Catalytic valorization of lignocellulose

Direct and sidestream upgrading approaches

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Academic dissertation for the Degree of Doctor of Philosophy in Organic Chemistry at Stockholm University to be publicly defended on Friday 10 September 2021 at 15.00 in Magnélisalen, Kemiska övningslaboratoriet, Svante Arrhenius väg 16 B.

Abstract
This work aims to explore different approaches for the valorization of lignocellulosic biomass. In this regard, two different strategies are presented: the catalytic upgrading of lignocellulose derivatives from industrial streams, such as pyrolytic oil and kraft lignin, and the direct catalytic fractionation of woody biomass. The first approach is explored in Paper I and II, while the second in Paper III and IV.

Different phenolic compounds were hydro-dearomatized using a heterogeneous catalytic system based on Pd/C and polymethylhydrosiloxane/H_2O as a liquid hydrogen source. High yields of either cyclohexanones or cyclohexanols were achieved in high selectivity by varying the concentration of water. To prove the broad applicability of the method, commercially available bio-oils such as beechwood tar creosote and cardanol oil underwent hydrodearomatization using the developed catalytic systems (Paper I).

Kraft lignin, a byproduct of the paper manufacturing industry, has been valorized by steering its solubility properties through the production of a lipophilic lignin oil suitable for hydrotreatment. The enhanced solubility allowed its blending in common refinery carriers and full hydrodeoxygenation yielding hydrocarbons in the gasoline-diesel range. A particular focus was set on the mechanistic study of the esterification where a ^{13}C labeling analysis was performed (Paper II).

Untreated birch wood was fractionated into its components while lignin was consequently depolymerized into monophenolic compounds. Cobalt was scrutinized to replace noble metals in reductive catalytic fractionation by synthetizing a heterogeneous catalyst supported on nitrogen-doped carbon. We found that adjusting the pH of the reaction medium affected the yields of the reaction. Under optimized conditions, monophenolic compounds could be obtained in up to 34 wt% yield relative to initial lignin. The role of the catalyst and reductants was investigated (Paper III).

The last chapter describes a pulping system able to parallelly perform the glucan purification and the catalytic upgrade of the lignin by-products while avoiding the contamination of the pulp with the heterogeneous catalyst. The system is based on a high-pressure Soxhlet combined with the ethanol-water organosolv, where Pd/C was selected as the heterogeneous catalyst. Using only CO_2 as the acid source, lyocell grade dissolving pulp was produced in addition to lignin oil (Paper IV).

Keywords: *Lignin, biomass, catalytic fractionation, dearomatization, heterogeneous catalysis.*

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Keep breathing.
That's the key.
Breathe!
Gimli, son of Glóin

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Populärvetenskaplig sammanfattning

I denna avhandling har jag undersökt två tillvägagångssätt för att använda förnybara resurser som ersättningsråvara för fossil olja. Den höga efterfrågan på förnybara resurser gör lignocellulosamassa till den optimala kandidaten med tanke på dess stora tillgänglighet. Att producera bränsle och material från växter skulle leda till en koldioxidneutral situation där koldioxiden som alstras vid förbränning av dessa produkter motsvarar samma mängd koldioxid som binds från atmosfären av en annan växande växt. För att göra detta måste biomassan separeras i dess komponenter: cellulosa (används redan för papperstillverkning), hemicellulosa och lignin.

I den första delen av min avhandling redogör jag för hur sidoströmmar av biomassabehandling ytterligare kan omvandlas till värdefulla produkter. Den andra delen av avhandlingen handlar om direkt utnyttjande av trä för att producera mervärdesprodukter, såsom massa av upplösningskvalitet för textilproduktion och fenolföreningar som kan användas i polymersyntes.

List of publications

This thesis is based on the following publications, referred to in the text by their roman numerals I-IV. The author's contribution to each publication is described in Appendix A. Reprints of the articles were made with permission from the publishers, as reported in Appendix B:

I. **Ductile Pd-Catalysed Hydrodearomatization of Phenol-Containing Bio-Oils into Either Ketones or Alcohols using PMHS and H_2O as Hydrogen Source**
D. Di Francesco, E. Subbotina, S. Rautiainen, J. S. M. Samec
Adv. Synth. Catal. **2018**, 360, 3924.
https://doi.org/10.1002/adsc.201800614

II. **De-bottlenecking a pulp mill by producing biofuels from black liquor in 3 steps**
D. Di Francesco, C. Dahlstrand, J. Löfstedt, A. Orebom, J. Verendel, C. Carrick, Å. Håkansson, S. Eriksson, H. Rådberg, H. Wallmo, M. Wimby, F. Huber, C. Federsel, M. Backmark and J. S. M. Samec
ChemSusChem **2021**, 14, 2414.
https://doi.org/10.1002/cssc.202100496

III. **Lignin Valorization by Cobalt-Catalyzed Fractionation of Lignocellulose to Yield Monophenolic Compounds**
S. Rautiainen,† D. Di Francesco,† S. N. Katea, G. Westin, D. N. Tungasmita, J. S. M. Samec
ChemSusChem **2019**, 12, 404
† Authors contributed equally
https://doi.org/10.1002/cssc.201802497

IV.   **OrganoSoxhlet: a circular fractionation to produce pulp for textiles**

D. Di Francesco, K. Reddy Baddigam, S. Muangmeesri and J. S. M. Samec
Manuscript

Related publications by the author, not included in this thesis:

Sustainable sources need reliable standards

M. V. Galkin, D. Di Francesco, U. Edlund and J. S. M. Samec.
Faraday Discuss. **2017**, 202, 281–301.
https://doi.org/10.1039/C7FD00046D

Thermal and mechanical properties of esterified lignin in various polymer blends

A. Orebom, D. Di Francesco, P. Shakari, J. S. M. Samec and C. Pierrou.
Molecules **2021**, 26, 3619.
https://doi.org/10.3390/molecules26113219

Previous documents based on this work

This thesis is based partly upon the author's half-time report (presented on January 19, 2020). The literature review has been updated (in Chapters 1, 2, and 4). Of the papers included in this thesis, only Paper I and III were part of the half-time. By chapters, the contribution from the half-time report thesis is as follows:

Chapter 1: This chapter was included in the half-time report; for this thesis, it has been reviewed and updated, and around 20% of the text and references are new.

Chapter 2: This chapter was included in the half-time report; for this thesis, it has been reviewed and updated.

Chapter 3: This Chapter is new.

Chapter 4: This chapter was included in the half-time report; for this thesis, it has been reviewed and updated.

Chapter 5: This Chapter is new.

Contents

Abbreviations

barg	bar gauge
BL	Black liquor
CC	Collecting cup
Co-phen/C	Cobalt supported on nitrogen-doped carbon
CUB	Catalytic upstream biorefining
EC	Extracting cup
ECCL	Early-stage catalytic conversion of lignin
EDG	Electron donating group
EWG	Electron withdrawing group
HDA	Hydrodearomatization
HDO	Hydrodeoxygenation
ICP	Inductively coupled plasma
KL	Kraft lignin
LCC	Lignin-carbohydrate complex
Mt/y	Million tons per year
Pd/C	Palladium on activated charcoal
PMHS	Polymethylhydrosiloxane
RCF	Reductive catalytic fractionation
SRF	Short rotation forestry
XPS	X-ray photoelectron spectroscopy

