodium hydroxide (NaOH). In this basic environment at 130 to 180 °C, the lignin ether intralinkages are cleaved, eliminating soluble fragments from the wood matrix. By these non-catalytic stoichiometric reactions, a degraded, highly condensed, sulfur-containing type of lignin is obtained, which is often referred to as Kraft lignin.

With a worldwide production of 130 million ton pulp per year, Kraft pulping is the most important pulping process. It generates about 85% of the worldwide lignin. However, the solubilized lignin (black liquor) produced by this highly energetically integrated industrial process is directly burned, providing required internal energy. Moreover, it is utilized in the recovery of the pulping agents. Nowadays, though, an electricity surplus is often generated, which could be an incentive for further valorizing the lignin that causes this margin. Nevertheless, the condensed, sulfur-rich (1-3%) nature of Kraft lignin turns efficient catalytic upgrading into a very challenging task.

1.2.1.2 Sulfite pulping
In a pH range from 2 to 12, sulfite salts (e.g. CaSO$_3$, MgSO$_3$) are employed for the generation of lignosulfonate, the product of the sulfite pulping process. Lignosulfonate, in which lignin is mixed with carbohydrates and ash, contains a wide variety of functional groups, including sulfonate groups, phenolic hydroxyl groups and carboxylic groups. At the operating temperature of 130 to 150 °C, condensation reactions can take place. Although the produced lignin is of significantly higher molecular weight than the Kraft lignin, the presence of the functional groups renders lignosulfonate water-soluble.

Despite the sulfur content of 3-8%, which is even higher than that of Kraft lignin, some additional applications have been found for lignosulfonate. The polymer can, for example, be utilized as dispersing agent in the cement and concrete production. This potential use has raised new interest for lignosulfonate, aiming for enhancing the quality for this application, but also for finding new applications.

1.2.1.3 Soda pulping
The feedstock of the soda pulping process consist mainly of annual and non-woody plants. In an alkaline aqueous medium and a temperature of 140 to 170 °C, sulfur-free soda lignin is generated. In presence of sodium hydroxide, intralignin ether bonds are broken, resulting in soluble lignin with a low molecular weight.

1.2.1.4 Organosolv pulping
In the organosolv process, biomass is subjected to an organic solvent, a mixture of organic solvents or a mixture of organic solvents and water. Organic solvents include alcohols and diols, ketones and cyclic ethers. This environmentally more benign method does not make use of sulfur containing chemicals and produces high purity lignin without modifying the structure to a large extent. The temperatures of organosolv processes vary from 180 to 200 °C.

Acids and bases can be added to the organosolv process as catalyzing agents. However, condensation reactions are expected to occur in their presence.
1.3 Lignin valorization

The current biorefinery is predominantly focused on valorization the carbohydrate fraction. Platform chemicals and fuels such as levulinic acid and ethanol can be obtained from cellulose upgrading. Lignin, isolated by one the techniques discussed in Section 1.2.1, is mostly combusted for internal energy. Nevertheless, during the production of for example bioethanol, a lignin surplus of approximately 60% of the combusted fraction is generated. For achieving economic viability of biorefineries, further valorization of this lignin fraction is crucial.

Figure 1.4b shows potential valorization approaches and their margins. Even isolated lignins with lower purities could be upgraded to useful, high-value products. An overview of the technologies that have been developed for this purpose is discussed in this section. These techniques yield aromatic lignin monomers, dimers and oligomers that can be (de)functionalized yielding fuels or chemicals. These chemicals can be applied as raw materials and additives for polymers, for example. In the end, however, the most interesting lignocellulose-based chemicals are the aromatic platform chemicals benzene, toluene, xylene and phenol.

Two other valorization approaches which are not included in Figure 1.4b are gasification and pyrolysis. Gasification yields synthesis gas, a mixture of hydrogen and carbon monoxide. This gas mixture is an important platform for the production of fuels via Fischer-Tropsch synthesis and for the production of methanol. Supercritical water (377 °C and 217 bar) is considered to be a suitable medium for this catalytic or thermal conversion.

Pyrolysis is decomposition of biomass upon heating it to 300-900 °C in absence of air. This thermal conversion yields products in three phases: a liquid bio-oil, a solid char residue and gaseous CO\textsubscript{2}, CO and hydrocarbons. The liquid bio-oil consists of more than 300 compounds, including oxygen-rich products (e.g. phenol, aldehydes, ketones, alcohols) and aromatic hydrocarbons (e.g. benzene, toluene, naphthalene). Because of the high oxygen content, the heating value of pyrolysis oil is low. Moreover, due to its immiscibility with diesel and gasoline, chemical instability, low volatility and corrosive nature it is not directly applicable as substituent for fuels.

1.3.1 Valorization of isolated (technical) lignins

With the various types of isolated lignins, several catalytic methods have been developed to crack these further into smaller fragments. This depolymerization is a second key step in the lignin valorization approach, but the recalcitrant isolated lignin utilized already poses significant limits. One restriction is caused by recondensation reactions that have taken place in the harsh conditions of the delignification step. Furthermore, repolymerization should also be prevented in the depolymerization step. Finally, taking into account catalyst activity and stability, mild reaction conditions are highly desirable.

1.3.1.1 Acid-catalyzed/Base-catalyzed depolymerization

A classical method for depolymerization is acidolysis, or acid-catalyzed hydrolysis This method is capable of cleaving β-O-4 bonds present in technical lignins. Both Brønsted and Lewis acids have been applied in acidolysis processes, as well as solid acids.

Base-catalyzed depolymerization also catalyzes the cleavage of β-O-4 bonds. Aqueous solutions of homogeneous Brønsted bases (e.g. NaOH) are applied in these processes, leading to defunctionalization.
of the aromatic products.\textsuperscript{46} However, base-catalyzed depolymerization requires harsh conditions. The processing temperature exceeds 300 °C, while pressures are higher than 200 bar.\textsuperscript{46}

A common drawback of acid and base catalyzed processes is repolymerization and recondensation of the produced lignin fragments.\textsuperscript{46} Reactive products and intermediates such as phenolic OH groups\textsuperscript{49}, ketones and aldehydes\textsuperscript{45}, double bonds and radicals\textsuperscript{50} are found to make the reaction mixture prone to these undesired reactions. Moreover, formaldehyde is an undesired by-product, as it could be a crosslinking agent, enhancing repolymerization.\textsuperscript{49}

To prevent the occurrence of these reactions, scavenging formaldehyde is one method for steering the reaction towards the desired products.\textsuperscript{49,51} Although formaldehyde is often seen as a yield hampering species, recent work by Shuai \textit{et al.} resulted in a method to turn formaldehyde into a stabilizing agent in an acidic environment. In their catalytic process, acid-catalyzed depolymerization products react with formaldehyde in a first step, forming 1,3-dioxane intralignin structures. During a second step, these are converted by Ru/C hydrogenolysis.\textsuperscript{52}

Three methods for suppressing repolymerization by reactive carbonyl compounds are revealed by the work of Deuss \textit{et al.} First, the aldehydes formed by triflic acid catalyzed depolymerization are converted into more stable acetals by a reaction with ethylene glycol. The second method is the reduction of reactive species by Ru/C, in presence of hydrogen. A third method elucidated is decarbonylation by a homogeneous $[\text{IrCl-(cod)}]_2/P\text{Ph}_3$ catalytic system.\textsuperscript{35}

1.3.1.2 Reductive depolymerization/hydroprocessing

Bearing in mind the success of hydroprocessing technologies developed for oil upgrading (e.g. hydrocracking, hydroforming), a popular lignin valorization method is the depolymerization in a reductive environment.\textsuperscript{39} In these systems, a high pressure hydrogen atmosphere can be utilized, but the use of hydrogen donating reagents or solvents such as formic acid, tetralin and isopropanol is explored as well.\textsuperscript{46,53,54} Temperatures range from 300 to 600 °C.\textsuperscript{41}

Reductive upgrading of lignin can be traced back to the 1930s, when Harris \textit{et al.} employed a Cu-Cr catalyst for converting an organosolv lignin into cycloalkanes. The conditions applied in this process are rather harsh, as temperatures of 250 to 260 °C and hydrogen pressures of 200 to 350 bar are used.\textsuperscript{55} In 1952, the first commercial reductive lignin upgrading technology was developed in Japan. This so-called Noguchi process produced simple monophenols in decent 44 wt\% yields from desulfonated lignin, employing an iron(II)sulfide catalyst with one or more promoting co-catalysts. Although commercializing this process was also attempted in the U.S. by Crown-Zellerbach, ultimately, this process could not withstand the harsh competition against oil-derived phenols.\textsuperscript{39}

In the presence of hydrogen and a hydroprocessing catalyst, several reactions can take place, including hydrogenolysis, hydrogenation and hydrodeoxygenation.\textsuperscript{36} By hydrogenolysis, carbon-carbon or carbon-heteroatom bonds can be cleaved upon addition of hydrogen to both the carbon atom and the heteroatom. The lignin polymer, to a large extent linked by ether bonds, is therefore susceptible for this reaction type, which can be catalyzed by Ni, Ru, Rh, Pd and bimetallic variants.\textsuperscript{36,47} Furthermore, the hydrotreating catalysts Co-Mo and Ni-Mo have received quite some attention. Being applied before for the elimination of sulfur and nitrogen from fossil feedstocks, these (sulfided) catalysts remove oxygen from lignin via hydrodeoxygenation, a type of hydrogenolysis.\textsuperscript{29}
Previously, our research group also reported a CuMgAl mixed oxide catalyst for the conversion of soda lignin in supercritical ethanol. In this system, hydrodeoxygenation is efficient, while ring-hydrogenation is limited. Ethanol is a hydrogen donor and a scavenger for reactive intermediates, preventing condensation reactions.\textsuperscript{51,56}

Tandem catalytic systems have also been developed that combine reductive depolymerization catalysts with acids or bases. An example is the application of nickel, an active hydrogenolysis/hydrogenation catalyst, on HZSM-5, an solid acid support.\textsuperscript{57} Homogeneous acids are elucidated by the work Zakzeski \textit{et al.}, depolymerizing lignin over Pt/\(\gamma\)-Al\(_2\)O\(_3\) assisted by H\(_2\)SO\(_4\),\textsuperscript{58} and Xu \textit{et al.}, using formic acid in combination with Pt/C.\textsuperscript{53} Wang \textit{et al.} focused on the effect of basic solvents on depolymerization. It was reported that Lewis bases hinder the activity of Raney Ni. This characteristic can steer the reaction towards hydrogenolysis instead of hydrogenation.\textsuperscript{59} Other examples of base promoted depolymerization systems are NiAu and Ru/C assisted by NaOH.\textsuperscript{60,61}

### 1.3.2 Reductive fractionation

A relatively new approach for valorizing lignin is the lignin-first or catalytic reductive fractionation approach. Instead of isolating lignin which is likely to result in recalcitrant technical lignins, lignin is processed in its native form, in which it contains 67-73\% reactive ether linkages bonds.\textsuperscript{62} As a consequence, higher yields in desired aromatic fragments can be obtained via hydrogenolysis. Moreover, due to sulfur free-nature, other catalysts can be applied that would be deactivated by the presence of sulfur (e.g. noble metal catalysts).\textsuperscript{63}

Up to date, a few catalytic systems have been reported. Almost one decade ago, Yan \textit{et al.} already found carbon supported noble metal catalysts (e.g. Pt, Ru, Pd, Rh) to be active in the hydrogenolysis of birch wood. Aromatic monomer yields of 46 wt\% could be obtained after 4 hours in a 1:1 mixture of dioxane and water at a temperature of 200 °C and a pressure of 40 bar. Aiming for cycloalkanes and methanol instead of methoxylated aromatics, the product mixture of the first step was subjected to a second hydrogenation step, which was also catalyzed by noble metals.\textsuperscript{64} Li \textit{et al.} built further on this work and developed an aqueous hydrocracking method. A Ni-W\(_2\)O/AC catalyst upgraded lignin into 46 wt\% monoaromatics, while cellulose and hemicellulose were converted into diols in a yield of 76 wt\% (4h, 235 °C, 60 bar H\(_2\)). A significant advantage of this approach is the reusability of the catalyst.\textsuperscript{65}

Song \textit{et al.} followed a more fundamental approach and hypothesized a fragmentation/hydrogenolysis mechanism. First, alcohol solvents are employed for releasing soluble lignin fragments, which can subsequently be cleaved further by hydrogenolysis over a Ni/C catalyst. Ultimately, this resulted in a 50\% conversion of lignin into alkylmethoxyphenols in the absence of hydrogen (6h, 200 °C). Ferrini \textit{et al.} also conducted reactions in the absence of hydrogen. They made use of a Raney Ni catalyst and a two-step method. In a 3:7 H\(_2\)O/isopropanol mixture, poplar wood is delignified, resulting in a soluble oil, rich in phenol derivatives, and a solid, carbohydrate-rich residue. Subsequently, the oil is converted further in isopropanol by the same Raney Ni catalyst. Because of the magnetic properties of Raney Ni, catalyst recovery and reuse is possible via this approach.\textsuperscript{66}

A study of Van den Bosch \textit{et al.} returned to noble metal catalysts Pd and Ru, both on a carbon support. By their work, the dependency of the product composition on the hydrogenolysis catalyst was revealed. Ru/C preferably produced phenolic monomers with a propyl side chain, while Pd/C yielded monomers with a propanol group. For both catalysts, the monomer yield was close to 50\%, based on the carbon content of the products and birch wood feedstock (3h, 250 °C, 30 bar H\(_2\)).\textsuperscript{67}
1.4 Acid-assisted reductive fractionation

In line with the developments in reductive depolymerization of technical lignins, tandem catalytic systems consisting of a heterogeneous hydrogenation/hydrogenolysis catalyst and an acid are also explored in the reductive fractionation processes. This results in a complex yet effective interplay of reactions, yielding the desired low molecular weight aromatics in a relatively mild environment.