1 Introduction

For thousands of years, humankind has been exploiting woody biomass as construction material and energy. The first industrial revolution made coal the main fossil source of energy and chemicals until the second half of the 19th century when fossil oil and natural gas appeared as a better alternative in terms of heating value and processability (Figure 1.1).[1] Nowadays, fossil oil is the most exploited feedstock for the production of liquid fuels and chemicals.[2] Indeed, a broad spectrum of products is manufactured using distillation fractions of fossil oil as substrate, *e.g.* plastics, textiles, and bulk chemicals. However, most of it is burnt to produce heat, electricity, and as fuel generating one of the largest contributions to the anthropogenic CO_2 in the atmosphere. In respect to fossil-derived plastics, several environmental issues concerning their disposal have become an object of public interest, such as pollution by micro-plastic and plasticizers, landfill accumulation, and marine life endangerment. Therefore, the waste-to-energy approach (WtE)[3] has been proposed as a feasible option to eliminate plastic waste. Even though fossil-derived material accounts only as a small fraction of the oil-derived products, this method is beneficial to the environment and able to lower the overall CO_2 flux only if they come from renewable sources.[4]
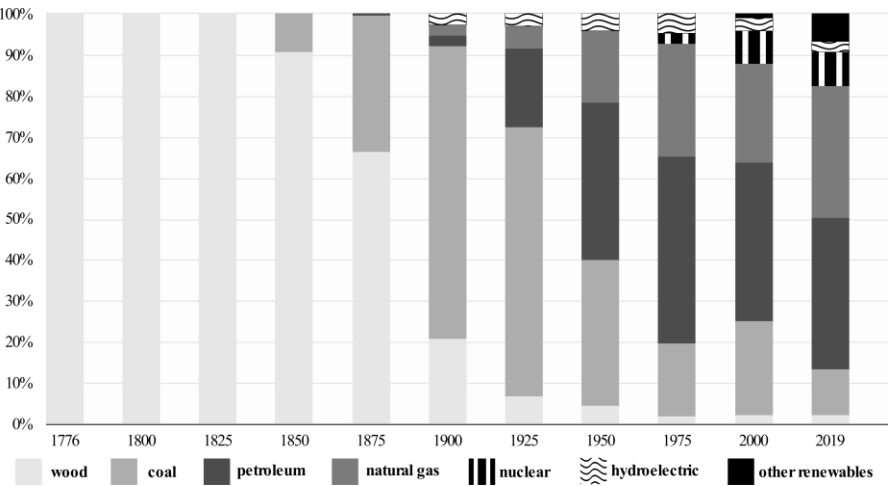

Figure 1.1. Shares of total energy consumption by major sources in selected years (1776-2019).[1]

On the other hand, the technology of electric energy production has improved during the last century and new renewable sources of energy can now be exploited such as wind, hydropower, geothermal heat, and of course the sun. Renewable energy production has constantly increased during the past few years, but the majority of the energy is still produced from non-renewable sources. For instance, in the US only 11% of the energy came from renewable sources in 2019.[5] Despite that, an oil-free world is not yet economically competitive and the full electrification of transportation will require decades before its completion.[6,7] Recently, the above-mentioned environmental concerns, the political instability of the extraction regions, and the oil price fluctuations have renewed the interest in biomass, and wood in particular. This time, it is not considered only as a source of fibers and construction materials, but also as a valid alternative carbon source helpful in the replacement of chemicals derived from petrochemistry and liquid fuels distilled from fossil oil.

Chemical industries will most likely need to follow the sustainability directives mentioned above in a not too distant future. Therefore, striving towards independence from crude oil will become a common target for most manufacturing companies. For this reason, many research groups have focused their efforts on the investigation of materials and precursors derived from sustainable sources as well as biofuels.[8] These thoughts were summarized in the Biorefinery Concept: old crude oil refineries converted into or substituted by a new generation of environmentally friendly bio-refineries.[9]

1.1 Biomass

The term biomass is used to describe any organic source of energy that is produced or derived from renewable sources such as living organisms.[10] Below the biomass umbrella can be found: agricultural by-products, biogenic solid waste, bio-ethanol, vegetal oils, manure, landfill gas, wood, and wood processing wastes. A promising carbon bio-source is plant biomass, *i.e.* herbaceous and woody biomasses (lignocellulose). Nowadays, the largest industrial fields based on plants are forestry and crop agriculture. Lignocellulosic biomass(es), like by-products derived from forestry and crops, have the potential and the production magnitude to be alternative feedstocks to petroleum. However, if these sources are considered renewable, still, not all of them are sustainable. For instance, the production of first-generation bioethanol, derived from the fermentation of edible plants, comes with several environmental and social issues. Deforestation and competition with food crops are the main ones.[11] A competitive bio-diesel has been found in vegetal oils, where palm oil is leading the market.[12,13] In March 2019, the EU commission has declared palm oil not fulfilling the sustainability criteria and

therefore not to be used for bio-fuels within European countries from 2030.[14] Deforestation was the main reason behind the ban. Even the production of vegetal fibers has drawbacks. As an example, cotton fibers production is associated with extreme water consumption (10 tons of water per kilo of cotton), erosion of soil, pollution from pesticides and fertilizers, and competition with food crops.[15–17] A bio-based alternative to cotton fabrics is the regenerated cellulose, *e.g.* Lyocell, which can be produced by dissolving grade pulp derived from woody biomass.

1.2   Lignocellulosic biomass

Lignocellulose is the constituent of the plant's cell walls. It is mainly composed of cellulose, hemicellulose, and lignin in different proportions depending on the taxonomy of the plant.[18] It provides the plant the ability to grow vertically, transport water and nutrients. The largest differences are found among hardwood, softwood, and herbaceous plants. Generic lignocellulosic biomass is composed of 38–50% of cellulose, 15–35% of lignin, and 23–32% of hemicellulose. All of these components are bonded to create lignin-carbohydrate complexes (LCC).[19,20] This extensively available feedstock is exploited in different industrial processes on large scale, however, all the relevant ones are focusing on the carbohydrate fraction. The largest industry is pulp and paper, where the biomass is converted into pulp and then transformed into paper by a separation process called pulping. Second-generation bio-ethanol is produced by the fermentation of non-edible sources of glucose.[21] Crop and forest residues and wood manufacturing waste can be considered as non-edible lignocellulosic feedstocks. Nonetheless, the exposure of the sugar fractions to the enzymes performing the hydrolysis is still a critical step of the process.[22] Even though composites and plastics derived from cellulose have gained industrial relevance lately, fossil-derived polymers are still leading the market due to better cost of production and higher performances. Textile manufacturing extensively employs plant biomass, an example is cotton fibers for fabric production. In this case, the bio-derived product overtakes the synthetic surrogate in terms of performance and quality, remaining optimal on the market.

1.2.1   Cellulose

Cellulose is a linear high molecular weight polysaccharide made of D-glucose units connected through β(1–4') glycosidic bonds (Scheme 1.1).[23] Due to its ubiquity in Plantae's kingdom, cellulose is the most abundant natural polymer. Despite its hydrophilic character, it remains insoluble in water due
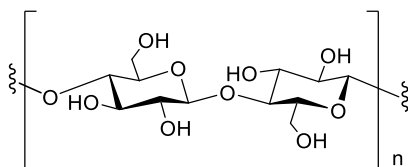
Scheme 1.1 Cellulose molecular structure.

to the massive presence of intermolecular hydrogen bonds that stack the polymer chains in a typical supramolecular structure, the microfibril.[24] This supramolecular structure provides the tensile strength required for the vertical growth of the plant. Cellulose naturally occurs in different crystalline forms with relatively high thermal stability, *e.g.* α and β.[25] The glass transition temperature in water is around 300 °C.[26] The cellulose contained in woody biomass is exploited in the paper industry and as a substrate in the production of fabrics, via dissolving grade pulp, and microcrystalline cellulose.[27] It is also used for the production of bio-ethanol by hydrolysis into simple glucose and subsequent fermentation.[28]

1.2.1.1 Dissolving grade pulp

High purity cellulose can be obtained by removing both hemicellulose and lignin from the lignocellulose. Usually, hemicellulose is extracted from the biomass by acidic pre-hydrolysis.[29] The obtained materials incorporate a low amount of residual lignin and hemicellulose (both <5 wt%). The glucan and the α–cellulose content are generally higher than 90%. When optimizing the pulping conditions, the intrinsic viscosity of the dissolved product is targeted within the range of 400-600 g/L to obtain a material that can be spun to generate yarns.[30] As mentioned above, dissolving grade pulp is considered a valid alternative to cotton fibers for textile production.[31,32]