A first indication of the promoting effect of acids was revealed by the work of Parsell et al. A bimetallic catalyst, combining Pd nanoparticles on a carbon support with Zn, was found to be efficiently cleaving model compounds. Upon catalyst characterization by XANES and EXAFS, it was concluded that not the Pd-Zn alloy is the active phase. Yet Zn is hypothesized to be present as Zn\(^{2+}\) and acts as Lewis acid co-catalyst.\(^{58}\) Later, this catalyst was applied in reductive fractionation of several types of wood, resulting in monomer yields up to 54 wt\% (12h, 225 °C, ca. 35 bar H\(_2\)). Interestingly, these reactions were carried out in a reactor that had a microporous cage filled with the biomass, enabling separation of catalyst and solid residue.\(^{69}\) Moreover, a mechanism for this Zn/Pd/C catalytic system is proposed by the same research group.\(^{70}\)

As successful Lewis acid promotion was observed, Renders et al. investigated the effect of acids and bases into more detail, comparing the promotion by H\(_3\)PO\(_4\) and NaOH with a neutral Pd/C catalyzed reaction. Whereas acidic conditions were found to significantly enhance the monomer yield from 26 mol\% to 42 mol\%, the base assisted system resulted in a decrease of the monomer yield. Especially the delignification increased upon addition of the acid (3h, 200 °C, 20 bar H\(_2\)).\(^{71}\)

Recently, a non-noble bimetallic catalytic system has been explored by Zhai et al. Inspired by the previous Ni-catalyzed systems and reported promotion by Fe or FeCl\(_3\), a potentially cheap 1:1 Ni-Fe/AC catalyst was prepared, affording yields of almost 40 wt\% (6h, 200 °C, 20 bar H\(_2\)). Fe was indeed confirmed to act as an acid in this bimetallic catalyst, promoting deoxygenation of the lignin products.\(^{72}\)

Previous work in our research group by Huang et al. also focused on acid-assisted reductive fractionation. Lewis acidic metal triflates (e.g. Yb(OTf)\(_3\), Al(OTf)\(_3\)) are identified as efficient co-catalysts, in combination with heterogeneous Pd/C. An optimal aromatic monomer yield of 46 wt\% was obtained and the suitability of several wood types for this method is confirmed.\(^{73}\) Later, a more detailed model compound study elucidated the role of both catalysts of this tandem catalytic system (Figure 1.5). Based
on this work, acids are concluded to be playing a major promoting role in delignification, while the released fragments are cleaved further by hydrogenolysis over Pd/C. However, acids also promote this hydrogenolysis step. Therefore, the Pd/acid ratio is an important parameter in order to steer the reaction.\(^\text{74}\)

From a more fundamental catalytic viewpoint, two main depolymerization reaction pathways can be followed in acid-assisted reductive fractionation processes. After acid-catalyzed solvolytic release of lignin fragments, the \(\beta\)-O-4-linked solubilized lignin oligomers can either undergo acidolysis (Figure 1.6a) or hydrogenolysis (Figure 1.6b). For acidolysis, activation of the \(\alpha\)-carbon by hydrolysis of the \(\alpha\)-OH is the essential first step of the reaction sequence. After this step, a nucleophile (i.e. the removed water in the reaction mechanism of Figure 1.6a) can add to the reactive \(\text{C-O-C}_{\text{aryl}}\). Because reactive intermediates are formed, condensation reactions are very likely to occur.\(^\text{35}\)

Hydrogenolysis over the Pd/C surface is highly simplified in Figure 1.6b, because the mechanism is still rather controversial. Several mechanisms have been proposed in literature, mainly in the absence of molecular hydrogen. A dehydrogenation step is required in this reaction sequence. However, whilst Galkin et al. suggest that dehydrogenation takes place before hydrogenolytic cleavage of the \(\beta\)-O-4 bond\(^\text{75}\), Zhou et al. propose a dehydrogenation of the cleavage product.\(^\text{76}\) Based on the DFT study of Lu et al., the preferred pathway is dehydrogenation prior to hydrogenolysis.\(^\text{77}\)

When combining acidolysis and hydrogenolysis, side reactions expected for the acidolysis pathway can be hindered by stabilizing hydrogenation of reactive intermediates by the hydrogenation/hydrogenolysis catalyst (Figure 1.7).\(^\text{71}\) For balancing stabilization and activation, the earlier mentioned Pd/acid ratio should be optimized. This particular feature was already discussed in acid-catalyzed depolymerization reactions by triflic acid and Ru/C. If too much Ru/C is present, reactive intermediates might be rapidly hydrogenated, stabilizing these fragments (i.e. species 2 converted into 11 in Figure 1.7). Unfortunately, these species become unreactive for acidolysis.\(^\text{35}\)

---

**Figure 1.6a** Simplified acidolysis mechanism of a \(\beta\)-O-4 model, potentially leading to recondensation. Hydrolysis reactions resulting in further removal of OH-groups are not included in this scheme; **b** Simplified hydrogenolysis mechanism of a \(\beta\)-O-4 model over a Pd/C catalytic surface. Hydrodeoxygenation resulting in further removal of OH-groups are not included in this scheme.
1.5 Scope

In this master thesis, acid co-catalyzed fractionation of woody biomass into streams of aromatic monomers, dimers and oligomers, methylated sugars and cellulose pulp is explored. Earlier work by our group showed that low concentrations Lewis acidic metal triflates enhance the aromatic monomer yield of reductive fractionation catalyzed by Pd/C. A potential show-stopper, though, is the price of metal triflates, given the contribution of the catalyst to the process economics.

Anticipating to this downside, first, substitution of the metal triflates by formic acid (HCOOH) is considered in Chapter 2. This simple carboxylic acid is weak (pKₐ = 3.77)\(^{16}\). An attractive property of formic acid is its hydrogen donor capacity. Moreover, the recyclability of formic acid within the integrated biorefinery could be a benefit for this process.

After this investigation into one particularly interesting acid, a more systematic approach is employed to compare a variety of Brønsted and Lewis acids aiming for optimal acidic environments. Results on woody biomass are combined with model compound results in order to obtain a more fundamental understanding of the trends observed in the real biomass cases. Moreover, the effect of acids on the crystallinity and morphology of the solid residues is examined. In Chapter 3, the results of this extensive study are summarized and discussed.
Although yield is of course an important parameter for assessing the process feasibility, completing this study requires characterization of the spent catalyst (Chapter 4). Leaching of palladium from the support could undermine the optimal process conditions. Moreover, acids could cause corrosion of the autoclave. Various analysis techniques (e.g. ICP-AES, TEM, XPS) are used to assess the catalyst properties after reaction. Furthermore, the stability of Lewis acids under reaction conditions is determined.

Finally, in Chapter 5, two small steps to industrial application are discussed. One is a move to another attractive acid, \( p \)-toluenesulfonic acid (\( p \)-TsOH). The other is a feedstock modification, from sawdust towards larger wood particles. This opens new opportunities for mechanically separating catalyst and solid residue.

1.6 References

Acid-Assisted Catalytic Fractionation of Lignocellulosic Biomass / Version Final
2 Formic Acid as Co-Catalyst and Hydrogen Donor

Lignin is one of the main constituents of lignocellulosic biomass, covering up to 30 wt% of this abundant feedstock. As lignin is a polymer network of propylphenols, renewable aromatic building blocks could be obtained from cracking lignin.\(^1\) Exploring methods to valorize this currently underutilized fraction of wood, pathways have arisen that convert lignin in its native form, linked for 67-73% by ether linkages.\(^2,3\) In these so-called lignin-first or reductive fractionation processes, lignin fragments are released by solvolysis and subsequently, supported metal catalysts cleave ether bonds that link the ether fragments by hydrogenolysis.\(^3\)

Although these so-called lignin-first methods require only very mild conditions, addition of a Brønsted or Lewis acid co-catalyst can make lignin-first valorization processes even gentler.\(^4-6\) For this work, the metal triflate-Pd/C tandem system recently reported by our research group is selected as the benchmark for acid-assisted catalytic reductive fractionation.\(^6,7\) Metal triflates are stable and active Lewis acids that can be recovered and reused.\(^8\) A concentration as low as 0.79 mM of aluminum triflate afforded high aromatic monomer yields from birch sawdust (45 wt%, based on the lignin fraction) and a high delignification while the temperature was well below 200 °C. Moreover, the cellulose fraction remains largely unaffected in this mildly acidic environment.\(^6\)

An attractive substitute for the expensive metal triflates, however, could be formic acid. Revising the production pathways for levulinic acid (Figure 2.1), an important incentive for considering this simple carboxylic acid as acid co-catalyst is immediately obvious. The formation of every molecule of this cellulose-derived platform chemical is accompanied by the formation of one molecule of formic acid.\(^9\) Application of formic acid in the catalytic fractionation process could be a motivation for recovery and utilization of this by-product "on-site", in the biorefinery where it is produced.

Furthermore, an advantage of formic acid is its capability to serve as a hydrogen donating agent. This particular characteristic of formic acid has been exploited in several valorization methods reported for isolated lignin,\(^10-15\) where both in situ formic acid decomposition and catalytic hydrogen transfer pathways

\[\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{H}_2 \]

\[\text{C} = \text{O} \quad \text{H} - \text{C} = \text{O} \quad \text{H} - \text{C} = \text{O} + \text{H}_2\text{O} \rightarrow \text{C} = \text{O} \quad \text{C} = \text{O} \quad \text{C} = \text{O} + \text{H}_2\text{O} \rightarrow \text{C} = \text{O} \quad \text{C} = \text{O} \quad \text{C} = \text{O} \]

\[\text{Formic acid} \quad \text{Levulinic acid} \quad \text{Cellulose} \quad \text{Glucose} \quad \text{Cellobose} \quad \text{H}^+ \quad \text{H}^+ \quad \text{Formic acid} \quad \text{5-HMF} \quad + \text{H}_2\text{O} \]

*Figure 2.1. In the levulinic acid scheme, one molecule of formic acid is produced per levulinic acid molecule.*\(^9\)
can provide hydrogen.\textsuperscript{13} In situ decomposition can be provoked by thermal and catalytic pathways, yielding carbon dioxide and hydrogen required for the hydrogenolysis reactions; unfortunately, decomposition into carbon monoxide and water is also possible.\textsuperscript{14} Eventually, this change in hydrogen source could increase the commercial feasibility of catalytic biomass conversion processes, as the cost of hydrogen is found to be a major barrier for the implementation of lignocellulosic biorefineries.\textsuperscript{16}

Comparing formic acid to Brønsted acids previously reported for catalytic fractionation processes, formic acid is relatively weak, (pK\textsubscript{a} = 3.77). Renders et al., for example, reported the application of the weak phosphoric acid (pK\textsubscript{a} = 2.12) as acid co-catalyst in relatively low concentrations of 2.5 g L\textsuperscript{-1}.\textsuperscript{5,17} However, based solely on the difference in pK\textsubscript{a}, measured in water, the concentration of the acid should be increased by more than one order of magnitude to obtain a similar acidic environment.

In this chapter, the prospects for formic acid in a dual function (e.g. catalyst and reactant) in the catalytic fractionation of woody biomass are experimentally probed. In an early stage of the reaction, it is hypothesized that formic acid can act as an acid co-catalyst, facilitating delignification. Later in the process, it can decompose either thermally or catalytically, by involvement of Pd/C which was found to be active in catalyzing decomposition in aqueous environment.\textsuperscript{18} To validate these hypotheses, the effect of concentration and pressure on the yield in aromatic monomers and the weight of residual biomass is determined. Then, model compound reactions are performed in order to gain fundamental understanding of the carbohydrate-lignin bond cleavage by this acid.

2.1 Experimental

2.1.1 Chemicals and materials

The oak sawdust was obtained from houtzagerijmennen.nl; its composition was analyzed by the Celignis Limited Nexus Innovation Centre, University of Limerick, Ireland (www.celignis.com). In Table 2.1, the detailed composition of the oak sawdust is shown.

Catalyst Pd/C (5 wt% Pd) and co-catalysts aluminum trifluoromethanesulfonate (aluminum triflate or Al(OTf)\textsubscript{3}) and formic acid (>98%) were purchased from Sigma-Aldrich. Analytical grade methanol was purchased from VWR. The gases hydrogen and nitrogen were both obtained from Linde Gas and have a purity of 5.0, which corresponds to 99.999%.

Model compounds glyceryl trioleate (>97.0%) and phenyl β-D-glucopyranoside (>97.0%) were purchased from Sigma-Aldrich.

All commercial chemicals were used without further purification. The sawdust, though, is subjected to pretreatment steps to remove the extractives and to obtain a well-defined particle size.(Details in Section 2.1.2)

<table>
<thead>
<tr>
<th>Total sugars</th>
<th>Glucose</th>
<th>Xylose</th>
<th>Mannose</th>
<th>Arabinose</th>
<th>Galactose</th>
<th>Rhamnose</th>
<th>Klason lignin</th>
<th>Acid soluble lignin</th>
<th>Extractives</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>56.8</td>
<td>37.6</td>
<td>15.7</td>
<td>1.8</td>
<td>0.4</td>
<td>1.0</td>
<td>0.3</td>
<td>23.3</td>
<td>3.0</td>
<td>8.8</td>
<td>0.3</td>
</tr>
</tbody>
</table>
2.1.2 Feedstock pretreatment

Oak sawdust is dried overnight at 105 °C and sieved to obtain a feedstock for reaction with a particle size ranging from 125 µm to 300 µm. The reaction feedstock was then subjected to Soxhlet extraction by water and ethanol, both for approximately 6 hours. The extracted wood was collected and again dried overnight at 105 °C.

2.1.3 Catalytic reactions

All catalytic reactions discussed in this chapter are batch experiments carried out in a 100 mL autoclave (Parr Instruments Company). For the benchmark Al(OTf)$_3$ experiment, the autoclave is filled with 2.0 g extracted oak, 15 mg Al(OTf)$_3$ (0.0316 mmol), 100 mg Pd/C (5 wt%) and 40 mL of methanol. Moreover, 30 µL n-dodecane is added as internal standard. After sealing the autoclave, it is purged four times with nitrogen and hydrogen and subsequently, a hydrogen pressure of 30 bar is applied, at room temperature. When no leak is observed, it takes approximately 30 minutes to heat the pressurized autoclave to 180 °C by an oven. The autoclave is continuously stirred at 500 rpm and after 2 hours of reaction (excluding heating time), the autoclave is cooled to room temperature in an ice bath. In order to record the course of the reaction, samples are taken and analyzed by GC-MS/GC-FID (Section 2.1.5.1).

For the formic acid experiments, the conditions are very similar to the benchmark. The autoclave is filled with 2.0 g extracted oak, 100 mg Pd/C (5 wt%), 40 mL of methanol, 30 µL n-dodecane and varying amounts of formic acid. The first experiment is performed in 30 bar hydrogen atmosphere, with 1.0 g formic acid (21.7 mmol). Later experiments are carried out in a 1 to 20 bar nitrogen atmosphere instead of the 30 bar hydrogen. The formic acid loading is varied from 1.0 g to 5.0 g.

For the model compound experiments, the reaction medium created is equal to the reaction medium for the wood experiments. The autoclave is charged with 100 mg glyceryl trioleate and 100 mg phenyl β-D-glucopyranoside, 100 mg Pd/C (5 wt%), 40 mL of methanol, 30 µL n-dodecane and again 1.0 to 5.0 g formic acid, at 1 to 20 bar nitrogen.

2.1.4 Work-up procedure

Figure 2.2 schematically describes the work-up procedure that is created for obtaining analyzable product fractions from the reaction mixture. The reaction mixture is collected from the autoclave and filtered over a glass fiber filter. The undiluted liquid filtrate is then transferred into a vial and the solid residue, consisting of residual biomass and Pd/C, is washed with methanol. After air-drying the solid residue for one week, the residue weight is determined.

For some analyses, further work-up of the liquid filtrate is required. After evaporation of methanol, the viscous, oil-like product is extracted by water and ethyl acetate, three times; a water-soluble sugar fraction and an ethyl acetate-soluble lignin fraction are obtained.
2.1.5 Product analysis

2.1.5.1 GC-MS/GC-FID
A Shimadzu 2000 GC-MS system with RTX-1701 column (60 m x 0.25 mm x 0.25 μm) is applied for the identification and quantification of products in the liquid reaction mixture, by means of a mass spectrometer (MS) and a flame ionization detector (FID), respectively. Quantification of the amount of lignin monomers and methylated monosaccharides is based on the peak area of the internal standard and the peak area and response factor (RF) of a particular compound:

\[
\frac{\text{Peak area}_{\text{product } i}}{\text{Peak area}_{\text{STD}}} = \frac{m_{\text{product } i}}{m_{\text{STD}}} \times RF_{\text{product } i}
\]

\[
\text{Monomer yield} = \frac{x_{\text{lignin}} \times m_{\text{wood}}}{m_{\text{monomers}}} \times 100\%
\]

Response factors of the woody biomass products are determined experimentally, by injecting a known amount of commercially available compound and n-dodecane. In case the compound was not commercially available or unknown, the response factor is based on the response factor for a product with a similar structure or molecular weight.

The response factors of model compound products are determined by the Effective Carbon Number (ECN) method.

2.1.5.2 \(^1\text{H}-^{13}\text{C}\) HSQC NMR
NMR samples are prepared from the ethyl acetate phase, containing the methanol-soluble lignin products (Details in Section 2.1.4). Ethyl acetate is evaporated for part of the solution and approximately 10 mg of the residual viscous, oil-like product is dissolved in 0.6 mL DMSO-d6.

The samples were analyzed by a Bruker 400 MHz spectrometer. For this analysis, a \(^1\text{H}\) NMR sample of 32 scans with a relaxation delay of 2 seconds is coupled to a \(^{13}\text{C}\) HSQC analysis of 16 scans and a relaxation delay of 2 seconds (HSQC EDETGPSISP). Both methods applied are standard analysis methods of the NMR apparatus.
The data processing software used is MestReNova. The assignment of peaks to particular compounds, building blocks or bonding fragments is based on literature.

2.2 Results and discussion

2.2.1 Formic acid-assisted reductive fractionation of oak sawdust

Figure 2.3 is an overview of two reductive fractionation processes. In the benchmark case, with Al(OTf)$_3$ as acid co-catalyst, gaseous hydrogen is provided at 30 bar pressure. After delignification, which is found to occur predominantly via acid-enhanced solvolysis, lignin fragments are cleaved via combined hydrogenolysis and acidolysis. Hence, hydrogen is employed by Pd/C for either hydrogenation of reactive intermediates formed by acidolysis or hydrogenolysis. Subsequently, the γ-OH products PG-OH and PS-OH can be converted into γ-ethers PG-OCH$_3$ and PS-OCH$_3$ by acid catalyzed etherification or into γ-H products PG-H and PS-H. The formation of γ-H products is expected to occur by combined dehydration and hydrogenation or by hydrodeoxygenation.