1.2.2 Hemicelluloses

Hemicelluloses are heteropolymers constituted of hexoses and pentoses. The structure and the components vary from plant to plant, where the major monosaccharides are xylose, mannose, galactose, rhamnose, and arabinose (Scheme 1.2).[33,34] A study on the composition of hemicellulose in birch found the following distribution of sugars: xylose (81.0%), uronic acids (10.4%), mannose (7.4%), and galactose (1.2%).[35] Hemicelluloses have a lower molecular weight as compared to cellulose. They are partially water-soluble materials and present a characteristic hygroscopicity when dried. Hemicelluloses are branched and not crystalline. Their role in plants has

4

been discussed for a long time, and it has been proposed that hemicelluloses act as a linker between cellulose and lignin. This idea has been supported by the isolation of several LCCs.[36,37]
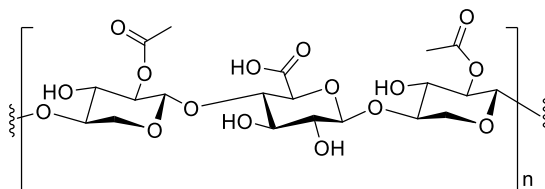
Scheme 1.2 Simplified representation of the structure of (glucorono) acetylxylan, the main component of hardwood hemicellulose.

1.2.3 Lignin

The name lignin is given to the compound resulting from the radical coupling of monolignols and their oligomers. Main monolignols are *p*-coumaryl-, coniferyl-, and sinapyl-alcohols; those correspond to H-, G- and S- units once included in the polymeric chain (Scheme 1.3). Their average distribution varies according to the botanical nature of the organism. The largest differences are found among hardwood, softwood, and herbaceous plants (Table 1.1).[38] Lignin is an amphiphilic and highly aromatic macromolecule that shows an anti-oxidant character.[39] These properties allow the plant to contain water and resist microbial infections and light-promoted oxidations. The radical coupling is initiated by non-specific enzymes, *i.e.* peroxidase and laccase, resulting in a heterogeneous and branched oligomer.[40]
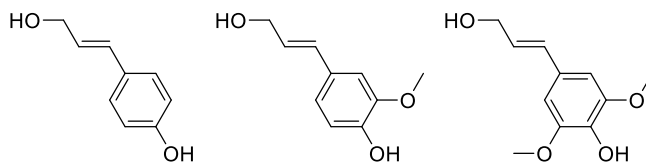
Scheme 1.3 Left to right: *p*-coumaryl alcohol (H-unit), coniferyl alcohol (G-unit), and sinapyl alcohol (S-unit).

Table 1.1 Distribution of phenolic units in plants.

Source	H-unit [wt%]	G-unit [wt%]	S-unit [wt%]	Lignin [wt%]
Hardwood	0–8	25–50	45–75	16–24
Softwood	<5	>95	Traces	25–31
Herbaceous	5–33	33–80	20–54	10-25
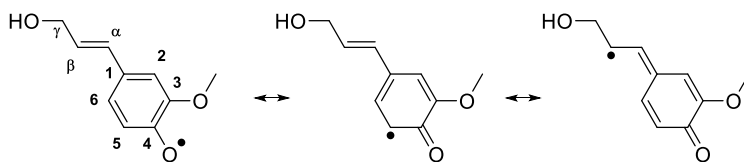
Scheme 1.4 Most reactive resonance structures of a monolignol radical.

Due to the presence of several reactive resonance structures, monolignols react with each other forming different inter-unit linkages (Scheme 1.4). The most abundant inter-unit motif is the β–O–4' (up to 70–80%), but there are other notable interlinkages in lignin. The most representative units are pinoresinol (7–17%) and phenylcoumaran (2-3%) while others are present in trace amounts (Scheme 1.5).[41] Lignin can be isolated as a by-product of pulp and paper production. Several pulping processes have been specifically designed to dissolve lignin in the process liquors and other components of the wood to isolate the purest cellulose fibers with optimal yields.
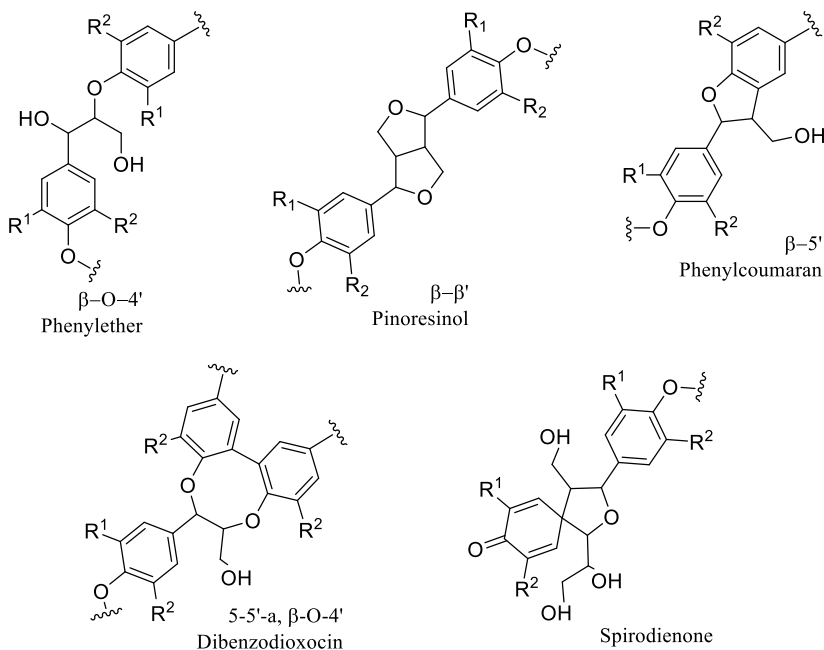
Scheme 1.5 Most common inter-unit motif of lignin.

1.2.4 Extractives

As the class name suggests, this group of molecules includes all the chemical components soluble in organic solvents that can be directly extracted from lignocellulose. The extractive group includes terpenes, polyphenols (lignans and tannins), and waxes (mainly fatty alcohol and fatty acid esters) (Scheme 1.6).[42] Their presence in biomass ranges between 2 and 10%,[43] 3% for birch wood.[44] Other than having antioxidant and antimicrobial activity,[45] it has been proposed that this class of compounds is responsible for the control of certain plant properties, *i.e.* wettability, moisture content, and shrinkage.[46,47]
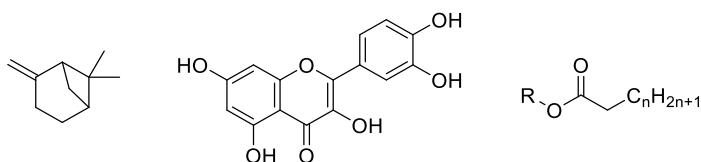
Scheme 1.6 Example of (left to right) terpene (pinene), tannin (quercetin), and generic fatty ester.

1.3 Pulping

The pulp consists of a lignocellulosic material that is disintegrated in order to liberate fibers that can be dispersed in water and produce a web.[48] The process of liberating and isolating such fibers is known as pulping. Different industrial methodologies are currently being used to produce different pulps with disparate applications. Two main classes of pulping are operating: mechanical pulping and chemical pulping. The mechanical pulping consists of the physical breakdown of the biomass until the liberation of fibers is achieved. The resulting material is obtained in very good yields (90–96%), has scarce mechanical properties, and is used in newspapers and magazine production. On the other hand, chemical pulping is able to produce higher purity pulps with higher mechanical performance. Indeed, these materials can find applications in corrugated cardboard and paper bags. Among the chemical pulping processes kraft and sulfite are the largest. However, the yields of chemical pulping are in the range of 45–50%, where the rest of the biomass is treated as a byproduct with the only exception of the technical lignin derived from the sulfite process (see Section 1.3.2).
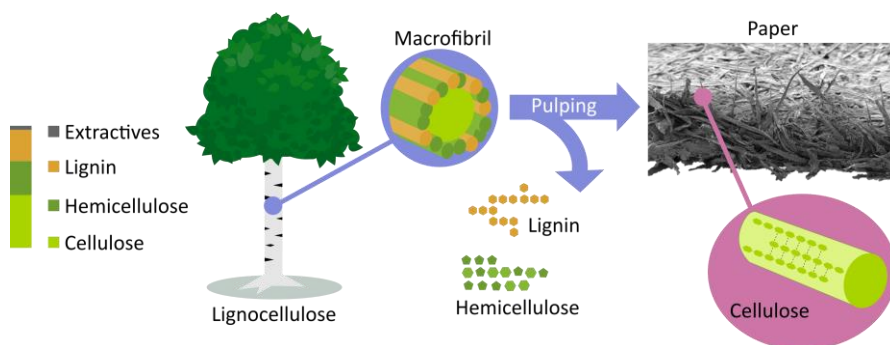
Figure 1.2 Schematic representation of pulping.