Changing to a hydrogen-free system, complexity increases as the number of reactive species in the reactor grows. Al(OTf)$_3$ is no longer present, but formic acid is expected to take over its role as delignification aid. Then, hydrogenolysis of the lignin fragments and hydrogenation of the acidolysis products are hypothesized to yield aromatic monomers, requiring formic acid to decompose selectively into hydrogen and carbon dioxide.

![Figure 2.3. Proposed catalytic process for the reductive fractionation, comparing formic acid as acid co-catalyst and hydrogen donor (purple), with the benchmark process co-catalyzed by Al(OTf)$_3$ and in H$_2$ atmosphere (green). (*) refers to the specific acid co-catalyst under investigation, formic acid or Al(OTf)$_3$.](image)
2.2.1.1 Influence of the formic acid concentration

During this series of experiments on formic acid as substituent for Al(OTf)$_3$, oak sawdust was selected as woody biomass feedstock. As previous results in the Al(OTf)$_3$-Pd/C reductive fractionation system were all based on birch wood,$^6$ new monomer yield and residual biomass weight benchmarks for this tandem system were set. The conditions for these benchmark were based on the optimal conditions for birch wood: converting 2.0 g wood by 15 mg Al(OTf)$_3$ and 100 mg Pd/C in 40 mL methanol in a 30 bar H$_2$ atmosphere and 180 °C. This resulted in a benchmark monomer yield of 47 wt%, while the biomass residue amounted 1057 mg. (Figure 2.4a). Typically, the product composition of these experiments is highly shifted towards etherified products PS-OCH$_3$ and PG-OCH$_3$, formed upon acid-catalyzed etherification of the γ-OH (Figure 2.4b).

In Figure 2.4a, monomer yield and biomass residue of the benchmark oak sawdust experiment are compared with formic acid experiments. Obviously, addition of formic acid could significantly enhance the aromatic monomer yield, compared to the acid-free scenario. When the formic acid concentration is 75 g/L, an maximum monomer yield of 28 wt% is obtained (10 bar N$_2$). Further increasing the formic acid concentration further did not result in a yield increase.

![Figure 2.4a](image1)

![Figure 2.4b](image2)

*Figure 2.4a) Effect of formic acid concentration and imposed nitrogen or hydrogen pressure on the aromatic monomer yield and the weight of the residual biomass after 2 hours of reaction. Benchmark experiments are based on Pd/C without any acid (no acid) and Pd/C with 0.38 g/L Al(OTf)$_3$. b) Typical product composition of experiments without acid co-catalyst (30 bar H$_2$), with Al(OTf)$_3$ as co-catalyst (30 bar H$_2$) and with formic acid as co-catalyst and hydrogen donor (10 bar N$_2$).*
Comparing the product compositions obtained for the no-acid and Al(OTf)$_3$ co-catalyst case to the product composition for the formic acid co-catalyzed reaction, a shift can be observed to the γ-H products PG-H and PS-H (Figure 2.4b). Based on Figure 2.3, this means that dehydration/hydrogenation or hydrodeoxygenation is preferred over etherification in this reaction mixture. In contrast to this observation, for Al(OTf)$_3$, etherification is the preferred pathway, while for the reaction mixture without acid both etherification and dehydration/hydrogenation or hydrodeoxygenation products are hardly found.

One explanation for the trends in monomer yield could be derived from the biomass residues. Delignification and alcoholysis of hemicellulose are reactions that disconnect respectively lignin and sugar fragments from the wood matrix, resulting in the decrease in residual biomass weight. Addition of the acid is expected to promote these reactions, but minor delignification enhancement is observed upon formic acid assistance. Only in the highest yield scenario of 75 g/L formic acid, the biomass residue is found to be lower than 1500 mg. For investigating the functioning of formic acid as delignification agent in more detail, two model compounds that resemble sugar-lignin interlinkages are selected and subjected to similar reaction conditions as the native wood (Section 2.2.2).

2.2.1.2 Influence of atmosphere and pressure

Another parameter limiting the yield of the formic acid co-catalyzed system is the hydrogen donation by formic acid. In a 30 bar H$_2$ atmosphere, the monomer yield is found to be 6% higher than in the best 10 bar N$_2$ experiment with the same concentration of formic acid (25 g/L). Besides its role as reacting agent in combination with Pd/C, hydrogen plays an important role in the stabilizing hydrogenation of reactive
intermediates. Thus, if the hydrogen supply is not sufficient, undesired side reactions, like aldol condensations, might take place, resulting in recondensation products that cannot be cleaved anymore.\textsuperscript{20} This hampers the monomer yield and it could account for some discrepancies in the mass balances, as the yield of aromatic dimers and oligomers that are formed by these reactions is not analyzed for the reaction mixtures obtained.

Based on the \textsuperscript{1}H-\textsuperscript{13}C HSQC NMR spectra, solvolysis by methanol in a hydrogen atmosphere results in unsaturated fragments, denoted by C in Figure 2.5a. When Pd/C is added, these fragments do not appear, implying that these species are converted by hydrogenation (Figure 2.5b). The species denoted by C are also not observed for the product mixture of the formic acid co-catalyzed reaction in nitrogen atmosphere (Figure 2.5c). Hence, hydrogen donation seems to sufficient for hydrogenation of the unsaturated intermediates and products in the 75 g/L experiment. Nevertheless, it can be concluded that hydrogenolysis of the β-O-4 bond does not reach full conversion. In Figure 2.5a-c, the uncleaved β-O-4 species A\textalpha and A\textbeta are present. Previously, though, it was found that the Lewis acid Yb(OTf)\textsubscript{3} and H\textsubscript{3}PO\textsubscript{4} could yield (nearly) complete cleavage of these bonds, resulting in aromatic monomer yields near the theoretical maximum.\textsuperscript{5,6}

The nitrogen pressure affects the results to a great extent. For all formic acid concentrations, a cold pressure of 10 bar is found to be providing the highest monomer yields. Of course, heating the reactor to 180 °C leads to profound increase of the pressure, because of methanol evaporation and expansion. Moreover, as formic acid decomposition results in formation of gas, the reaction pressure is an important parameter indicating the decomposition conversion of formic acid. Therefore, the pressure is recorded whenever a sample is taken: after heating (30 minutes), after one hour of reaction, after two hours of reaction and after autoclave cooldown. For the 10 bar cold pressure reaction, the maximum pressure increases from 26.5 bar for a concentration of 25 g/L increasing formic acid to 28.7 g/L for a 125 g/L concentration, indicating that more gas is formed. A second indication for gas formation is the small rise in pressure, when comparing the initial cold pressure with the final cold pressure, after autoclave cooldown.

When the cold nitrogen pressure is reduced to 1 bar, the maximum pressure during the reaction is still found to be close to 26 bar. Therefore, the amount of methanol present in the liquid phase is significantly lower than in the 10 bar experiments. Delignification via solvolysis of the lignin fragments from the wood matrix might be impeded, which is confirmed by the solid biomass residue. A pressure rise of the full reaction is observed for these reactions as well, again indicating that gas is produced during the reaction.

At the elevated pressure of 20 bar, a maximum pressure during the reaction approximately 35 bar. The 15 bar pressure rise is similar to pressure rise of the 10 bar experiments. However, in contrast to the lower pressure experiments, a reduction in pressure is detected upon comparison of the initial cold pressure to the final cold pressure. Hence, it is hypothesized that the higher nitrogen pressure restricts gas formation, which is also in line with the lower yields: if too little hydrogen is present for completely stabilizing the reactive intermediates in the 10 bar cold pressure case by hydrogenation, an even lower hydrogen supply could lead to further hydrogenation and hydrogenolysis limitations.

2.2.1.3 Influence of side-reactions

Even though the limiting factors discussed can explain some of the trends encountered, the reason why this strongly acidic medium shows the volcano-like curve with the drop in monomer yield at higher formic acid concentrations is not elucidated yet. The origin can probably be deduced from simple ester chemistry. By increasing the formic acid concentration, more acid is present at the start of the reaction,
which could co-catalyze reductive fractionation reactions and donate hydrogen. However, as methanol is
the solvent in this reaction system, biomass contains many hydroxyl groups and concentrations of formic
acid are relatively high, extensive formylation reactions can take place that consume formic acid. In fact,
for these acid-catalyzed esterifications, formic acid is also both catalyst and reactant. Therefore, the
conversion of formic acid becomes more favorable and faster at higher concentrations of itself. Figure
2.5c confirms formation of these formylated products, as a peak at 62.86/3.84 is observed which can be
assigned to acetylated species A'γ. Moreover, methyl formate peaks are observed by GC-MS/GC-FID.

Some previous work on the application of formic acid in lignin depolymerization reactions has been
dedicated to formylation reactions.12,13 It is found that a stable intermediate is formed by fast formylation
of the α- or γ-carbon. Subsequently, the formate group has to be eliminated for activating the compound
for cleavage of the β-O-4 bond by hydrolysis13 or hydrogenolysis12. Based on DFT calculations, the
elimination of the formate group required for cleavage of the β-O-4 bond has a high energy barrier of 38.8
kcal mol⁻¹, making this the rate-limiting step.12,21

The challenge of this high barrier deformylation was also faced in recent work of Oregui-Bengoechea et
al. and work of Rahimi et al., but their results did not really suffer from it. In the former case, the reactions
are performed at high temperatures (320 °C), making it more likely that the barrier is overcome.12 In the
latter case, though, formylation of the γ-carbon is elegantly turned into an advantage. In contrast to our
work, they made use of lignin of which the α-carbon hydroxyl group is oxidized, yielding an α-carbonyl
group. Moreover, sodium formate is added to reaction mixture in order to facilitate the removal of the γ-
formyl group.13 Based on DFT calculations, the oxidation reduces the energy barrier for elimination to
20.8 kcal mol⁻¹ and thus, directly increases the rate of the rate-limiting step.21 As high temperatures,
oxidized lignin and bases are not provided in our work, irreversible formylation seems a reasonable cause
for the disappointing aromatic monomer yields and the drop in yield while the co-catalyst concentration is
increased.

2.2.2 Catalytic cleavage of carbohydrate-lignin interlinkage models

Because delignification was found to be a major yield limiting step, delignification is assessed by a model
compound approach. One compound, glyceryl trioleate, is a model for the carbohydrate-lignin γ-ester
bonds, the other, phenyl β-D-glucopyranoside, represents the phenyl glycoside bond between
carbohydrate and lignin.

Figure 2.6 shows the observed yields for ester and ether bond cleavage after 90 minutes of reaction as a
function of the formic acid concentration. Without any acid present in the reaction mixture (formic acid
concentration is 0 g/L), the cleavage yield for both model compounds is lower than the cleavage yield with
formic acid. In case no formic acid is added as co-catalyst, methyl oleate is obtained, which is an
unsaturated methylated fatty acid. Only the saturated methylated fatty acid methyl stearate is found upon
adding formic acid to the reaction mixture, which indicates that formic acid definitely has hydrogen
donating characteristics in this reaction medium.

Remarkably, cleavage of the ester bonds of glyceryl trioleate by acid-catalyzed transesterification shows
a decreasing trend for the formic acid concentration. Formylation reactions, discussed in Section 2.2.1.3,
could be contributing to this observation. As the rate of formation increases with increasing concentration,
formic acid is converted more rapidly for higher concentrations, which might, in the end, result in a lower
availability of formic acid, while the initial concentration is higher.
This reasoning is not in line with the phenyl glycoside cleavage which shows an increasing trend. Cleavage of this ether bond is found to be promoted by acids, but occurs via hydrogenolysis as well. The hydrogen required for this reaction should be donated by the decomposition of formic acid. Although sufficient hydrogen seemed to be present for hydrogenation of the fatty acids, hydrogen donation is apparently too limited to lead to hydrogenolytic cleavage of the phenyl glycoside bonds. The increasing trend could be due to the increasing availability of hydrogen because of formic acid decomposition.

### 2.2.3 Catalytic process

Based on the biomass and model compound results obtained in this chapter, the proposed catalytic process of Figure 2.3 is updated, resulting in the process overview of Figure 2.7. In this figure, by-product formation is included. Furthermore, in essence, the process is similar to the Al(OTf)₃ co-catalyzed process. The first step, delignification by cleaving γ-ester bonds and phenyl xyloside ether bonds, is slower, though, and the final conversion of the γ-OH species PG-OH and PS-OH, is highly biased to γ-H products, while γ-OCH₃ monomers are hardly formed.
2.3 Conclusion

As Brønsted acid co-catalyst, formic acid can double the aromatic monomer yield, compared to the neutral scenario. Interestingly, no hydrogen has to be added, as formic acid serves as a hydrogen donor. The product composition is quite remarkable. Whereas mostly γ-OH aromatic monomers are found for the reaction without acid and etherification is preferred when Al(OTf)₃ is the co-catalyst, γ-H products typically constitute the largest fraction of aromatic monomers when the reaction is co-catalyzed by formic acid. This implies that dehydration/hydrogenation and hydrodeoxygenation are promoted by formic acid.

Despite the significant yield enhancement compared to the acid-free benchmark, it should be noted that the optimal acid concentration (g/L) is 200x higher than the Al(OTf)₃ concentration of the benchmark experiment. In this reaction, the autoclave contains more formic acid than biomass. Moreover, the complexity of the reductive fractionation system is increased. The reactions required, i.e. decomposition of formic acid to form hydrogen and acid-catalyzed delignification take place, but their rate and extent of reaction seem insufficient. The formation of hydrogen is not very high, as only slight pressure increases are observed during the reactions. Moreover, the observed delignification is low, as even high formic acid concentrations are not sufficient for cleaving the ester and phenyl glycoside bonds in models for the interlinkages between lignin and sugars.

The formation of formylated products is suggested to hamper the reaction, especially at high concentrations of formic acid. By formylation reactions, the acid co-catalyst and hydrogen donor formic acid is converted, while reactants and intermediates become less active. Therefore, formylation could be disadvantageous for this process via three ways.

Figure 2.7. Process overview of the catalytic fractionation process, co-catalyzed by formic acid. In blue and red, common carbohydrate-lignin interlinkages are indicated; by-products are denoted in green.
2.4 References

3 Comparing acid co-catalysts for the catalytic fractionation of oak sawdust

*This chapter is based on:* X. Huang, X. Ouyang, B.M.S. Hendriks, O.M.M. Gonzalez, J. Zhu, T.I. Korányi, M.D. Boot, E.J.M. Hensen, Selective Production of Mono-aromatics from Lignocellulose over Pd/C Catalyst: On the Influence of Acid Co-catalysts. *Faraday Discuss.*, 2017 (Accepted manuscript)

The propylphenolic biopolymer lignin has often been recognized as a high-potential resource for the production of renewable aromatics. Therefore, considerable efforts are made in lignin research in both academia and industry. At the same time, the commercial interest in second-generation biorefineries is increasing. In these biorefineries, the cellulose fraction of lignocellulosic biomass is converted into biobased chemicals and fuels. This obviously creates new opportunities for simultaneously implementing lignin conversion processes that would increase the profitability of the biorefinery. Unfortunately, despite the commitment to lignin research for many years, biorefineries hardly apply the lignin valorization technology that is developed. A commercially feasible valorization method is still lacking. Combustion of lignin for energy generation is a commonly used low-value alternative.

Although the valorization methods aiming for high-value fuels or chemicals are not yet commercially successful, lignin research continues. Previous research has demonstrated that pretreatment of the feedstock imposes the major challenges for lignin valorization. Fractionation of lignocellulose into its three main components is mostly focused on obtaining high-purity cellulose, coproducing lignin that has been severely degraded. Reactive ether bonds are broken and recondensed lignin with recalcitrant C-C crosslinks is formed, making selective upgrading of isolated lignin a challenging task.

For developing methods to efficiently crack the isolated lignin, application of mild pretreatment methods is a generally considered option in order to prevent lignin condensation. In addition to these processes still focusing on isolation of lignin, lignin-first approaches have emerged which directly process raw lignocellulose that contains native lignin. After solvolysis of lignin fragments by the alcohol solvent, a reduction catalyst (*e.g.*, Ni, Ru, Pd) stabilizes the reactive intermediates and assists in further breakdown via hydrogenolysis.