1.3.1 Kraft pulping

The kraft process is the most extensively exploited technology in the pulp and paper industry which produces the strongest fibers used to make cardboard.[49] The process consists of a high-temperature reaction between wood chips and an alkali aqueous solution of sodium sulfide.[50] The resulting product is a highly delignified solid dispersed into an alkali solution of lignin derivatives called black liquor (BL).
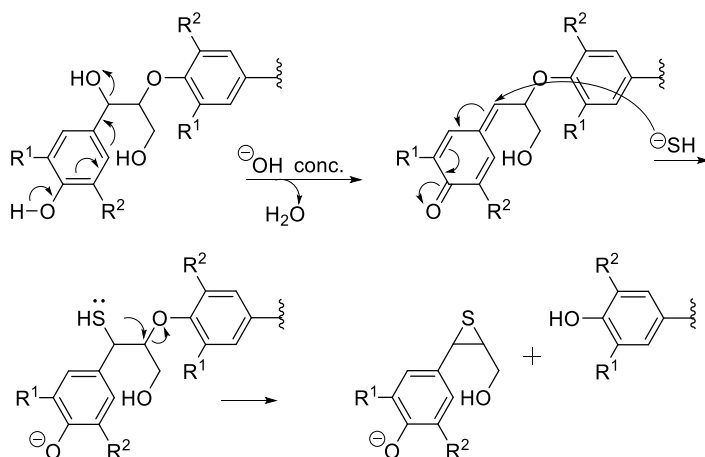
Scheme 1.7 β–O–4' depolymerization scheme during the kraft process.

During the depolymerization, the β–O–4' bonds are targeted and cleaved (Scheme 1.7). This results in a higher amount of free phenolic moieties and a higher solubility of the oligomers in an alkaline aqueous solution. However, the high reactivity of these molecules leads to an immediate re-condensation with the consequent formation of new carbon–carbon bonds among the freshly generated compounds. After the completion of the kraft pulping, the BL is usually concentrated by the means of evaporators giving MeOH and tall oil as side products. The concentrated BL is then burnt to a low value to recover the inorganic chemicals. Because of this, the name given to technical lignin extracted by the abovementioned process is known as kraft lignin (KL).[50,51] Thus, to isolate kraft lignin as a standalone material, the pH of the BL is lowered to 9–10, where the kraft lignin becomes insoluble in aqueous solutions and precipitates. The final product of the kraft process is the kraft fibers. The procedure aims to selectively remove lignin from the biomass keeping the hemi- and the cellulose (holocellulose) as a solid residue. Kraft pulp is commonly produced from softwood, *e.g.* southern pine.

1.3.2 Sulfite pulping

In contrast to alkali-based kraft pulping, sulfite pulping can be run under a wide pH range. The biomass undergoes cooking in presence of SO_3^{2-} and HSO_3^- anions where several cations are currently used. The goal of this process is to functionalize the lignin with sulfonate moieties increasing its solubility in water. The resulting pulp is known to be high in brightness. In the

case of the acidic sulfite process, most of the hemicellulose is also hydro-lyzed yielding a solid residue with high content of cellulose. The residual lignin can be isolated as a salt named lignosulfonate. This material bears amphiphilic properties and it finds application as dispersants[52] and as feed-stock for vanillin production.[53]
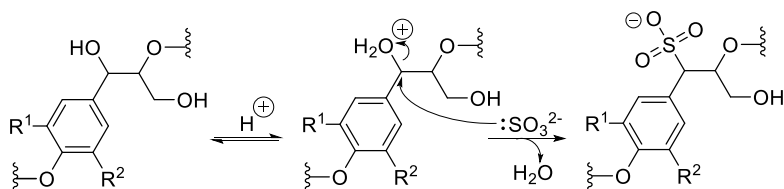
Scheme 1.8 Simplified reaction scheme of the acidic sulfite process.

1.3.3 Organosolv pulping

To perform a pulping process with reduced utilization of chemicals, a frac-tionation procedure based on solvolysis has been developed.[54] The process is called organosolv and consists of reacting biomass with water and benign organic solvents. Common solvents are acetone, methanol, ethanol, butanol, ethylene glycol, formic acid, and acetic acid.[54] The process involves the sol-volysis of lignin and hemicelluloses under acidic conditions. The organic solvents, which constitute the main cost of the process, can be recovered by distillation with the consequent lignin/hemicellulose (or both) precipitation in the water phase. In the same way as for kraft lignin, the organosolv lignin undergoes re-condensation reactions.
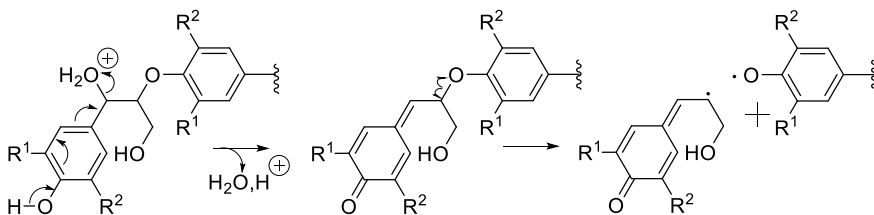
Scheme 1.9 One of the possible β–O–4' depolymerization pathways occurring dur-ing the organosolv process.

1.4 Lignin-first

As described in the above Sections, most of the industrial effort is within cellulose retention, downgrading lignin to a by-product role. In recent years, the focus on the valorization of lignin has increased and a new view has emerged: the "*lignin-first*" approach.[55–62] The idea behind this concept is to consider lignin, which is the most abundant source of aromatics in nature, a valuable material and not just a side product. This approach consists of the fractionation of biomass and the valorization of lignin *in-situ*. The fractionation is performed by organosolv methodology.[63,64] The resulting fragments of lignin and carbohydrates, monomers and oligomers, are further transformed into stable compounds by a catalytic system. Several studies have been published on different catalytic systems using precious metals but also Cu and Ni, reporting from moderate to good yields of monophenolic compounds. [65] Based on the β–O–4' content of the native lignin, these yields correspond to very good when compared to the theoretical maximum yield of lignin (ESI Paper III, Section 5.3).[66–68] Catalytic Upstream Biorefining (CUB),[69] Reductive Catalytic Fractionation (RCF)[64] and Early-stage Catalytic Conversion of Lignin (ECCL)[70] are other names for the same concept.[71] Currently, an example of *lignin-first* technology based on RCF at pilot scale has been demonstrated.[72] However, this strategy has not been developed on large scale yet. The reasons behind this are mainly the unprofitability of the *lignin-first*, the process produces a low-quality pulp when compared to kraft and involves a large amount of solvent.[73] In addition, the utilization of a heterogeneous catalyst makes the purification of the solid residues tedious requiring extra solvent.[74] Better exploitation of the solvents used for these procedures is therefore desirable and needed.
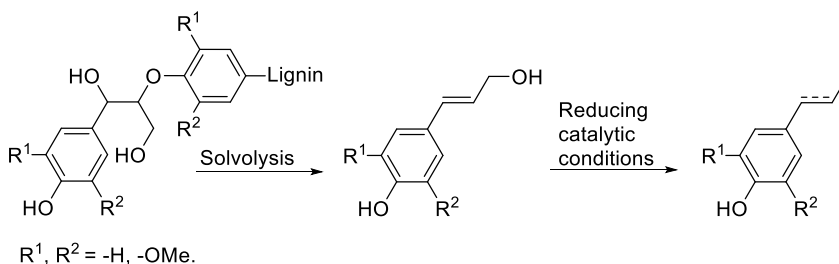
Scheme 1.10 Reductive catalytic fractionation simplified scheme.

1.5 Aim of the thesis

This work aims to increase the understanding of fundamental events occurring in catalytic fractionations of biomass and biomass-derived side streams and explore new valorization strategies of these substrates. More particular goals are to:

- Reach ductile chemoselectivity in the HDA of a complex mixture of biomass-derived phenolic compounds with an alternative H_2 source.

- Develop an analytical methodology to elucidate the mechanism of kraft lignin esterification with fatty acids by monitoring the reaction in real-time using semi-quantitative ^{13}C NMR spectroscopy.

- Study whether first-row transition metals can replace noble metals in hydrogenation/hydrogenolysis reactions during RCF of biomass.

- Investigate a solvent efficient pulping system able to produce dissolving grade pulp from SRF biomass with a benign acid.

- Propose a lignin-first approach that addresses both solvent efficiency and valorization of the cellulose fraction.

2 Ductile Pd-catalyzed hydrodearomatization of phenol-containing bio-oils into either ketones or alcohols using polymethylhydrosiloxane and H_2O as H_2 source (Paper I)

2.1 Background

The liquefaction product of biomass is called bio-oil, it is also known as pyrolytic oil or bio-crude.[75] Fast pyrolysis is considered one of the most efficient processes for biomass direct valorization due to the high bio-oil/gas yield and low charcoal production.[75,76] Typical fast pyrolytic process consists of thermal treatment of biomass (300–700 °C) under an inert atmosphere for a short reaction time. The outcome of the thermal decomposition of the biomass is a mixture of gases (syngas, CO_2, and C_{1-3} alkanes), a condensable liquid fraction (bio-oil), and a solid fraction (bio-carbon/char).[77] The liquid fraction is composed of water, the products from the decomposition of sugars, and the decomposition of lignin (mono-, di-,and poly-phenolic molecules).[78] In this chapter, the focus was set on the valorization of the phenolic fraction of a bio-oil. Phenolic bio-oils cannot be directly utilized as fuel or polymer precursors due to the high oxygen content and the complexity of the mixture. Therefore, to become a suitable liquid fuel or an industrial feedstock a preliminary hydrotreatment step is required.[79,80] Commonly, hydrogenation of phenols is carried out by using high-pressure gaseous hydrogen with the consequent requirement of expensive equipment.
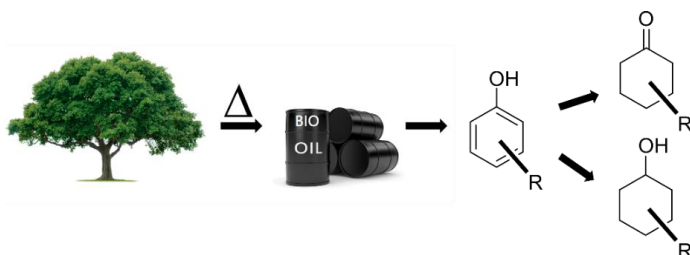

Figure 2.1 Proposed bio-oil valorization concept.

Several catalytic systems have been reported to achieve either cyclohexanones or cyclohexanols from phenols. Heterogeneous catalysts based on noble metals such as Pd,[81] Pt,[82], and Ru[83] have been shown to give very good yields of either ketones or alcohols. However, to the best of our knowledge, no reports have shown the ability to tune the selectivity between ketone and alcohol only through a marginal change in the reaction conditions. We investigated a catalytic system that can selectively produce cyclohexanones or cyclohexanols combined with the formation of H_2 *in situ*.

2.2 Optimization

The proposed catalytic system is based on Pd/C as a hydrogenation catalyst and a mixture of polymethylhydrosiloxane (PMHS) and water as the hydrogen source. PMHS is a non-toxic hydride source and it is widely available since it is produced as a by-product of silicon and dimethicone manufacturing industries. Hydrogen can be generated *in situ* by reacting PMHS with water (Scheme 2.1)[84] or *via* the formation of Pd hydride.[85] Together with Pd/C, PMHS has already been reported as an effective reducing system for the deoxygenation of aromatic ketones and aldehydes.[86,87] To date, however, no report has shown the possibility to use this catalytic system to dearomatize phenolic moieties.
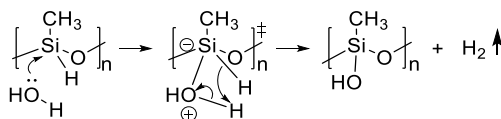
Scheme 2.1 Hydrogen production from PMHS/water mixture.

Meta-cresol (**1**) was chosen as a representative model of phenolic bio-oil in the initial screening. First, we optimized the reaction conditions to generate ketone **1a**. Hence, compound **1** was successfully transformed into **1a** with excellent yield (97%) by reacting it with 3 equiv of PMHS and 125 μL of water for 6 h (Table 2.1, entry 1). Second, since the theoretical amount of hydride donor to achieve full hydrogenation was already present in the reaction mixture we tried to obtain 4-methylcyclohexanol **1b** by varying the other reaction parameters. Increasing the reaction time to 20 h resulted in a scarce 15% yield of **1b** (Table 2.1, entry 2). Still, when PMHS was increased to 5 equiv only 35% of alcohol was obtained after 18 h (Table 2.1, entry 3). Gratifyingly, 64% yield of the fully dearomatized products was obtained when using 5 equiv of PMHS combined with 500 μL of water (Table 2.1, entry 4). Letting the same reaction mixture react for 18 h gave >99% yield

of **1b** (Table 2.1, entry 5). Reactions using Pd/C demonstrated the highest yields for both ketone and alcohol when compared to other noble metals. Under the reaction conditions optimized for **1a**, Ru/C showed only 20% conversion of **1** and selectivity towards **1b** despite the lower catalyst amount used, *i.e.* 2.5 mol% (Table 2.1, entry 6). However, >99% yield of **1b** was obtained when using the same solvent system with 5 equiv of PMHS for 24 h (Table 2.1, entry 7). Pt/C used under the same conditions demonstrated a poor selectivity giving 80% of **1b** and 20% of **1a** (Table 2.1, entry 8). Thus, ductile selectivity was achieved only when using Pd. By slightly changing the reaction conditions, either 3-methylcyclohexanone (**1a**) or the corresponding cyclic alcohol (**1b**) could be formed in excellent yields starting from *m*-cresol **1** (Table 2.1, entries 1 and 5).

Table 2.1 Optimization of *m*-cresol (**1**) HDA.

Entry	THF:H$_2$O v/v	Metal	t [h]	PMHS [equiv]	Conv. [%]	Ketone 1a [%]	Alcohol 1b [%]
1	4:1	Pd[a]	6	3	>99	97	3
2	4:1	Pd[a]	20	3	99	85	15
3	4:1	Pd[a]	18	5	>99	65	35
4	1:1	Pd[a]	6	5	>99	36	64
5	1:1	Pd[a]	18	5	>99	-	>99
6	4:1	Ru[b]	6	3	20	3	97
7	4:1	Ru[a]	24	5	>99	-	>99
8	4:1	Pt[a]	24	5	>99	20	80

Reaction conditions: 80 °C, magnetic stirring 600 r.p.m., substrate 0.46 mmol, THF 500 μL, H$_2$O 125–500 μL. [a] Catalyst amount 5 mol%. [b] Catalyst amount 2.5 mol%. Yields were determined by ^{1}H NMR spectroscopy using an internal standard.