Due to the mild conditions of these reductive fractionation processes, extracting lignin fragments from the lignocellulose matrix (delignification) is slow. Acids have been identified as promising co-catalysts that facilitate delignification. However, the nature of the acid required is still not clear. Lewis acids, like Zn(OAc)$_2$ and Al(OTf)$_3$, function perfectly in low concentrations, enhancing both delignification and cleavage of β-O-4 linkages. Moreover, adding a weak Brønsted acid such as H$_3$PO$_4$ to the reaction mixture also promotes delignification. In contrast to these promising examples of acid-assisted reductive fractionation, the previous chapter suggests that acids should meet certain requirements to be suitable co-catalysts.

In order to identify these requirements and find cheap alternatives for Al(OTf)$_3$, the performance of a range of Brønsted acid co-catalysts is explored via both native oak wood experiments and model compound studies. By varying the concentration from approximately 0.80 mM to 25 mM, the acids HCl, H$_2$SO$_4$, H$_3$PO$_4$ and CH$_3$COOH are compared with the Al(OTf)$_3$ benchmark, based on their activity in...
cleaving the ester and ether interlinkages between carbohydrate and lignin and their capability of assisting in the cleavage of β-O-4 intralignin bonds. Moreover, the crystallinity and morphology of biomass residues are analyzed for reactions with optimal acid concentration.

### 3.1 Experimental

#### 3.1.1 Chemicals and materials

The detailed composition of the oak sawdust, obtained from houtzagerijmenten.nl, is analyzed by Celignis Limited Nexus Innovation Centre, University of Limerick, Ireland (www.celignis.com). For the results of this analysis, please consult Table 2.1.

Catalyst Pd/C (5 wt% Pd) and acids aluminum trifluoromethanesulfonate (aluminum triflate or Al(OTf)$_3$), CH$_3$COOH (≥99%) and H$_3$PO$_4$ (85 wt% in water) were purchased from Sigma-Aldrich. Furthermore, the acids HCl (37 wt% in water) and H$_2$SO$_4$ (95-97%, 99.99% trace metals basis) were purchased from Merck Emsure. Analytical grade methanol was purchased from VWR. The gasses hydrogen and nitrogen were both obtained from Linde Gas and have a purity of 5.0.

Model compounds glyceryl trioleate (>97.0%), phenyl β-D-glucopyranoside (>97.0%) were purchased from Sigma-Aldrich. Guaiacylglycerol-β-guaiacyl ether (≥97 %) was purchased from TCI.

All commercial chemicals were used without further purification. The sawdust is subjected to pretreatment steps to remove the extractives and to obtain a well-defined particle size (Details in Section 3.1.22.1.2).

#### 3.1.2 Feedstock pretreatment

Oak sawdust is dried overnight at 105 °C and sieved to obtain a feedstock for reaction with a particle size ranging from 125 µm to 300 µm. The reaction feedstock was then subjected to Soxhlet extraction by water and ethanol, both for approximately 6 hours. The extracted wood was collected and again dried overnight at 105 °C.

#### 3.1.3 Acid insoluble lignin (Klason lignin)

A pressure tube is filled with 300 mg of the wood sample and 3 mL of a 72 wt% H$_2$SO$_4$ solution. For one hour, the solution is heated to 30 °C by an oil bath and stirred every 10 minutes with a glass rod. Then, the solution is diluted by 84 mL water and heated for another hour, now at 121 °C.

After cooldown to room temperature, the mixture obtained is filtered over a glass fiber filter with a known weight. The solid residue is dried overnight at 105 °C and weighted. After calcination at 575 °C for 24h, only acid insoluble ash remains. This ash content is subtracted from the weight of the solid residue found before, resulting in the Klason lignin content.
3.1.4 Catalytic reactions

All wood reactions discussed in this chapter are batch experiments carried out in a 100 mL autoclave (Parr Instruments Company). For the benchmark, neutral experiment, the autoclave is filled with 2.0 g extracted oak, 100 mg Pd/C (5 wt% Pd) and 40 mL of methanol. Moreover, 30 µL n-dodecane is added as internal standard. After sealing the autoclave, it is purged four times with nitrogen and hydrogen and subsequently, a hydrogen pressure of 30 bar is applied, at room temperature. When no leak is observed, it takes approximately 30 minutes to heat the pressurized autoclave to 180 °C by an oven. The autoclave is continuously stirred at 500 rpm and after 2 hours of reaction (excluding heating time), the autoclave is cooled down to room temperature in an ice bath. In order to record the course of the reaction, samples are taken and analyzed by GC-MS/GC-FID (Section 2.1.5.1).

For the acid experiments, the conditions are very similar to the benchmark. The autoclave is filled with 2.0 g extracted oak, 100 mg Pd/C (5 wt% Pd), 40 mL of methanol, 30 µL n-dodecane and varying amounts of Al(OTf)₃, HCl, H₂SO₄, H₃PO₄ and CH₃COOH in a 30 bar hydrogen atmosphere. The acid concentration is optimized by applying an initial acid loading of 0.0316 mmol (1 equivalent, the optimum for Al(OTf)₃) and increasing this to 4, 16 and 32 equivalents. Samples are taken and analyzed by GC-MS/GC-FID to follow the time course of the reaction.

For the model compound experiments, 12 mL mini-autoclaves are used. The acid concentration of reaction media created is equal to the acid concentrations applied in the native wood experiments. The mini-autoclaves are charged with either 25 mg glyceryl trioleate or 25 mg phenyl β-D-glucopyranoside or guaiacylglycerol-β-guaiacyl ether, 10 mg Pd/C (5 wt% Pd), 5 mL methanol and 10 µL n-dodecane. After sealing the autoclave and purging it three times with nitrogen and hydrogen, the autoclave is pressurized with 30 bar hydrogen at room temperature. After that, heating is started and the reactions run for 2 hours at 160 °C. After the reaction, one liquid phase sample was quantitatively analyzed by GC-MS/GC-FID.

3.1.5 Work-up procedure

The work-up procedure described in Section 2.1.4 and Figure 2.2 is applied for obtaining the product fractions suitable for analysis.

3.1.6 Product analysis

3.1.6.1 GC-MS/GC-FID

A Shimadzu 2000 GC-MS is used for identification and quantitative analysis of the liquid phase products. More information on the apparatus and the procedure is found in Section 2.1.5.1.

In contrast to Chapter 2, the lignin monomer yield is not based on the total percentage of lignin present in the wood, but on the Klason lignin:

$$\text{Monomer yield} = \frac{m_{\text{monomers}}}{x_{\text{Klason lignin}} \times m_{\text{wood}}} \times 100\%$$
Furthermore, the total mass balance is calculated:

\[
\text{Mass balance} = \frac{m_{\text{residue}} + m_{\text{monomers}} + m_{\text{sugars}}}{m_{\text{wood}}} \times 100\%
\]

3.1.6.2 \( ^{1}\text{H}-^{13}\text{C} \) NMR analysis

NMR analysis of liquid phase products is performed by a 400 MHz Bruker spectrometer. More information on the preparation of samples and the apparatus is found in Section 2.1.5.2.

3.1.6.3 GPC

Samples for Gel Permeation Chromatography are prepared from the ethyl acetate phase, containing the methanol-soluble lignin products (Details in Section 2.1.4). Ethyl acetate is evaporated for part of the solution and the residual viscous, oil-like product is dissolved in tetrahydrofuran, in a concentration of approximately 2 mg/mL. The samples were filtered with 0.45 µm syringe membranes.

A Shimadzu apparatus equipped with two columns in series (Mixed-C and Mixed-D, polymer laboratories) and a 254 nm UV-Vis detector was used for the analysis of the samples. Calibration was performed on the column by polystyrene standards. The flow rate of the eluent THF was 1 mL/min.

3.1.6.4 XRD

X-Ray Diffraction is performed by a Bruker 2D Phaser. Using Cu Kα radiation, the detector angle 2θ is varied from 5° to 50° in 2227 steps and a slit of 0.6 mm.

Based on the diffraction pattern, the crystallinity index (CI) is determined by the peak height method on residues of the reactions with a high aromatic monomer yield and benchmarks (Figure 3.1):

\[
\text{CI} = \frac{I_{002} - I_{\text{AM}}}{I_{002}} \times 100\%
\]

\( I_{002} \) denotes the intensity of the crystalline peak corresponding to the 002 plane; \( I_{\text{AM}} \) is the intensity found at the minimum between the 002 peak and the 101/101i peak.

![Figure 3.1. The peak height method determines the crystallinity index (CI) by the ratio of the peak intensity of \( I_{002} \) and \( I_{\text{AM}} \).](image)

37 Acid-Assisted Catalytic Fractionation of Lignocellulosic Biomass / Version Final
3.1.6.5 SEM

A FEI Quanta 3D FEG microscope was employed for taking Scanning Electron Microscope (SEM) images for verifying the morphological stability of the high aromatic monomer yield results. The accelerating voltage was 1.50 kV and the background pressure in the microscope was maintained at around $5 \times 10^{-5}$ mbar. No additional coating of the surface was applied.

3.2 Results and discussion

3.2.1 Acid-assisted catalytic cleavage of model compounds

![Image of chemical structures](image)

**Figure 3.2a** Cleavage of phenyl β-D-glucopyranoside; **b** Cleavage of phenyl glyceryl trioleate. Conditions: 40 mL methanol, 100 mg Pd/C and different acid co-catalysts (2h, 160 °C, 30 bar $H_2$). 1 eqv. acid loading corresponds to a concentration of 0.79 mM. The colors of the products in the reaction equation correspond to the colors of the bars.

Common interlinkages between the carbohydrate and lignin fraction in woody biomass are phenyl glycoside and γ-ester bonds. As the extraction of lignin from the biomass matrix is a slow step in the catalytic fractionation process, an acid could be added to the reaction mixture in order to facilitate this delignification. Two model compounds representing the interlinkages, e.g. phenyl β-D-glucopyranoside and glyceryl trioleate, respectively, are applied for estimating the delignification potential of the acidic mixtures.

By varying acid concentrations, clear trends are observed for the cleavage of the two model compounds in a 12 mL mini-autoclave in 2h at 160 °C (Figure 3.2). When Pd/C is the only catalyst present in the reaction mixture, cleavage of phenyl β-D-glucopyranoside is limited to 28% (Figure 3.2a, No acid). The mechanisms for this cleavage are considered to be hydrogenation and hydrogenolysis, while the activity of methanol in this conversion is very low. Upon addition of the acid co-catalysts $Al(OTf)_3$, HCl, $H_2SO_4$
and H₃PO₄, the yield increases rapidly, to yields exceeding 70%, indicating the powerful catalytic action of these acids in cleavage of the phenyl glycoside bond.

Furthermore, from Figure 3.2a, it can be concluded that acids significantly alter the hydrogenation activity of the heterogeneous Pd/C catalyst. Whilst H₂SO₄ and H₃PO₄ stimulate ring hydrogenation, HCl hampers it. Different effects of acids are also observed for etherification of the products. Whereas H₃PO₄ and HCl are seemingly not active in etherification, H₂SO₄ is very active.

The cleavage yield of glyceryl trioleate by Pd/C is even lower than for phenyl β-D-glucopyranoside: 5% (Figure 3.2b, No acid). This transesterification reaction is acid-catalyzed, and therefore, a decent yield improvement is observed when acid is added. In this case, the increase is significantly lower for the weaker acid H₃PO₄ (pKₐ = 2.12)¹⁷. However, the trend is increasing, so this conversion might simply require higher concentrations of the acid.

In the discussion above, the trends for CH₃COOH are not included. For this carboxylic acid, two decreasing trends are observed, which is opposite to the trends found for the other acids. Although the pKₐ of this acid is much higher than that of the other acids,¹⁷ increased concentrations are still expected to result in increased cleavage. Side-reactions, like acetylation of reactants, products and methanol are hypothesized to play a limiting role, as these reactions cause the conversion of the catalyst. Formation of methyl acetate is confirmed by GC-MS.

Further cleavage of the lignin fragments released from the wood matrix by delignification occurs by depolymerization. The influence of different acid co-catalysts can also be revealed by model reactions, using guaiacylglycerol-β-guaiacyl ether. By this model compound, the cleavage of the β-O-4 linkage is exemplified, which is the most abundant linkage in hardwood (ca. 65%).¹⁸ At 160 °C and 30 bar H₂ pressure, Pd/C is a quite active catalyst for hydrogenolytic cleavage (Figure 3.3, No acid: 40% yield). Low

![Figure 3.3: Cleavage of lignin-lignin intralinkage model compound guaiacylglycerol-β-guaiacyl ether by Pd/C and different acid co-catalysts (2h, 160 °C, 30 bar H₂). 1 eqv. acid loading corresponds to a concentration of 0.79 mM.](image-url)
concentrations of acids enhance the reaction yield, as yields higher than 50% are observed for 1 equiv. Al(OTf)$_3$ and 4 equiv. of H$_2$SO$_4$, H$_3$PO$_4$ and CH$_3$COOH. As explained in the introduction, two reaction pathways can be followed to crack the β-O-4 upon addition of the acid: hydrogenolysis by Pd/C and acidolysis by the acid co-catalyst. Increasing the concentration of the Brønsted acids ultimately resulted in yields very close to the 40% yield of only hydrogenolysis (Figure 3.3, No acid), contradictorily suggesting that β-O-4 cleavage is hampered by a higher concentration of acid.

In accordance with the hydrogenation trends observed for phenyl β-D-glucopyranoside, acids can promote hydrogenation of the aromatic ring. For H$_2$SO$_4$, this hydrogenation promotion is the strongest, as almost no aromatic products are found. HCl, however, shows a decreasing ring hydrogenation trend which was also observed for phenyl β-D-glucopyranoside.

Interestingly, enhanced hydrogenation could play a role in the suggested hampered β-O-4 cleavage at high acid concentrations. Based on the theoretical work of Lu et al., hydrogenolysis starts by binding both aromatic rings on the solid catalyst. If rings get hydrogenated, the interaction with the Pd/C catalyst for hydrogenolysis is weaker. Moreover, enhanced hydrogenation could lead to stabilization of acidolysis intermediates. The rate of formation of these intermediates becomes faster as acid-catalyzed dehydration is enhanced. However, hydrogenation of the intermediates results in the formation of compounds that are resistant for complete acidolysis.

Based on Figure 3.2a and Figure 3.3, HCl does not seem to amplify but reduce hydrogenation. This is in line with this hypothesis, as an increasing guaiacylglycerol-β-guaiacyl cleavage yield is found for increasing concentrations.

Concluding, based on this model compound study, acids differ mostly in their delignification properties. Therefore, strong acids H$_2$SO$_4$ and HCl seem to be attractive alternatives for Al(OTf)$_3$. It is expected that the delignification by H$_2$PO$_4$ will be too limited for obtaining very high monomer yields, as H$_3$PO$_4$ is not very effective in cleaving the γ-ester. CH$_3$COOH could assist in cleavage of the β-O-4 bond, but delignification will probably very low, as neither phenyl glycoside bonds nor γ-ester bonds are broken to a reasonable extent in presence of this acid.

### 3.2.2 Acid-assisted catalytic fractionation of oak sawdust

Oak sawdust experiments are performed to confirm the applicability of the model compound findings in acid-assisted catalytic fractionation of real feedstocks. For these experiments, 2.0 g oak wood is mixed in a 100 mL autoclave with 100 mg Pd/C (5 wt%), 40 mL methanol and varying concentrations of the four Brønsted acids under investigation (e.g. H$_2$SO$_4$, HCl, H$_3$PO$_4$ and CH$_3$COOH) and the benchmark Lewis acid Al(OTf)$_3$. Reactions take place at 180 °C under 30 bar H$_2$ pressure, for 2 hours. Aromatic monomer yield, C5 sugar yield, total yield and delignification and amount of solid residue are the parameters that determine the performance of the applied conditions.

Table 3.1 summarizes the main results of these oak sawdust experiments. Without any catalyst or acid, solvolysis by methanol can result in a 6% monomer yield and a delignification of 35% (Entry 1, Table 3.1). Addition of the solid hydrogenolysis catalyst Pd/C already enhances this methanolysis by more than 20%, based on the delignification determined by Klason lignin content of the solid residue. Moreover, it induces a significant increase in monomer yield (Entry 2, Table 3.1). Relating this effect to the model compound study (Section 3.2.1), it is confirmed that application of this catalyst/solvent system leads to a decent cleavage of phenyl glycoside bonds (Figure 3.2a) and β-O-4 models (Figure 3.3). However, in contrast to these model compounds, the woody biomass reactant is solid. In this suspension of both oak and catalyst
particles, the methanolysis enhancement by Pd/C will probably be limited by the slow solid-solid mass transfer. Therefore, the impact on the solid biomass residue mass is not very strong.

If few lignin fragments are released from the wood matrix, a desirably high monomer yield can never be obtained. Hence, the main aim of addition of a homogeneous acid co-catalyst is to overcome the limitation imposed by slow methanolysis. As elucidated by the model compound experiments (Section 3.2.1), the acid concentration and acid type affect the delignification characteristics rather than the cleavage of intralignin β-O-4 bonds. Because Pd/C is found to be sufficiently active in cleaving β-O-4 bonds of methanol-soluble fragments in absence of the acid, a highly optimized tandem catalytic system can be obtained, in which the acid is the main delignification catalyst, while Pd/C targets the released fragments and cleaves these by hydrogenolysis. By tracking the effect of the acid concentration on the biomass residue, it can be concluded that the addition of acid co-catalysts significantly contributes to the delignification and also to release of sugars. Delignification, quantified by determining the Klason lignin content, is based on Klasson lignin content (22.4 wt%) of the pre-extracted oak sawdust.

Except for CH$_3$COOH, an increasing trend in lignin monomer yield and delignification is observed for increasing acid concentrations, ultimately resulting in promising yields. Based on the model compound study, strong Brønsted acids or the Lewis acid Al(OTf)$_3$ are preferred as delignification catalysts over weaker acids, evidenced by the high cleavage yields found for both phenyl glycoside bonds and γ-esters (Figure 3.2). In line with this conclusion, H$_2$SO$_4$, HCl and Al(OTf)$_3$ show the lowest biomass residue and the highest delignification based on Klasson lignin in the concentration range under investigation. These high delignification results directly result in the three optimal aromatic monomer yields revealed: 1 equiv. of

<table>
<thead>
<tr>
<th>n$^a$</th>
<th>Solid cat.</th>
<th>Acid co-catalyst</th>
<th>Type</th>
<th>Amount (mmol)</th>
<th>pH $^b$</th>
<th>Solid residue mass (mg)</th>
<th>Lignin monomers yield wt%</th>
<th>Methy l CS sugars (mg)</th>
<th>Total yield (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.6</td>
<td>1655 35</td>
<td>1 5 6 (26)</td>
<td>4 84</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Pd/C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.6</td>
<td>1619 57</td>
<td>4 14 19(81)</td>
<td>4 85</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Pd/C</td>
<td>HCl</td>
<td></td>
<td>0.0316 (1x)</td>
<td>3.0</td>
<td>1546 N/A</td>
<td>4 11 14(62)</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Pd/C</td>
<td>HCl</td>
<td></td>
<td>0.0316 (1x)</td>
<td>3.0</td>
<td>1546 N/A</td>
<td>4 11 14(62)</td>
<td>5 80</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Pd/C</td>
<td>HCl</td>
<td></td>
<td>0.126 (4x)</td>
<td>2.2</td>
<td>1422 N/A</td>
<td>5 15 18(78)</td>
<td>20 76</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Pd/C</td>
<td>HCl</td>
<td></td>
<td>0.506(16x)</td>
<td>1.7</td>
<td>1211 N/A</td>
<td>12 21 23(100)</td>
<td>133 72</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Pd/C</td>
<td>HCl</td>
<td></td>
<td>1.011(32x)</td>
<td>1.4</td>
<td>1148 75</td>
<td>21 41 44(194)</td>
<td>249 80</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Pd/C</td>
<td>H$_2$SO$_4$</td>
<td></td>
<td>0.0316 (1x)</td>
<td>2.9</td>
<td>1562 N/A</td>
<td>4 9 10(44)</td>
<td>5 81</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Pd/C</td>
<td>H$_2$SO$_4$</td>
<td></td>
<td>0.126 (4x)</td>
<td>2.2</td>
<td>1017 76</td>
<td>23 31 35(153)</td>
<td>257 71</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Pd/C</td>
<td>H$_2$SO$_4$</td>
<td></td>
<td>0.506(16x)</td>
<td>1.7</td>
<td>328 N/A</td>
<td>28 35 40(176)</td>
<td>46 28</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Pd/C</td>
<td>H$_3$PO$_4$</td>
<td></td>
<td>0.0316 (1x)</td>
<td>3.6</td>
<td>1761 N/A</td>
<td>1 6 13(55)</td>
<td>20 92</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Pd/C</td>
<td>H$_3$PO$_4$</td>
<td></td>
<td>0.126 (4x)</td>
<td>3.1</td>
<td>1600 N/A</td>
<td>3 9 13(55)</td>
<td>19 84</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Pd/C</td>
<td>H$_3$PO$_4$</td>
<td></td>
<td>0.506(16x)</td>
<td>2.8</td>
<td>1448 N/A</td>
<td>3 13 17(75)</td>
<td>30 78</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Pd/C</td>
<td>H$_3$PO$_4$</td>
<td></td>
<td>1.011(32x)</td>
<td>2.6</td>
<td>1358 69</td>
<td>5 14 26(116)</td>
<td>31 77</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Pd/C</td>
<td>CH$_3$COOH</td>
<td></td>
<td>0.0316 (1x)</td>
<td>5.0</td>
<td>1598 N/A</td>
<td>4 10 15(65)</td>
<td>5 88</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Pd/C</td>
<td>CH$_3$COOH</td>
<td></td>
<td>0.126 (4x)</td>
<td>4.1</td>
<td>1577 N/A</td>
<td>3 8 10(41)</td>
<td>8 81</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Pd/C</td>
<td>CH$_3$COOH</td>
<td></td>
<td>0.506(16x)</td>
<td>3.7</td>
<td>1639 N/A</td>
<td>1 5 8(35)</td>
<td>7 84</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Pd/C</td>
<td>CH$_3$COOH</td>
<td></td>
<td>1.011(32x)</td>
<td>3.5</td>
<td>1649 40</td>
<td>1 4 6(26)</td>
<td>3 84</td>
<td></td>
</tr>
</tbody>
</table>

Note: $^a$ pH values were measured by replacing 20 vol% of the acidic methanol solution with water and measured at room temperature using an electronic pH meter; $^b$ mass of the residue excluding Pd/C catalyst; $^c$ Delignification was determined by analyzing the Klasson lignin content of solid residue assuming the Pd/C is homogenously mixed with biomass residue; $^d$ heating time (30 min); $^e$ Lignin yield is based on Klasson lignin content (22.4 wt%) of the pre-extracted oak sawdust.
Al(OTf)$_3$, 32 eqv. of HCl and 4 eqv. of H$_2$SO$_4$ (Entries 3, 7 and 9, Table 3.1). Yet, at the lowest concentration of acid added (0.79 mM), much lower lignin monomer yields are obtained for the Brønsted acids under consideration than for Al(OTf)$_3$. For this Lewis acid, a very low concentration was found to be the optimum$^{16}$, yielding 46 wt% aromatic monomers (Entry 3, Table 3.1).

According to the guaiacylglycerol-β-guaiacyl ether experiments (Figure 3.3), low concentrations of both strong and weak acids could be strong promoters for the cleavage of the β-O-4 bond, the most prevalent intralignin linkage. As these low acid concentrations were found to be optimal as well for catalytic fractionation assisted by Al(OTf)$_3$ and H$_2$SO$_4$, these reactions may benefit from this characteristic. However, an opposite trend is observed for HCl (e.g. cleavage of the β-O-4 bond is facilitated by high acid concentrations). The optimal reaction for this acid is at relatively high concentration (32 eqv., Entry 7, Table 3.1). The β-O-4 cleavage yield is reasonably high at this concentration (Figure 3.3). $^1$H-$^{13}$C HSQC NMR analysis of these samples confirms the efficient conversion of β-O-4 bonds in by 1 eqv. of Al(OTf)$_3$, 32 eqv. of HCl and 4 eqv. of H$_2$SO$_4$, but also the decent cleavage of these linkages by Pd/C only (Figure 3.4a-e). Some low-intensity signals can still be found in the region covering the β-O-4 related shifts, though, which points at a conversion lower than 100%. For Al(OTf)$_3$ and H$_2$SO$_4$, the conversion of β-O-4 linkages seems to be slightly higher than for HCl.

Despite the decent performance of the weak acids (H$_3$PO$_4$ and CH$_3$COOH) in β-O-4 model compound cleavage, especially in low concentrations (Figure 3.3), this effect is hardly observed in the oak sawdust experiments. When these low concentrations are applied, insufficient delignification obstructs the reaction and the acids do not even get the chance to show their promoting effect on cleavage of the intralignin linkages. At the highest concentration of this series of experiments, the yield for H$_3$PO$_4$ increases up to 26 wt% and the delignification achieved is 69% (32 eqv., Entry 14, Table 3.1). Therefore, H$_3$PO$_4$ promotion is evident, but the yield deviates substantially from the 46 wt% yield of the Al(OTf)$_3$ benchmark. Considering the $^1$H-$^{13}$C HSQC NMR again, the presence of some β-O-4 intralignin linkages is more obvious in the reaction mixture obtained with H$_3$PO$_4$ as co-catalyst than with strong acids or Al(OTf)$_3$ as co-catalyst (Figure 3.4a-f).

The use of H$_3$PO$_4$ as co-catalyst has been reported earlier by Renders et al. for acid-assisted reductive fractionation of poplar wood.$^{12}$ A concentration of 2.5 g/L (= 27.8 eqv.) and 200 mg Pd/C were found to be yielding 40 mol% aromatic monomers. The difference in aromatic monomer yield between their work and our work could be caused by a few reasons. First of all, the reaction conditions are not exactly the same, as their reaction temperature is set to 200 °C and their catalyst loading is 200 mg in contrast to our 180 °C and 100 mg, respectively. Moreover, their calculation is based on mol% instead of wt%. Finally, the chosen feedstock could account for some differences. Nevertheless, both studies show that H$_3$PO$_4$ can promote the reductive fractionation process.

For CH$_3$COOH, the general trend observed is the opposite of the trend observed for other acids. Increasing the CH$_3$COOH concentration hampers the monomer yield, possibly because extensive acetylation takes place. This esterification reaction, closely related to the formylation reactions by formic acid elaborately discussed in Section 2.2.1.3, consumes the catalyst, as the catalyst could react with hydroxyl groups present in biomass and methanol.
Figure 3.4. $^1$H-$^{13}$C HSQC NMR spectra of liquid phase products of oak sawdust fractionation in methanol at 180 °C at 30 bar $H_2$ for 2h: a) without catalyst (methanol solvolysis); and catalyzed by b) by Pd/C; c) Pd/C and 1 eqv. Al(OTf)$_3$; d) Pd/C and 32 eqv. HCl; e) Pd/C and 4 eqv. $H_2$SO$_4$; f) Pd/C and $H_3$PO$_4$. The labels correspond to the added molecular structures.
An upper acid concentration limit is found as well. In Entry 10 (16 eqv. H\textsubscript{2}SO\textsubscript{4}), the biomass is almost completely broken down (solid residue is only 328 mg). This means that lignin and hemicellulose sugars are released from the wood matrix, but cellulose is converted as well. A complex methanol-soluble product mixture is obtained, containing a significant amount aromatic monomers (176 mg, 40%), but sugars are non-selectively degraded in the strong acidic environment into products like furfural, levulinic acid and small alcohols.

Mass balances, denoted in Table 3.1 by Total yield (wt%), are slightly lower than expected. Earlier work on birch wood mostly resulted in higher mass balances, but an important difference is the extent of extraction. The oak sawdust feedstock contains quite a significant amount of extractives (Table 2.1) and it takes a relatively high number of extraction cycles and thus long extraction times (ca. 48h) to remove these completely. Therefore, extractives can still be present in the product mixture and these are not taken into account for determining the total yield. For Entry 10, the low total yield is not very surprising as lots of unknown carbohydrate degradation products are formed.

In other cases, though, a total yield below 80% suggest formation of products that are not visible by GC-MS/GC-FID, like aromatic dimers and oligomers. For establishing qualitatively whether oligomers and dimers are formed during the reactions, the reaction mixtures of optimal cases are analyzed by GPC (1 eqv. Al(OTf)\textsubscript{3}, 32 eqv. of HCl and 4 eqv. of H\textsubscript{2}SO\textsubscript{4}), just like the reaction mixtures of 32 eqv. H\textsubscript{3}PO\textsubscript{4} and 32 eqv. CH\textsubscript{3}COOH. These are compared to the scenario in which no acid is added. As could be concluded from Figure 3.5a, the average molecular weights are significantly smaller than the average molecular weight (M\textsubscript{w}) found for the reaction mixture when no acid is added. The average M\textsubscript{w} is very similar for the Al(OTf)\textsubscript{3}, HCl, of H\textsubscript{2}SO\textsubscript{4} and H\textsubscript{3}PO\textsubscript{4} co-catalyzed systems. Yet, remarkably, the addition of 32 eqv. of CH\textsubscript{3}COOH results in the lowest M\textsubscript{w}, whereas the monomer yield is very low in this case (Table 3.1, Entry 18). From this result, it could be derived that the lignin fragments released from the wood matrix...
are efficiently cleaved, but that the first step, the extraction of the fragments, limits the reaction. Some differences can be observed from the shape of the curve, though. Especially in case 32 eqv. of HCl are co-catalyzing the reaction, a curve is obtained which substantially deviates from the others. While the dimer peak seems to be shifted to the left, the monomer peak is shifted to the right, resulting in overlap of these peaks. Moreover, no clear oligomer peak is observed.

Although the trends in monomer yield seem to follow the pH, as presented in Table 3.1, it should be noted that pH is a parameter for assessing the acidity of an aqueous mixture. Upon replacing 20 vol% of the of mixture with water, the pH is measured by an electronic pH meter. Based on this analysis, an acidity in methanol corresponding to a pH of 1.5 to 2.0 in a 1:5 water-methanol solvent system seems to be required for obtaining a high monomer yield for a Brønsted acid co-catalyzed reaction. However, acid decomposition is solvent dependent and therefore, these pH values cannot be translated directly into the acidity of the methanol solution. Moreover, this measurement is conducted at room temperature, while the reaction temperature is 180 °C, which might shift the dissociation equilibria.\(^{22}\)

### 3.2.3 Residue quality

As explained in the introduction, a biorefinery aims for production of valuable product streams from biomass.\(^{23}\) By catalytic reductive fractionation of lignocellulose, a mixture of relatively low molecular weight monoaromatics, aromatic dimers, aromatic oligomers and methylated hemicellulose sugars dissolved in methanol is obtained. However, the solid residue forms a second valuable product stream. As current biorefineries are highly focused on valorization of the cellulose fraction, the quality of this (partially) delignified pulp, intended to contain mostly cellulose, is highly important.\(^{12}\) This fraction should still be suitable for maximum valorization as paper, (platform) chemicals or biofuels.\(^{5}\) Because currently no mature method is known that could separate the solid Pd/C catalyst from the solid residue, the possibility to directly apply the process under investigation industrially is simply excluded. Pd/C is an undesired pollutant for further cellulose processing and moreover, catalyst recovery and recyclability are major conditions for economically feasible operation this process. As development of proper catalyst-residue separation methods is an essential step in making this process attractive for commercial application, some efforts in this field have been reported. Ferrini and Rinaldi reported a Raney Ni depolymerization catalyst that can be separated from the pulp by magnetic forces.\(^{8}\) Moreover, Van den Bosch et al. utilized their Ru/C hydrogenolysis catalyst as catalyst for reductive conversion of the pulp into a mixture of polyols.\(^{5}\)

As the different acids applied in this work might affect the quality of the residue to varying extents, the crystallinity and morphology of the residue are characterized in this early stage by XRD and SEM respectively. The samples selected for analysis are the solid residues of the reactions of Pd/C, combined with 1 eqv. Al(OTf)\(_3\), 4 eqv. of H\(_2\)SO\(_4\), 32 eqv. of HCl and 32 eqv. of H\(_3\)PO\(_4\). These are compared with four benchmark cases: non-extracted oak, extracted oak, oak after methanol solvolysis and oak after treatment with only Pd/C. Most residues still contain Pd/C, which is assumed to be homogeneously mixed with the wood residue.
The XRD pattern of wood is a sum of the different crystalline and amorphous phases present. The shape of the curve is very similar to the shape found for cellulose. Based on the XRD results displayed in Figure 3.6, the main diffraction peaks for this oak sawdust are found at 2θ of approximately 15°, 22°, 34° and 44°. Below these peaks corresponding to crystalline phases, a broad range band is indicating an amorphous phase. In the XRD results, a significant difference is observed for the different wood and residue samples for the relative intensity of the amorphous phase peak to the crystalline peaks. The ratio of the intensity of the 22° peak (002) and the minimum between the 15° (101/10ī) and 22° peak is the so-called peak height method, for determining the crystallinity index (CI).