2.3 Hydrodearomatization of bio-oil model compounds into cyclohexanones

The scope of the reaction was investigated by reacting an array of substituted phenolic compounds, initially under the reaction conditions optimized for **1a**. A difference in reactivity was observed among compounds **1**, **2**, and **3** concerning the position of the methyl group, respectively *meta-*, *para-,* and *ortho-*. Ketones **1a** and **2a** were produced in excellent yields under the same reaction conditions, while prolonged reaction time (18 h) and increased hydride donor amount (5 equiv) were needed to achieve 85% of **3a** (Table 2.2, entries 1–3). Phenol (**4**) was found to be more reactive than the benchmark *m*-cresol (**1**), giving 90% of cyclohexanone (**4a**) in only 3 h (Table 2.2, entry 4). The reactivity trend observed for methylphenols was also valid for ethylphenols **5**, **6,** and **7**. Compounds **5a** and **6a** were obtained in excellent yields by using the same solvent system and running the reaction for 18 h, whilst 24 h, 5 equiv of hydride donor, and an increased amount of water were needed to fully convert 2-ethylphenol (**7**) into the corresponding cyclohexanone **7a** (Table 2.2, entries 5–7). A kinetic study performed on compounds **1** and **3** showed lower reactivity of the *ortho*-substituted phenols compared to the *meta*-substituted, confirming that substituents in the *ortho* position negatively affect the reactivity of the phenol under the employed reaction conditions (Paper I). Very good yields (85%) were obtained also with compounds **8** and **9** carrying bulkier substituents in the *para* position running the reaction for 18 h (Table 2.2, entries 8 and 9). Disubstituted phenols with both free *ortho* positions, compounds **10** and **11**, showed reactivity similar to *m*-cresol (**1**), giving very good yields of the corresponding cyclohexanones under the optimized reaction conditions for **1a** (Table 2.2, entries 10 and 11). Phenolic compounds with substituents on both the *ortho* positions, **12** and **13**, gave slightly lower yields towards the corresponding cyclohexanones (85% and 77% respectively). These two reactions were carried out by using 5 equiv of PMHS combined with 500 μL of water for 24 h (Table 2.2, entries 12 and 13). Compound **14** with a slightly EWG and compound **15** with EDG were successfully transformed into the corresponding methylcyclohexanones in comparable yields under the optimized reaction conditions for **1**, suggesting that the steric hindrance is the main parameter affecting the reactivity (Table 2.2, entries 14 and 15). Indeed, *o*-guaiacol, known to be resistant to chemo-selective HDA,[88,89] gave poorer conversion and selectivity towards the corresponding cyclohexanones and therefore was not included in this study.

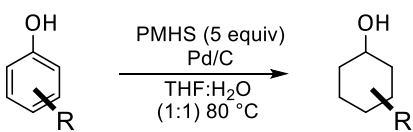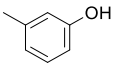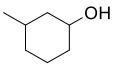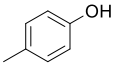**Table 2.2** Transformation of phenols to cyclohexanones.
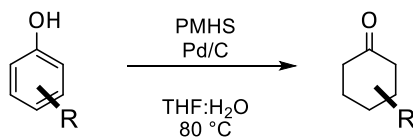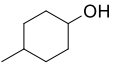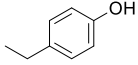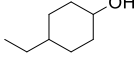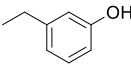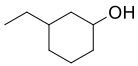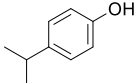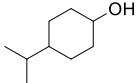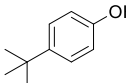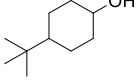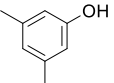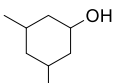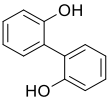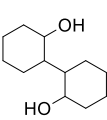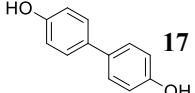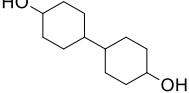
Entry	THF:H₂O, [v/v]	PMHS [equiv]	Substrate	t [h]	Ketone, yield [%]
1	4:1	3	**1**	6	**1a**, 97
2	4:1	3	**2**	6	**2a**, 95
3	4:1	5	**3**	18	**3a**, 85
4	4:1	3	**4**	3	**4a**, 90
5	4:1	3	**5**	18	**5a**, 93
6	4:1	5	**6**	18	**6a**, 95
7	1:1	5	**7**	24	**7a**, >99
8	4:1	5	**8**	18	**8a**, 85
9	4:1	3	**9**	18	**9a**, 85
10	4:1	3	**10**	6	**10a**, 93
11	4:1	3	**11**	6	**11a**, 80
12	1:1	5	**12**	24	**12a**, 85
13	1:1	5	**13**	24	**13a**, 77
14	4:1	3	**14**	6	**14a**, 85
15	4:1	3	**15**	6	**15a**, 83

Reaction conditions: 80 °C, Pd/C 10 wt% (5 mol%), substrate (0.46 mmol), THF (500 µL), H₂O (125–500µL). Yields calculated by ^{1}H NMR.

2.4 Hydrodearomatization of bio-oil model compounds into cyclohexanols

The reaction conditions optimized for cyclohexanones (Section 2.3) were applied to a series of *meta*- and *para*-substituted phenols to convert them into cyclohexanols (Table 2.3). Benchmark compound **1** gave >99% NMR yield of 3-methylcyclohexanol (**1b**) with 5 equiv of PMHS after 18 h (Table 2.3, entry 1). Very good to excellent yields of cyclohexanols (93–99%) were obtained with the *meta*- and *para*-substituted phenols **2**, **5**, **6**, **8**, and **9** under the same reaction conditions (Table 2.3, entries 2–6). Even di-substituted phenol **11** gave full conversion towards the corresponding cyclohexanol (Table 2.3, entry 7). Surprisingly, recalcitrant compound **3** gave a 90% yield of 2-methylcyclohexanol (**3b**) under the same conditions optimized for the synthesis of **3a** with only changing the water content from 125 to 500 µL (Table 2.3, entry 8). Noteworthy, *ortho*-substituted 2,2′-biphenyl **16** and *para*-substituted 4,4′-biphenyl **17** gave the corresponding fully saturated products in similar yields of 85% and 83% respectively (Table 2.3, entries 9 and 10). Moreover, no ketone intermediates were detected suggesting a different reaction mechanism for the HDA of bicyclic compounds. Besides, their successful transformation into bi-cyclohexanols opens up applications of the catalytic system to more advanced model compounds of biomass, such as the dimeric model compounds disclosed in Section 4.4. While aiming for the alcohol, the limitations of the catalytic system are the same as already elucidated in the previous Section since cyclohexanones are intermediates in the reaction. *Ortho*-substituted phenols gave poor yields, only compound **3** was successfully transformed into the corresponding alcohol. Moreover, no selectivity towards the *cis* product was observed when synthesizing substituted cyclohexanols, suggesting a 2 steps process, where the corresponding ketone leaves the catalytic center after being formed and the second adsorption will lead to full hydrogenation.

Table 2.3 Transformation of phenols to cyclohexanols.

Entry	Substrate	t [h]	Alcohol, yield [%]
1	**1**	18	**1b**, >99
2	**2**	18	**2b**, 95
3	**5**	18	**5b**, 93
4	**6**	24	**6b**, >99
5	**8**	24	**8b**, 95
6	**9**	24	**9b**, >99
7	**11**	18	**11b**, >99
8	**3**	18	**3b**, 90
9	**16**	24	**16b**, 85
10	**17**	24	**17b**, 83

Reaction conditions: 80 °C, in THF:H$_2$O (1:1 v/v, 1 mL), PMHS (5 equiv), Pd/C 5 mol%, substrate (0.46 mmol). Yields calculated by ^{1}H NMR.

2.5 Hydrodearomatization of cardanol

Cashew nut shell liquid (CNSL) is a by-product of the cashew nut manufacture and consists of a mixture of phenols and hydroxyl benzoic acids substituted with a C_{15} alkyl chain in the *meta*-position. After thermal decomposition, CNSL is transformed into a phenolic mixture of isomers called cardanol (Scheme 2.2).[90] We sought the cardanol mixture to be an interesting candidate to employ the developed HDA reaction. The cardanol mixture was completely transformed into 3-pentadecylcyclohexanone (**18**) using 10 equiv of PMHS to achieve >99% yield. A higher amount of hydrogen donor was needed due to the presence of double bonds in the aliphatic side chain. Under the reaction conditions, the double bonds in the side chain underwent hydrogenation and required additional hydrogen.