CIs for the samples under consideration are calculated and provided by Figure 3.6. These CIs confirm the observation from the patterns and show an increasing trend for the crystallinity of the sample upon addition of methanol, catalyst and acids. Extraction and solvolysis of the raw wood with methanol increases the crystallinity index by 15%. Further acid-assisted fractionation can lead to a maximum of 82% (4 eqv. H₂SO₄), which indicates a relative enrichment in cellulose. The amorphous lignin and hemicellulose phases are converted, though, while the crystalline cellulose is mainly unaffected by the acid. As cellulose is not fully crystalline, a CI of 100% could not be reached by full delignification and release of hemicellulose sugars. It is known in literature though that the peak height method is not the most accurate method available for establishing crystallinity: crystallinity indices obtained are high compared to the values found by other techniques and the reported values vary widely. Furthermore, the baseline subtracted can significantly influence the index.

Although the 44° peak is also clearly affected by the addition of strong acids, its appearance is not discussed in detail. As this peak is not reported in literature, the structure causing this signal is not identified. In native wood, this peak is observed as well, indicating that it is not corresponding to the crystalline Pd of our catalyst.
As crystallinity is closely related to morphology, SEM images are taken from the wood and residue samples as well. In Figure 3.7, six of those within the magnification range of 500 to 700 times are collected. For all wood particles, the morphology is very similar. In general, closely packed fibers are observed, but some defects are also clearly visible, like holes and disorganized fibers. These defects do not depend on the reductive fractionation conditions applied, as the wood samples that are only extracted are far from perfectly aligned as well. Therefore, treatment of the wood by acids does not seem to alter the morphology of cellulose fibers.

### 3.2.4 Catalytic process

Figure 3.8 shows the conceptual reaction pathways that can be derived from the model compound and woody biomass experiments performed in this work. Acid co-catalysts facilitate the methanolyis of lignin fragments, simultaneously yielding methylated C5 sugars and a solid residue. The lignin fragments are cleaved further by hydrogenolysis by Pd/C. Moreover, acidolysis combined with hydrogenation could assist in this reaction step, resulting in the γ-OH products PG-OH and PS-OH. These are found to be the main products of Pd/C catalyzed reductive fractionation, in absence of an acid (Figure 3.5b). For high concentrations of the weak acid H$_3$PO$_4$, etherification is slightly enhanced, resulting in small amounts of PG-OCH$_3$ and PS-OCH$_3$. However, as strong acids show major etherification of the products by methanol, it is concluded that the etherification step requires addition of a strong acid. Finally, the formation of PG-H and PS-H can occur via both Pd/C catalyzed hydrodeoxygenation and acid-catalyzed dehydration pathways. Therefore, a higher preference for PG-H and PS-H is observed upon addition of acids, but this shift in product composition is less distinct.
3.3 Conclusion

The strong acids HCl and H$_2$SO$_4$ are cheaper yet suitable substitutes for the Lewis acidic Al(OTf)$_3$ acid co-catalyst for catalytic reductive fractionation processes. Both acids perform well as delignification agents and promising monomer yields of 35 wt% and higher could be obtained. For using H$_2$SO$_4$ as acid co-catalyst, probably some further optimization is required, as activity of this acid is very concentration dependent and it tends to break down the cellulose fraction as well. This degradation of cellulose is not observed by analysis of the solid residues. Actually, the concentration of 4 equivalents of H$_2$SO$_4$ resulted in a highly crystalline residue, based on XRD.

H$_3$PO$_4$ functions as a co-catalyst as well, but higher concentrations are required to yield a desired amount of aromatic monomers. This weaker acid is found to be facilitating delignification, but not as efficiently as strong acids.

Based on the previous chapter, addition of high concentrations of formic resulted in decent but not very high yields, even when no hydrogen was added. In this chapter, CH$_3$COOH was tested at much lower concentrations and no significant promoting effect of this weak acid was observed. Therefore, the application of attractive, bioderived carboxylic acids as acid co-catalysts has not yet lead to very promising yields, probably due to extensive formation of esters by reaction with hydroxyl groups in the feedstock and solvent.

3.4 References

4 Stability of the tandem catalytic system: Investigating the fate of Pd/C and Lewis acid co-catalysts

In the introduction, an analogy is made between petrol refineries and biorefineries, as both are applying integrated catalytic processes aiming for producing the most valuable streams of products from its feedstocks. Although several similarities can be observed easily, translating processes of the conventional refinery into biorefinery processes is not always straightforward, as oil and biomass show significantly different properties.

An example of these properties is the thermal stability. Whereas vapor-phase processing at high temperatures is common for oil-derived species in conventional petrol refineries, biorefinery processes converting lignocellulose are often performed in the liquid phase, as biomass feedstocks suffer from much lower thermal stability. Although recovery of heterogeneous catalysts from liquid reaction media is easy, the reuse of this recovered catalyst can be inefficient, because the stability of the catalyst might be affected disruptively by the solution. Regarding economic and environmental performance of processes, catalyst stability is a major property of the catalyst. Therefore, the industrial feasibility of biomass conversion is strongly influenced by the limits of liquid processing.

Poisoning or deactivation of palladium catalysts is a widely investigated yet often uncontrollable phenomenon, unfavorably suppressing the activity of the catalyst. In the catalytic reductive fractionation process under consideration, Pd/C efficiently depolymerizes lignin fragments into monomers, dimers and oligomers in a liquid acidic methanol environment. In liquid processing, especially leaching (e.g. dissolution of active catalyst sites) is a serious issue, not only inhibiting catalytic reactions, but also generating waste and toxically contaminating products. As the spent catalyst could not be separated from the solid residue, direct characterization of the spent catalyst is impossible. Therefore, the degradation of the catalyst over multiple reaction cycles could not be assessed.

Besides Pd/C, the catalytic system requires the presence of an acid co-catalyst and both Brønsted and Lewis acids are found to be suitable for this role (Chapter 3). However, when selecting a Lewis acid, the co-catalyst could demonstrate instability as well. In aqueous environment or even in presence of moisture, for example, Lewis acids can react immediately with water, leading to decomposition of the Lewis acid. Over the last few decades, though, quite some exceptions have been found, commonly by applying sulfonated ligands. Examples of water-tolerant Lewis acids are rare earth triflates, such as Yb(OTf)₃ and Sc(OTf)₃ and indium complexes.

In this chapter, the degradation of the solid catalyst and Lewis acid co-catalyst for catalytic fractionation is investigated. First, the compositional change of the heterogeneous catalyst in the different acidic environments is investigated. Hereto, Pd/C is treated by the acidic media that were found to be optimal for obtaining high aromatic monomer yields in the previous chapter (32 eqv. HCl, 4 eqv. H₂SO₄, 32 eqv. H₃PO₄ and 1 eqv. Al(OTf)₃) and the spent catalyst is characterized by ICP-AES, TEM and XPS. Then, three Lewis acids are selected. At the optimal concentration for facilitating reductive fractionation, it is determined whether these acids are still present in their Lewis acidic form by quenching potential Brønsted acidity with a steric base.
4.1 Experimental

4.1.1 Chemicals and materials

The detailed composition of the oak sawdust, obtained from houtzagerijmenten.nl, is analyzed by Celignis Limited Nexus Innovation Centre, University of Limerick, Ireland (www.celignis.com). For the results of this analysis, please consult Table 2.1.

Catalyst Pd/C (5 wt% Pd) and acids Al(OTf)$_3$ (aluminum trifluoromethanesulfonate or aluminum triflate), CH$_3$COOH ($\geq$99%), H$_3$PO$_4$ (85 wt% in water), AlCl$_3$ (anhydrous) and FeCl$_3$ hexahydrate were purchased from Sigma-Aldrich. Furthermore, the acids HCl (37 wt% in water) and H$_2$SO$_4$ (95-97%, 99.99% trace metals basis) were purchased from Merck Emsure. The steric base 2,6-di-tert-butyl-4-methylpyridine (98%) was obtained from Sigma-Aldrich. Analytical grade methanol was purchased from VWR. The gasses hydrogen and nitrogen were both obtained from Linde Gas and have a purity of 5.0.

All commercial chemicals were used without further purification. The sawdust, though, is subjected to pretreatment steps to remove the extractives and to obtain a well-defined particle size.(Details in Section 4.1.4)

4.1.2 Acid treatment of catalyst

Pd/C is treated in methanol in a 12 mL mini-autoclave without adding biomass. For a typical reaction, 100 mg Pd/C is added in 8 mL solution of an acid in methanol. The mini-autoclave is purged four times with nitrogen and hydrogen and then pressurized with 30 bar H$_2$. Subsequently, the mixture stirred at 180 °C for 2h30. The concentration of the acids is based on the optimal monomer yield experiments of Chapter 3, which means that one fifth is taken from the 40 mL solutions of 1 eqv. Al(OTf)$_3$ (0.00632 mmol), 4 eqv. H$_2$SO$_4$ (0.0253 mmol), 32 eqv. HCl (0.202 mmol) and 32 eqv. H$_3$PO$_4$ (0.202 mmol). Moreover, Pd/C is also treated for 2h30 in neutral methanol at 30 bar H$_2$ pressure and 180 °C.

After this treatment, the solid catalyst is separated from the methanol phase by centrifuging the mixture for 30 minutes at 5000 rpm. Subsequently, the liquid is decanted from the solid and the residue dried in air for 4 days.

4.1.3 Spent catalyst characterization

4.1.3.1 ICP-AES

Inductively Coupled Plasma – Atomic Emission Spectroscopy is used for determining the amount of palladium present in the spent catalyst particles after treatment with methanol, eventually with acid. For the digestion of Pd metal, 20 mL of an aqueous 3 M HNO$_3$ solution is mixed with 20 mg treated Pd/C and stirred for 1 hour at ca. 80 °C. Subsequently, the solution is transferred into a volumetric flask of 50 mL and diluted. After the carbon residue has sunk to the bottom of the flask, the solution is diluted 10 times; no solids are present in this diluted solution anymore and the solution is ready for analysis.
The Ametek SPECTRO Spectroblue apparatus with autosampler is calibrated by a standard dilution series consisting of 5 aqueous solutions of 50 mL with 2 mL 3 M HNO₃ and a Pd concentration of 0 mg/L, 1 mg/L, 2 mg/L, 3 mg/L and 4 mg/L. Based on this calibration line, the Pd concentration of the treated Pd/C solutions can be determined, which directly corresponds to the amount of Pd on the catalyst.

4.1.3.2 TEM
The average Pd particle size distributions were determined using transmission electron microscopy (TEM). The catalyst samples were suspended in excess ethanol and suspension aliquots were deposited on 300 mesh carbon film Cu grids (EMS) and dried overnight under ambient conditions. Images were taken using a FEI Tecnai 20 equipped with a Schottky field emission gun operated at 200 kV and captured with a CCD camera. Particle size distributions were extracted from TEM images using image processing software (ImageJ). At least 250 particles were measured of at least 4 images. Based on this information, a particle size distribution and an average particle size are determined.

4.1.3.3 XPS
Samples of the spent catalyst and the fresh catalyst were distributed over carbon film and analyzed by ThermoScientific K-Alpha XPS apparatus. This X-ray Photoelectron Spectrometer (XPS) was equipped with a monochromatic X-ray source (Al Kα = 1486.6 eV). The background pressure was 2 x 10⁻⁹.

Analysis of the data is performed using CasaXPS.

4.1.4 Feedstock pretreatment
Oak sawdust is dried overnight at 105 °C and sieved to obtain a feedstock for reaction with a particle size ranging from 125 µm to 300 µm. The reaction feedstock was then subjected to Soxhlet extraction by water and ethanol, both for approximately 24 hours. The extracted wood was collected and again dried overnight at 105 °C.

4.1.5 Catalytic reactions
All wood reactions discussed in this chapter are batch experiments carried out in a 100 mL autoclave (Parr Instruments Company). For the benchmarks, the H₂SO₄ and Al(OTf)₃ co-catalyzed reactions, the autoclave is filled with 2.0 g extracted oak, 100 mg Pd/C (5 wt% Pd), 40 mL of methanol and either 12.4 mg H₂SO₄ or 15 mg Al(OTf)₃. Moreover, 30 µL n-dodecane is added as internal standard. After sealing the autoclave, it is purged four times with nitrogen and hydrogen and subsequently, a hydrogen pressure of 30 bar is applied, at room temperature. When no leak is observed, it takes approximately 30 minutes to heat the pressurized autoclave to 180 °C by an oven. The autoclave is continuously stirred at 500 rpm and after 2 hours of reaction (excluding heating time), the autoclave is cooled down to room temperature in an ice bath. In order to record the course of the reaction, samples are taken and analyzed by GC-MS/GC-FID (Section 2.1.5.1).

For the further Lewis acid experiments, the conditions are very similar to the benchmark. The autoclave is filled with 2.0 g extracted oak, 100 mg Pd/C (5 wt% Pd), 40 mL of methanol, 30 µL n-dodecane and varying amounts of AlCl₃ (anhydrous) and FeCl₃.6H₂O in a 30 bar hydrogen atmosphere. The acid concentration is optimized by applying an initial acid loading of 0.0316 mmol (1 equivalent, the optimum
for Al(OTf)$_3$ and increasing this to 4, 16 and 32 equivalents. Samples are taken and analyzed by GC-MS/GC-FID to follow the time course of the reaction.

For the quenching experiments, an equimolar amount of 2,6-di-tert-butyl-4-methylpyridine is added to the optimal acid scenario. Again, samples are taken and analyzed by GC-MS/GC-FID to follow the time course of the reaction.

4.1.6 Work-up procedure

The work-up procedure described by Section 2.1.4 and Figure 2.2 is applied for obtaining the product fractions suitable for analysis.

4.1.7 Product analysis

4.1.7.1 GC-MS/GC-FID

A Shimadzu 2000 GC-MS is used for identification and quantitative analysis of the liquid phase products. More information on the apparatus and the procedure is found in Section 2.1.5.1.

4.2 Results and discussion

4.2.1 Stability of Pd/C

Because it is not possible yet to obtain catalyst and biomass residue isolated from each other after a reaction, the stability of Pd/C in the reaction media is not based on a woody biomass experiment. Instead, the heterogeneous catalyst is stirred in a mixture of methanol and acid in a hydrogen atmosphere for 2h30. In Chapter 3, 1 eqv. Al(OTf)$_3$, 4 eqv. H$_2$SO$_4$, 32 eqv. HCl and 32 H$_3$PO$_4$ are found to be optimal acid concentrations at 180 °C and 30 bar H$_2$. Therefore, these conditions are also selected for these acid treatments.

![Figure 4.1. Pd recovery upon different acid treatments, as determined by ICP-AES. 100% recovery corresponds to the Pd concentration found by ICP on the fresh catalyst. 1 eqv. is a concentration of 0.79 mM.](image-url)
Subsequently, to verify catalyst stability in the different environments, the composition of the catalyst treated by these acidic methanol media is compared to the fresh catalyst and catalyst treated in neutral methanol. The bulk concentration of Pd is determined by ICP-AES (Figure 4.1). Obviously, the recovery of the HCl-treated Pd/C is much lower than the recovery obtained for the other samples (78%). This indicates that treatment by 32 eqv. of HCl (25.3 mM) in methanol leads to significant leaching, rendering HCl a less attractive acid co-catalyst for reductive fractionation. For the other four treatments, the recovery is more than 90%. Thus, some leaching is always observed, even upon treatment with methanol only. Whether the Pd recovery will decrease further after every reaction is not determined.

Along with leaching of the active metal, the dispersion of metal particles over the support is also influenced by the treatment of (non-)acidic methanol solution. As elucidated by TEM images, the average Pd particle size of the fresh catalyst is 2.70 nm, with a relatively high standard deviation of 2.09 nm (Table 4.1). Pd particles tend to grow in the (acidic) liquid environment and the reducing atmosphere. This growth is not excessive for MeOH/No acid, Al(OTf)₃ and H₂SO₄, as average growths of respectively 1.2 nm, 0.7 nm and 1.0 nm are obtained. However, for the HCl treated catalyst a very remarkable particle size increase is found, as these particles seem to grow by a factor 10. Comparing the appearances of the catalysts on the images, major changes are observed for this catalyst.

Table 4.1. TEM images are made from the fresh catalyst and (acid-)treated catalyst samples. With these images, a particle size distribution (PSD) is determined and an average particle size is calculated, based on the diameter of 250-300 particles.
In order to identify a reasonable explanation for this tremendous modification of the hydrogenolysis catalyst in actually quite promising reaction conditions (e.g. monomer yield exceeds 40 wt% for the 32 eqv. HCl reaction), XPS and again ICP-AES are performed on the samples.

Whereas the first series of ICP-AES analyses confirmed leaching of Pd, corrosion of the stainless steel autoclave (grade 316) is not analyzed. Acidic reaction media are known to be corrosive, and especially for HCl and oxidizing acids such as HNO₃ and concentrated H₂SO₄, major corrosion effects could be observed. Iron and nickel, the two main metals of which the autoclave consists, could be oxidized in the reaction environment. When these metals are present in the solution, deposition on the catalyst surface
can take place. Therefore, the ICP spectra measured for determining Pd leaching are reanalyzed, taking into account the content of iron and nickel. A semi-quantitative approach is used for the analysis. The presence of iron on the catalyst treated by a 32 eqv. HCl mixture is unambiguously confirmed. Relating the weight of iron and nickel to the weight of all metals found in this sample, approximately 13 wt% is iron and 2 wt% is nickel, while 85 wt% is Pd. In the fresh Pd/C catalyst, the concentration of both metals is far below 1 wt%. Moreover, for all other acid treatments, the iron fraction is significantly lower, with a maximum of ca. 1.6 wt% for H₂SO₄.

With the XPS spectra of the spent catalyst samples, the surface composition of the catalysts is determined (Table 4.2). In the calculation of relative abundances of surface elements, oxygen is not included, as samples are dried in air and thus expected to be oxidized to a large extent. The most abundant surface element is of course carbon, as carbon is the support material. Therefore, carbon is also not included in Table 4.2.

Pd, the active metal of this catalyst, appears in the highest surface concentration in every sample. Upon hydrotreating the catalyst in methanol and eventually acid, sulfur is always found on the catalyst surface. This can be attributed to either a contamination of the autoclaves used or the catalyst preparation method. After treatment in stronger acidic conditions, more sulfur is found. In the case of H₂SO₄, the sulfur elements present in the acid co-catalyst can provide this, but in the case of HCl another source should be supplying this sulfur. Furthermore, the element that is added via the acid co-catalyst is observed in all cases. More specifically, the Pd/C catalyst that is stirred in Al(OTf)₃ has some aluminum at the surface and the Pd/C stirred in HCl contains some chloride.

The most streaking result is the presence of surface iron in the HCl-treated sample, indicating autoclave corrosion and deposition of the autoclave metals on the catalyst. The ratio of Pd to contaminants Fe, Cl and S is approximately 55:45, explaining the highly modified nature of this catalyst as found by TEM.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pd (at%)</th>
<th>Fe</th>
<th>Al</th>
<th>Cl</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>No acid/MeOH</td>
<td>93.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.6</td>
</tr>
<tr>
<td>1 eqv. Al(OTf)₃</td>
<td>77.9</td>
<td>-</td>
<td>13.6</td>
<td>-</td>
<td>8.5</td>
</tr>
<tr>
<td>4 eqv. H₂SO₄</td>
<td>89.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10.3</td>
</tr>
<tr>
<td>32 eqv. HCl</td>
<td>55.8</td>
<td>16.3</td>
<td>-</td>
<td>12.2</td>
<td>15.7</td>
</tr>
</tbody>
</table>

4.2.2 Lewis acid co-catalyzed reductive fractionation

A second acid-screening is performed for finding optimal concentrations of Lewis acid co-catalysts for the catalytic fractionation of oak sawdust. For this screening, AlCl₃ and FeCl₃ are selected; the benchmark acid is Al(OTf)₃, another Lewis acid. All reactions are performed in 40 mL methanol at 180 °C and 30 bar H₂. In these conditions, 2.0 g sawdust is fractionated by 100 mg Pd/C (5 wt%) and the acids under consideration in a concentrations varying from 0.79 mM to 12.6 mM (i.e. 1 eqv. to 16 eqv.), yielding a methanol soluble mixture of monoaromatics, aromatic dimers and oligomers and methylated sugars. Moreover, a solid residue is obtained, which is mainly composed of cellulose.
By this series of experiments, the cheaper Lewis acid alternatives for Al(OTf)$_3$, have shown potential (Figure 4.2). Monomer yields exceeding 40 wt% of aromatic monomers (relative to the total amount of lignin in 2.0 g sawdust) were obtained. For AlCl$_3$, the trend is increasing up to 48 wt% for a 16 eqv. concentration. In case FeCl$_3$ is used, the concentration increase from 4 to 16 eqv. does not result in a further increase in monomer yield. Comparing the trends for these Lewis acids with the trends for the Brønsted acids in Chapter 3, relatively low acid concentrations result in high yields. Moreover, the selectivity towards production of lignin products is high, as the solid residue is still rather large.

In Figure 4.3, typical monoaromatic product mixtures of reactions with optimal concentration are summarized (1 eqv. Al(OTf)$_3$, 16 eqv. AlCl$_3$ and 4 eqv. FeCl$_3$). Al(OTf)$_3$ produces the most etherified product mixture. A quite large fraction of etherified aromatic monomers PG-OCH$_3$ and PS-OCH$_3$ is also obtained for AlCl$_3$. FeCl$_3$ is a much less effective etherification catalyst, though. This can be attributed to the fact that the hexahydrate of this Lewis acid is used. The presence of water can shift the reaction back, towards more γ-OH products.

![Figure 4.2. Aromatic monomer yield after 2h of reaction of 2.0 g extracted oak in 40 mL methanol at 180 °C and 30 bar H$_2$. Different co-catalysts in varying concentrations are applied, in combination with 100 mg Pd/C (5 wt%).](image1)

![Figure 4.3. Typical product composition of experiments without acid co-catalyst and with 1 eqv. Al(OTf)$_3$, 16 eqv. AlCl$_3$ and 4 eqv. FeCl$_3$ as co-catalyst (2h, 180 °C, 30 bar H$_2$).](image2)
4.2.3 Lewis acid stability

The goal of this chapter is not solely the identification of interesting Lewis acid co-catalysts, but also assessing the stability of these acids in the reaction environment. In presence of moisture, some Lewis acids decompose via hydrolysis, which could lead to the formation of related Brønsted acids via the exchange of ligands. That means that not Al(OTf)$_3$ might be co-catalyzing the reactions, but TfOH (triflic acid); similarly, for AlCl$_3$ and FeCl$_3$, the real catalyst could be the induced Brønsted acid HCl instead of the Lewis acid.

In order to find the species that is responsible for the catalytic action, 2,6-di-tert-butyl-4-methylpyridine is added to the reaction mixture. Because of the steric hindrance at the basic site (the nitrogen atom), it is expected that the rather bulky Lewis acids cannot react with this base, while protons, released by a Brønsted acid, can. A study of Williams et al. found for example that Al(OTf)$_3$ acquires its catalytic activity from a reaction with water, inducing Brønsted acidity.

Based on the monomer yields summarized in Figure 4.4, the steric base itself is not a suitable co-catalyst in reductive fractionation reactions. The aromatic monomer yield obtained is only 15 wt%, which indicates that the base does not have a promoting effect. Upon addition of the base to an acid co-catalyzed reaction, the aromatic monomer yield of the H$_2$SO$_4$ co-catalyzed reaction decreases significantly, whereas for the Lewis catalyzed reactions only a relatively small decrease is observed. Therefore, it seems that the Lewis acids are quite stable under the applied conditions. However, the expected full quenching of the Brønsted acid is not observed. This means that base quenching is not as effective as initially anticipated.

![Figure 4.4](image.png)

*Figure 4.4. Aromatic monomer yield after 2h of reaction is determined for 2.0 g extracted oak in 40 mL methanol at 180 °C and 30 bar H$_2$. An optimal acid concentration is used, in combination with 100 mg Pd/C (5 wt%), both in presence and in absence of an equimolar amount of base, to quench the acid.*
4.3 Conclusion

In an environment of 32 eqv. HCl in methanol, major degradation of the Pd/C catalyst is observed after 2h30 (180 °C, 30 bar H₂). Significant leaching of the active metal and deposition of metals from the autoclave modify the catalyst disruptively. Methanol with or without other acids also slightly modified Pd/C, as particles tend to grow and minor amounts of Pd leach. In retrospect, the applicability of HCl as acid co-catalyst in combination with Pd/C is doubted, whilst it showed high potential in biomass fractionation experiments.

Besides strong Brønsted acids and Al(OTf)₃, two more Lewis acids are highlighted as acid co-catalysts. Without acids, the yield is only 14 wt%. Upon addition of both AlCl₃ and FeCl₃, an aromatic monomer yield of more than 40 wt% can be obtained. This significant enhancement is accompanied by a decreased weight of the solid residue, suggesting improved delignification. Remarkably, this decrease is lower than the decrease found for Al(OTf)₃ which indicates that the selectivity towards lignin cleavage is higher for these acids.

The stability of Lewis acids in the reaction conditions applied is also promising. Quenching the Lewis acid with a base affects the monomer yield only slightly. Therefore, these reactions seem to be catalyzed by a Lewis acid and not by a Lewis acid-induced Brønsted acid.

4.4 References

5 \( p \)-Toluenesulfonic acid co-catalyzed reductive fractionation of birch wood chips

Reactive fractionation of hardwood is enhanced by acidic conditions. As for the strong Brønsted acids HCl and H\(_2\)SO\(_4\) and Lewis acids Al(OTf)\(_3\), AlCl\(_3\) and FeCl\(_3\), high monomer yields could be obtained from the reductive fractionation oak sawdust, it seems that actually many acids are suitable acid co-catalysts and that the factor mostly influencing the suitability of the acid is the required concentration (Chapter 3 and 4). However, for optimizing the conditions of the process to make an advance to economically viable processing, several crucial parameters, other than monomer yield, are to be investigated, especially to find the drawbacks of acidic liquid processing. The stability of the catalyst is one of those parameters, which is already studied in the previous chapter.

Finding optimal processing conditions also includes an investigation of the corrosive properties of the interesting acid co-catalysts. In 2016, NACE International estimated the worldwide cost of corrosion to be \$2.5 trillion, which is equivalent to approximately 3.4% of the total global GDP (Gross Domestic Product). Almost 60% of these costs are related to industrial corrosion. Solutions of inorganic acids are known corrosive environments. Both the nature and the concentration of the acid influence these metal degrading processes. Particularly hydrochloric acid requires careful handling in terms of corrosion, which is in line with the results of Section 4.2.1 of Chapter 4 where it was revealed that HCl causes significant corrosion of the autoclave. Moreover, higher temperatures lead to a significant increase in the rate of corrosion in acidic media.

Nevertheless, based on the experimental conclusions of Chapter 3, the strong acids HCl, H\(_2\)SO\(_4\) are cheap yet effective substitutes for Al(OTf)\(_3\) in the reductive fractionation process. As corrosion of the reactor is highly undesired, \( p \)-toluenesulfonic acid is investigated as acid co-catalyst, as this strong acid (pK\(_a\) = -2.6) is expected to be active, but less corrosive.

Finally, the woody biomass feedstock that could be converted effectively by the acid under consideration should not be limited to sawdust of a particle size below 300 µm. Therefore, chips of a size between 0.5 mm and 5 mm are subjected to reductive fractionation. As the particle size difference between catalyst and substrate is enlarged by this feedstock modification, sieving is tested as simple catalyst recovery technique.

*The feedstock change was part of a planned scale-up showcase at DSM. Because of the temperature and pressure limitations of their reactor, reactions were performed in milder conditions (\( T = 160 \) °C, \( P_{MAX} < 20 \) bar).*

60 Acid-Assisted Catalytic Fractionation of Lignocellulosic Biomass / Version Final
5.1 Experimental

5.1.1 Chemicals and materials

The detailed composition of the oak sawdust, obtained from houtzagerijmenten.nl, is analyzed by Celignis Limited Nexus Innovation Centre, University of Limerick, Ireland (www.celignis.com). For the results of this analysis, please consult Table 2.1.

Birch chips are obtained from Staatsbosbeheer (www.staatsbosbeheer.nl). The exact composition of these chips is not determined experimentally, but based on the composition of birch sawdust used before in this research project, analyzed as well by Celignis (Table 5.1).

Catalyst Pd/C (5 wt% Pd) and acids Al(OTf)$_3$ (aluminum trifluoromethanesulfonate or aluminum triflate), $p$-toluenesulfonic acid monohydrate (PTSA or $p$-TsOH) were purchased from Sigma-Aldrich. Analytical grade methanol was purchased from VWR. The gases hydrogen and nitrogen were both obtained from Linde Gas and have a purity of 5.0.

All commercial chemicals were used without further purification. The oak sawdust, though, is subjected to pretreatment steps to remove the extractives and to obtain a well-defined particle size (Section 5.1.2). The birch chips are not extracted.

Table 5.1. Composition analysis of birch sawdust, performed by Celignis (wt%)

<table>
<thead>
<tr>
<th>Total sugars</th>
<th>Glucose</th>
<th>Xylose</th>
<th>Mannose</th>
<th>Arabinose</th>
<th>Galactose</th>
<th>Rhamnose</th>
<th>Klason lignin</th>
<th>Acid soluble lignin</th>
<th>Extractives</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>63.77</td>
<td>40.00</td>
<td>21.12</td>
<td>1.29</td>
<td>0.32</td>
<td>0.66</td>
<td>0.39</td>
<td>20.12</td>
<td>3.64</td>
<td>-</td>
<td>0.28</td>
</tr>
</tbody>
</table>

5.1.2 Feedstock pretreatment

Oak sawdust is dried overnight at 105 °C and sieved to obtain a feedstock for reaction with a particle size ranging from 125 µm to 300 µm. The reaction feedstock was then subjected to Soxhlet extraction by water and ethanol, both for approximately 24 hours. The extracted wood was collected and again dried overnight at 105 °C.

Birch chips are dried overnight at 105 °C and sieved to obtain a feedstock for reaction with a particle size ranging from 0.5 mm to 5.0 mm. The feedstock was not extracted.

5.1.3 Catalytic reactions

All wood reactions discussed in this chapter are batch experiments carried out in a 100 mL autoclave (Parr Instruments Company). For the benchmarks, the Al(OTf)$_3$ co-catalyzed experiment, the autoclave is either filled with 2.0 g extracted oak sawdust or with 2.0 g birch chips, 100 mg Pd/C (5 wt%), 40 mL of methanol and 15 mg Al(OTf)$_3$. Moreover, 30 µL $n$-dodecane is added as internal standard. After sealing the autoclave, it is purged four times with nitrogen and hydrogen and subsequently, a hydrogen pressure of 30 bar is applied, at room temperature. When no leak is observed, it takes approximately 30 minutes to heat the pressurized autoclave to 180 °C by an oven. The autoclave is continuously stirred at 500 rpm.
and after 2 hours of reaction (excluding heating time), the autoclave is cooled to room temperature in an ice bath. In order to record the course of the reaction, samples are taken and analyzed by GC-MS/GC-FID (Section 2.1.5.1).