The developed HDA method demonstrates higher yields than those previously reported by Rahobinirina *et al.*, where 67% of **18** was obtained in two steps and the presence of H_2.[91] Due to the steric hindrance from the *meta*-substituent, 72 h were needed to achieve the full conversion of the cardanol mixture into the sole compound **18**. This product is an interesting candidate for the production of biopolymers.[91]
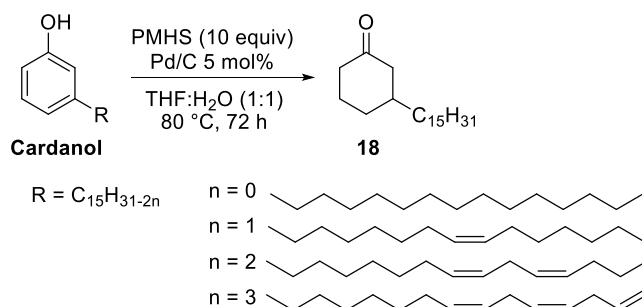
Scheme 2.2 Cardanol HDA into 3-pentadecylcyclohexanone.

2.6 Hydrodearomatization of beechwood tar creosote

Commercial beechwood tar creosote is a bio-oil mainly composed of aromatic compounds produced by pyrolysis of beechwood tar. Such a bio-oil is constituted by several mono- and poly-substituted phenols with a boiling point below 220 °C. Considering the complexity of the substrate mixture, full hydrogenation was targeted while optimizing the reaction conditions (Scheme 2.3). After the reaction was completed, the full conversion of the substrate was achieved, as determined by ^{1}H NMR spectroscopy. Ketone and aromatic moieties were not detected by NMR in the product mixture, confirming the presence of only saturated species.

OH
PMHS (12 equiv)
Pd/C 5 mol%
THF:H$_2$O (1:1)
80 °C, 72 h
OH

R^1 R

R = -H, -OCH$_3$, -CH$_3$, -CH$_2$CH$_3$.
R^1 = -H, OCH$_3$, -CH$_3$.
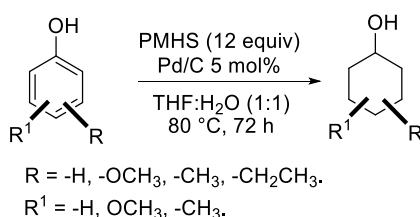
Scheme 2.3 Creosote from beechwood tar HDA into substituted cyclohexanols.

2.7 Summary

In conclusion, a series of phenolic bio-oil model compounds were successfully transformed into either the corresponding ketone or alcohol. An alternative hydrogen source was successfully used. Natural bio-oils were also treated to yield 3-pentadecylcyclohexanone from cardanol, and a cyclohexanols mixture from beechwood tar creosote. The proposed catalytic system showed a ductile selectivity with only adjusting the reaction parameters marginally, *i.e.* reaction time, water, and hydride donor content. Above mentioned yields are comparable with the ones previously reported. However, to date, no other system has been reported to achieve the adaptable production of either cyclohexanones or cyclohexanols from phenolic substrates using the same catalyst.

3 De-bottlenecking a pulp mill by producing biofuels from black liquor in 3 steps (Paper II)

3.1 Background

As mentioned in Section 1.3, the kraft industry leads the market of pulp and paper with an estimated annual production of 260 Mt of product.[92] The kraft pulping concept is well established all around the world since it was patented by C. F. Dahl in 1884.[93] It consists of a treatment of wood, usually from softwood and eucalyptus, under alkaline conditions (Figure 3.1). The logs, after being de-barked and reduced into chips, undergo a "cooking" step. During this phase, the biomass is treated in a solution of Na_2S and NaOH for up to 2 h at 165–175 °C.[94] Throughout the reaction time, lignin is mainly targeted and solubilized into the reaction liquors (BL). The solid residue, consisting of holocellulose, is then washed and considered the final product, *i.e.* kraft pulp. As its name suggests (kraft is a German word for force), the fibers in the kraft pulp are extremely strong due to the presence of residual hemicellulose which enhances the mechanical properties of the material. The BL is concentrated by the means of evaporators and burnt to a low value to recover the process chemicals as an inorganic smelt and generating steam.
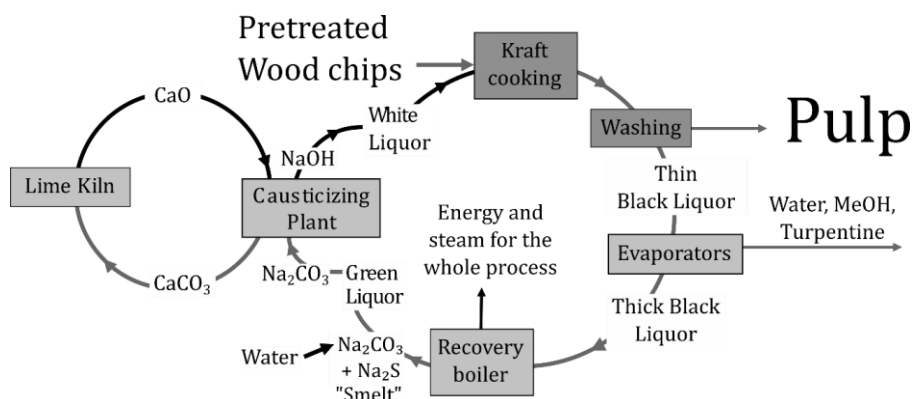


Figure 3.1 Kraft process scheme.

This procedure is performed in an operating unit called "recovery boiler", which is the most expensive unit of the infrastructure and it is the limiting step of the productivity in the whole process. Moreover, due to the extremely exothermic nature of the operation, the recovery boiler generates a surplus of energy in form of high-temperature process steam, which is not fully exploited. After being washed away by water, the smelt becomes "Green liquor" which is further treated with lime to yield back "White liquor" ready to be used in the next batch. The spent lime is also recycled by the means of a lime kiln operated with the process steam produced by the recovery boiler. A strategy to increase pulp production without investing in a new recovery boiler is the removal of lignin from the BL. To achieve a solid material, the pH of the liquors is reduced to precipitate the lignin, where carbon dioxide can be used as the acid source. In recent years, two main industrial procedures have been developed, with and without oxidation before the acidification of the BL with CO_2, named LignoForce and LignoBoost respectively.[95,96] In this study, Lignoboost KL is used. The resulting solid substance appears as a brown powder characterized by an average molecular weight of 1-3 kg/mol and scarce solubility in any solvents with few exceptions such as THF and DMSO. Several direct approaches, aiming at lignin valorization, have been investigated: the main ones are hydrothermal liquefaction and catalytic pyrolysis.[97–103] Up to date, there is no commercial use for this product and it is commonly utilized as an energy source for the lime kiln. The high oxygen content (heating value of 25 kJ/g versus 44 kJ/g of diesel), and its difficult handling when fully dry (it generates explosive atmospheres), hinder the KL utilization directly as a fuel outside the pulp mill. Moreover, the scarce solubility of KL in refinery carrier liquids (hydrocarbons) inhibits its valorization via the HDO process in a fixed bed reactor. A way to increase its compatibility with hydrocarbons is to functionalizing the most reactive moieties, aromatic and the aliphatic hydroxyl groups present in *c.* 6.5 mmol/g, with lipophilic functional groups consequently increasing the lipophilic character of the resulting KL based product. In this direction, KL esterification has been deeply investigated reporting up to quantitative yields of lignin esters. A known way to achieve lignin esterification is to use acyl chlorides produced in situ by reacting thionyl chloride with fatty acids.[104] However, the toxicity of the reactant and the large amount of hydrochloric acid produced as by-products limit its industrial application.