For the p-TsOH experiments, the conditions are very similar to the benchmark. The autoclave is filled with 2.0 g extracted oak, 100 mg Pd/C (5 wt%), 40 mL of methanol, 30 µL n-dodecane and varying amounts of p-TsOH in a 30 bar hydrogen atmosphere. The acid concentration is optimized by applying an initial acid loading of 0.0316 mmol (1 equivalent, the optimum for Al(OTf)₃) and increasing this to 4 and 16 equivalents. Samples are taken and analyzed by GC-MS/GC-FID to follow the time course of the reaction.

For the birch chips experiments, hydrogen pressure and reaction temperature of the optimal Al(OTf)₃ co-catalyzed system are varied. The temperature is first reduced to 160 °C and then, the hydrogen pressure is reduced to 8 bar. Moreover, the reaction time is increased to 6 hours.

One recyclability test is performed. All solids smaller than 0.5 mm are collected from the reaction mixture, dried and subsequently, added to a new reaction, instead of the 100 mg Pd/C.

5.1.4 Work-up procedure

The work-up procedure described by Section 2.1.4 and Figure 2.2 is applied for obtaining the product fractions suitable for analysis from the p-TsOH co-catalyzed reactions.

For the catalyst recyclability test, the work-up procedure is changed, as first, filtration is used to obtain a mixture of products and small particles in methanol and a residue of the delignified wood particles (Figure 5.1). The mixture of products and small particles in methanol is then separated into liquids and solids by centrifugation. Methanol is decanted and the solids are dried in air.

![Figure 5.1. Work-up procedure employed for separating the reaction mixture in order to recover the catalyst.](image)

5.1.5 Product analysis

5.1.5.1 GC-MS/GC-FID

A Shimadzu 2000 GC-MS is used for identification and quantitative analysis of the liquid phase products. More information on the apparatus and the procedure is found in Section 2.1.5.1.
5.2 Results and discussion

5.2.1 \( p \)-TsOH co-catalyzed reductive fractionation of oak sawdust

The concentration of \( p \)-toluenesulfonic acid (\( p \)-TsOH) is varied, in order to find an optimal concentration of this acid as co-catalyst for reductive fractionation (Figure 5.2a). In 40 mL methanol, 2.0 g oak wood is mixed with 100 mg Pd/C (5 wt\%) and the acid. After 2h of reaction at 180 °C and 30 bar H\(_2\), the optimum is found to be 4 eqv. of this strong acid, which corresponds to a concentration of 3.2 mM. A promising yield of 44 wt.\% was found for this relatively low concentration, which confirms the suitability of strong acids as co-catalysts for reductive fractionation. A further increase in acid loading could result in a higher aromatic monomer yield, but at 16 eqv., serious cellulose degradation takes place. Before, a similar trend was obtained for H\(_2\)SO\(_4\) (Section 3.2.2).

The main aromatic monomers formed are the \( \gamma \)-OH monomers PS-OH and PG-OH (Figure 5.2b). Etherification products PG-OCH\(_3\) and PS-OCH\(_3\) are also observed. However, compared to the Al(OTf)\(_3\) co-catalyzed reaction, extent of etherification of the \( \gamma \)-OH is not very high for this acid.

---

**Figure 5.2a** Aromatic monomer yield for \( p \)-toluenesulfonic acid (\( p \)-TsOH), compared to the neutral and Al(OTf)\(_3\) co-catalyzed reductive fractionation of oak (2h, 180 °C, 30 bar H\(_2\)); **b** Product composition obtained by \( p \)-TsOH co-catalyzed reductive fractionation of 2.0 g oak sawdust.
5.2.2 Al(OTf)$_3$ co-catalyzed reductive fractionation of birch chips

Along with a feedstock change to birch wood, the particle size of the wood is also increased. First of all, the chips are fractionated in the optimal reaction conditions for oak wood (180 °C and 30 bar H$_2$). Before, these reactions were performed on birch sawdust as well, which resulted in promising yields. As the impregnation of the acidic methanol and the release of lignin fragments probably takes longer for birch chips, the reaction time is prolonged to 6 hours.

After 2 hours, the yield is still slightly lower than the yield for oak sawdust in the same conditions (Figure 5.3a). However, after 6 hours, an aromatic monomer yield as high as 58 wt% is obtained. Unfortunately, this very promising yield was not observed for the lower temperature and pressure reactions that were required for a reaction scale-up. Delignification was limited in these cases, as biomass residues of approximately 1500 mg were obtained. Apparently, the cleavage of carbohydrate-lignin interlinkages is highly temperature dependent.

Whereas a high preference for the γ-OCH$_3$ products PG-OCH$_3$ and PS-OCH$_3$ was found for Al(OTf)$_3$ co-catalyzed reductive fractionation of oak sawdust, the reductive fractionation of birch chips selectively produces γ-OH products PG-OH and PS-OH (Figure 5.3b). Of course, the feedstock modification from oak to birch might be contributing to this change in product composition. Another contributor might be the water content of the particles. For the larger particles, overnight drying could be insufficient for removal of all water. In presence of moisture, dehydration or hydrodeoxygenation might be opposed, saving the products in their initial γ-OH form.

Because large difference in catalyst particle size and wood particle size, mechanical separation of these two solids is attempted via sieving and centrifugation. The solid residue of the 160 °C/30 bar H$_2$ experiment was separated into two phases: one phase consisting of particles larger than 500 µm, mainly the residual wood chips, the other consisting of particles smaller than 500 µm, including mostly catalyst particles. This second phase was dried and added to the reaction mixture again, as solid catalyst (133 mg). Although a lower yield is obtained (28 wt% vs. 34 wt%, Figure 5.4a), further optimization of this system can be imagined. As some particles of this catalyst are expected to be caught in the wood pores,
not all Pd/C can be recovered. However, by tuning particle size of the catalyst, this wood-catalyst interaction might be disturbed.

The smaller amount or lower activity of Pd/C is partly reflected by the product composition shift (Figure 5.4b). More etherification products, formed by acid catalyzed reactions, are found, which indicates that the relative activity of the acid is higher than that of Pd/C. In contrast to this observation, the fraction of γ-H products is also increased. The formation of these products requires Pd/C, as hydrodeoxygenation and dehydration/hydrogenation are the proposed pathways for the formation of PG-H and PS-H.

5.3 Conclusion

The high aromatic monomer yield obtained upon addition of p-toluenesulfonic acid (p-TsOH) confirms the applicability of strong Brønsted acids as acid co-catalysts for reductive fractionation of woody biomass. A low concentration of 4 eqv. (3.16 mM) is sufficient for this acid; increasing the concentration might assist degradation of cellulose, though. Just like with sulfuric acid, a strong concentration dependency is found which demonstrates the necessity of careful screening for the optimal conditions.

The feedstock change from sawdust to particles shows high potential. Whilst the aromatic monomer yield is mainly unaffected, it opens the possibility of mechanically separating the solid catalyst from the cellulose-rich residue. A second run resulted in a yield decrease of almost 20%, but catalyst synthesis targeting this separation could facilitate the separation.

5.4 References

5  NACE, 2016, 240.
6 Conclusion and outlook

During reductive fractionation of hardwood, soluble lignin fragments are released from the wood matrix by solvolysis. Subsequently, these fragments are cleaved further by hydrogenolysis over a solid reduction catalyst (e.g. Pd, Ru, Ni). Acid co-catalysts can facilitate the slow solvolysis of lignin fragments from whole biomass, in order to enhance the delignification of the feedstock. Both (weak) Brønsted acids and Lewis acids have been proposed before, but the true nature of the acid required for this purpose has not been reported yet. In order to identify suitable acid co-catalysts for reductive fractionation by Pd/C, an extensive screening is carried out in this master thesis.

The screening of acid co-catalysts is started with a study on formic acid assisted fractionation of oak sawdust. Formic acid is a carboxylic acid that is co-produced in the levulinic acid scheme. It has the potential to serve as a hydrogen donor as well. Upon addition of 75 g/L formic acid, the aromatic monomer yield increased from 14 wt% for the neutral Pd/C catalyzed reaction (30 bar H₂) to 28 wt% for the acid assisted reaction (10 bar N₂). Therefore, it can be concluded that formic acid can promote reductive fractionation significantly, even in absence of hydrogen. For this reaction, delignification is limiting, which is confirmed by the low cleavage yield of a phenyl glycoside model compound. Moreover, products of formic acid converting formylation reactions are observed.

As the delignification by formic acid is limiting the total aromatic monomer yield, a model compound study is performed in order to find acids that show better delignification activity. HCl, H₂SO₄, H₃PO₄, CH₃COOH and Al(OTf)₃ are selected for this purpose. The strong Brønsted acids HCl and H₂SO₄ and Lewis acid Al(OTf)₃ show outstanding performances in cleavage of γ-ester and phenyl glycoside models. This is perfectly translated into high aromatic monomer yields in oak sawdust experiments. Yields of respectively 44 wt%, 35 wt% and 46 wt% are obtained, based on the Klason lignin content. Especially for H₂SO₄, a strong concentration dependency is observed, which indicates that optimizing the concentration could increase this yield even further. Interestingly, the wood morphology seems rather unaffected by the treatment with acids, while the residual wood crystallinity increases upon addition of strong acids.

Although HCl shows a high potential based on aromatic monomer yield, side effects render its application in reductive fractionation processes less attractive. For this acid co-catalyst, serious Pd leaching from the hydrogenolysis catalyst is observed. Moreover, the acidic conditions initiate corrosion of the autoclave. For all other acid co-catalysts, these effects are negligible, but attention should be paid to these factors.

To extent the scope of suitable acid co-catalysts, the screening is expanded towards the Lewis acids AlCl₃ and FeCl₃ and the strong Brønsted acid p-toluenesulfonic acid (p-TsOH). These also show high potential for application as acid co-catalysts, as aromatic monomer yields of 48 wt%, 43 wt% and 44% were obtained, respectively. Remarkably, the residue weight of the Lewis acid co-catalyzed reactions is higher than the residue weight of HCl, H₂SO₄, p-TsOH and Al(OTf)₃ co-catalyzed reactions, indicating a higher selectivity towards lignin breakdown.

Bearing in mind the harsh conditions required for depolymerization of recalcitrant isolated lignin, reductive fractionation of native hardwood sawdust by Pd/C and a strong Brønsted or Lewis acid is an attractive alternative for valorizing lignin. In mild conditions, native intralignin ether linkages are easily cleaved, cracking lignin selectively into aromatic monomers. Furthermore, sugars are produced from hemicellulose, while the cellulose fraction remains mainly untouched. This so-called lignin-first route could
be a major step towards economically viable biorefineries, yielding maximum value via multiple product streams.

In this respect, a major challenge is the separation of the solid catalyst from the solid cellulose-rich residue. For economic and sustainability reasons, wasting the hydrogenolysis catalyst after one use is highly undesired. One solution for this challenge is the application of wood chips instead of sawdust. High monomer yields can still be obtained. Moreover, because of the particle size difference between catalyst and wood chips, mechanical separation by filtration and centrifugation can separate the catalyst from the residue. However, for full recovery of the catalyst, the particle size of the catalyst and the wood chips should be optimized further, taking into account the pore size of the wood, in order to reduce the interaction between the two.

Other separation options include the upgrading of the cellulose fraction in the presence of the hydrogenolysis catalyst and the reactor with a microporous cage filled with catalyst. Furthermore, a return to a two-stage process could be interesting, in which first lignin fragments are generated by acid catalyzed delignification, in absence of Pd/C. Subsequently, these are cleaved in a second hydrogenolysis step in the presence of Pd/C. Early results reveal that the aromatic monomer yield is much lower than for a one-step approach. Probably recondensation reactions take place in the first step that hamper the yield of the second step, because instable intermediates are not hydrogenation in the first step. Protecting reactive species can a be method to overcome this challenge, but an engineering approach using kinetic studies and new reactor designs could also be interesting.

Furthermore, investigating mechanisms with model compounds will remain an important part of lignin research. Ring hydrogenation which is not observed in reductive fractionation of real biomass, is an example of a phenomenon that is not fully understood yet. Model compounds sometimes get hydrogenated prior to cleavage of the bond representing the lignin structure. Therefore, using these model compound reactions for deriving a mechanism might lead to incorrect or incomplete assumptions. Performing model compound reactions in presence of sugars, a more complex yet more realistic environment, is already found to influence ring hydrogenation. Extending this study could reveal some new, interesting insights on the catalytic mechanism.
7 Acknowledgments

This master thesis is the result of almost 9 months of research in the Inorganic Materials Chemistry group. Of course this work summarizes and discusses all results obtained, but actually, they don’t say anything about what effort was made by whom for acquiring, analyzing and interpreting all data.

First of all, prof. Emiel Hensen, I really appreciate it that you offered me the master project in this great field of research. Your critical view and motivating comments on the results really helped me to make progress. Your questions and remarks were very valuable for obtaining a fundamental catalytic understanding of the processes under investigation. Moreover, you offered me the opportunity to attend two very interesting scientific meetings, the CatchBio symposium and the NCCC. At the latter one, I even presented a poster, which was a very good experience for me.

Dr. Xiaoming, a very special thank you to you, for being my daily supervisor. Especially in the first few months, the results were somewhat disappointing. At well-timed moments, you encouraged me to continue and created new, fresh spirit for solving the issues we faced: I think this is one of the most important characteristics of a master thesis supervisor. Besides these master thesis related notes, I should not forget to thank you again for the wonderful dinner we shared at your place for celebrating the Chinese New Year. Kaituo, you are a great cook! I wish you two (and very soon three©) all the best and, herewith, I invite you to share a Dutch dinner in the future as well, at my place.

Of course, I would also like to thank the other committee members: dr. Evgeny Pidko, dr. Fernanda Neira d’Angelo and dr. Michael Boot. Thank you very much for reading and assessing my work and attending my presentation.

I am very happy to say that I really liked my master project. Of course the topic is a major contributor to this, but I think the working atmosphere and friendship are even more important. Therefore, your contribution was indispensable, Xianhong. Our extensive lab discussions on scientific, political, socio-cultural, personal and especially culinary topics were great. I hope we can have a legs day in the sports center again and that you will be my guide whenever I will visit China! And now, I almost forgot to mention your most important scientific contribution to my thesis: thanks for your model compound data and allowing me to use these in Chapter 3.

The lignin group, then! Panos, my office mate, thanks for the ride to Noordwijkerhout to NCCC and introducing me into the fabulous lignin odor. Danil, thanks for helping me with repairing the GC and for the nice lab talks. Tim, thanks for your British humor. I heard TU/e offered you a PhD position in the fabulous field of pyrolysis, so perhaps we’ll meet again!

A special note also for you, Emma. Hallo!? What would this research group without your positivism! I really enjoyed the coffee discussions and the candies and talks. Moreover, thanks for all your secretary-related help, like inviting the committee, arranging meetings, planning the group seminars, inviting us for lectures and conferences etc.

Johan, Tiny, Adelheid and Brahim, thanks for your technical support. Your expertise about safety, Swagelok connections, analysis techniques, gas leaks and all those other things I forget now was very valuable.
This brings me to the rest of the group. Andrey (SEM), Jan, Arno, Tobias, Jiadong (TEM) and Longfei (XPS), thank you for doing measurements for me and help me analyzing the results. Anyone I did not mention yet should know: I did not forget you!

Bakker! Vrijdag 17u? This message or something similar I sent to you every week, PC. Thank you for being my “taxi driver” from Eindhoven to Hulst every Friday. I always enjoyed the scientific discussions we had on our ride to our beloved Zeeuws-Vlaanderen and of course also the gossip 😊 Moreover, I really appreciate the effort you made as reviewer of my work.

M’n laatste stukje ga ik toch maar in het Nederlands schrijven. Dankzij jouw steun, lieve Anne, ben ik de afgelopen vijf jaar vrijwel altijd een heel gemotiveerde student geweest. Ondanks dat het niet echt paste bij jouw interesses, toonde je altijd belangstelling voor mijn dagelijkse bezigheden. Soms kwam je tijdelijk op de tweede plaats, na mijn studie, maar daarvoor heb je altijd geweldig begrip gehad. Het is voor ons allebei nog afwachten waar we terecht zullen komen, maar zolang we maar vaak genoeg samen kunnen zijn, denk ik dat we ons overal thuis kunnen voelen.


Bart Hendriks
1 May 2017