Our group has already contributed to a method that compatibilizes KL with LGO, a common refinery carrier liquid, by esterification with fatty acids, overcoming the need for halides.[105] In that report, KL was pretreated by transfer hydrogenolysis with *i*PrOH catalyzed by nickel. That procedure aimed to deoxygenate the carbonyl groups into sp³ carbons. The activated lignin was then reacted with tall oil fatty acids (TOFA) and acetic anhydride in presence of imidazole as organocatalyst yielding a lignin ester. However, the pretreatment of KL and the utilization of high boiling imidazole

(b.p. 256 °C) are still drawbacks that need to be solved. To overcome these issues, we developed a new methodology able to yield a fully esterified KL with enhanced solubility in commonly used refineries' carrier liquids using easily recyclable pyridine (b.p. 115 °C) as the organocatalyst and Ligno-Boost KL directly without any catalytic pretreatment.

3.2 Kraft lignin esterification

The reaction is a multistep one-pot process. LignoBoost KL and fatty acid were mixed to achieve a slurry. Pyridine, as an organocatalyst, was added while the temperature was raised to 130 °C and Ac_2O was continuously added to the mixture. The competition between the formation of fatty ester lignin and acetylated lignin results in a fully esterified lignin with different fatty ester loading (Scheme 3.1).
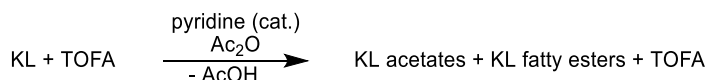
Scheme 3.1 KL esterification with TOFA.

To move the equilibrium towards the fatty esters, vacuum was applied and AcOH was selectively distilled off as well as the remaining catalyst, yielding esterified lignin solubilized in unreacted fatty acid. Different reactions can occur under the reaction conditions (Scheme 3.2).
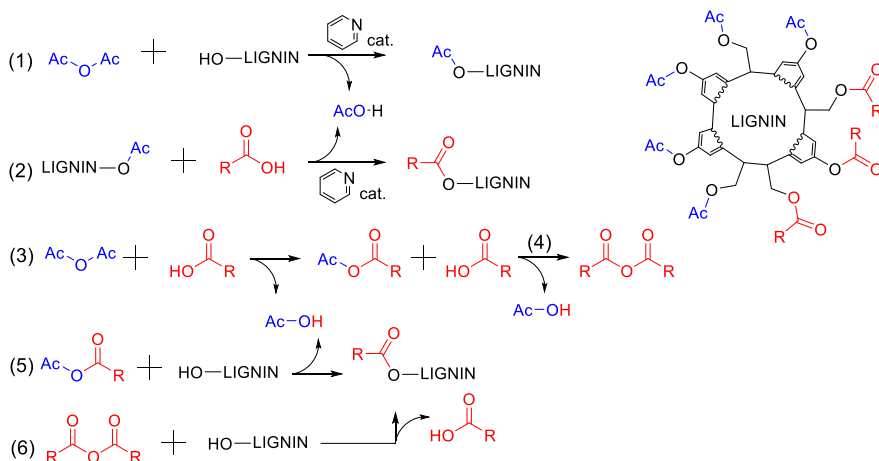
Scheme 3.2 Reaction scheme showing possible pathways occurring under the reaction conditions.

24

Lignin can undergo pyridine catalyzed acetylation in presence of Ac_2O (Scheme 3.2, reaction 1) and consequent transesterification of acetate with a fatty acid (Scheme 3.2, reaction 2). In parallel, Ac_2O can react with fatty acid to yield mixed and symmetric fatty anhydrides (Scheme 3.2, reactions 3 and 4). These anhydrides can react with lignin to generate lignin fatty esters (Scheme 3.2, reactions 5 and 6) in analogy to the previous proposal. Therefore, to better understand the reaction, a mechanistic study was performed.

3.2.1 Kraft lignin esterification mechanistic study

In our previous report on KL esterification, a reaction mechanism was proposed (Scheme 3.3).[105] In this reaction mechanism, the acetic anhydride would react with the fatty acids to produce fatty anhydride (Scheme 3.2, reaction 3 and 4) which consequently would react with the free hydroxyl group left on lignin to generate the corresponding esters and a free fatty acid (Scheme 3.2, reaction 5 and 6).[105–108]
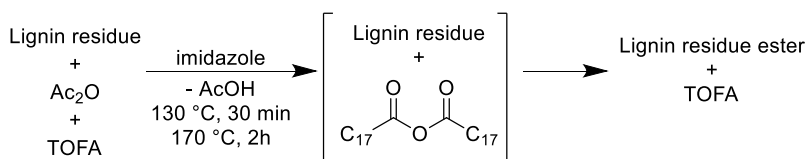
Scheme 3.3 Previously reported reaction mechanism.[105]

To elucidate the mechanism of the KL esterification under our reaction conditions, several reactions were performed. For simplicity, stearic acid was chosen as the source of fatty acid in this study. The blank reactions showed no reactivity when no activator and/or catalyst was involved (Table 3.1, entries 1 and 2). When using an excess of activator in absence of fatty acid, fully acetylated lignin was achieved as the final product (Table 3.1, entry 3). The reaction between KL and stearic anhydride gave scarce results (Table 3.1, entry 4), probably due to the high steric hindrance on the electrophilic carbonyl carbon of the stearyl group. These results differ from our previous mechanistic proposal. Changing the substrate to fully acetylated kraft lignin (KLA) and reacting it with stearic acid in absence of catalyst resulted in a scarce transesterification degree too (Table 3.1, entry 5). Including pyridine in the reaction mixture led to promising 30% hydroxyl groups converted into fatty esters, confirming the activity of the chosen catalyst towards the desired transformation (Table 3.1, entry 6). The results obtained from the control

reactions supported a mechanism where lignin acetylation (Scheme 3.2, reaction 1) is followed by pyridine catalyzed transesterification of the acetate moiety (Scheme 3.2, reaction 2). However, further investigations were needed to fully understand the reaction mechanism.

Table 3.1 Control reactions.

Entry	substrate	Stearic acid	Anhydride	Pyridine	Esterification [%]
1	KL	+	-	-	0
2	KL	+	-	+	0
3	KL[a]	-	Acetic (excess)	+	>99 (KLA)
4	KL[a]	-	Stearic (excess)	+	<5 (stearic ester)[b]
5	KLA[c]	+		-	<5 (stearic ester)[b]
6	KLA[c]	+		+	≈30 (stearic ester)[b]

Reaction conditions: kraft lignin (667 mg, TS 66%) was added to stearic acid (1 g, 1.1 equiv) under vigorous stirring at 130 °C until a homogenous slurry was reached. Then vacuum was applied to remove water and kept for 5 min. The system was then vented and, when required, pyridine (75 mg, 0.15 equiv) and anhydride were added. The reaction mixture was heated up to 180 °C. After 30 min vacuum was applied to remove acetic acid and pyridine until completion. [a] Dry KL, substrate amount: 500 mg. [b] Estimated by ^{1}H NMR spectroscopy. [c] Fully acetylated kraft lignin, substrate amount: 636 mg.

3.2.2 ^{13}C labeling study

To confirm the reaction mechanism proposed in the previous Section, and also to get more details about the different steps, real-time quantification of both lignin acetates and fatty esters was needed. However, common NMR analytical techniques do not allow such a study, since the ^{1}H NMR signals of the α protons overlap, and quantitative ^{13}C NMR spectroscopy is not applicable, mainly because of low sensitivity due to the scarce abundance of ^{13}C (1.1%) and smaller gyromagnetic ratio compared to ^{1}H (γ_n ^{1}H/ γ_n ^{13}C = 3.98). To overcome these issues, we exploited ^{13}C labeled activator (^{13}C acetic anhydride) and fatty acid (^{13}C oleic acid) to allow semi-quantitative ^{13}C 1D NMR analysis of the esters generated on the lignin. The integration regions were determined by using the HMBC cross-peaks of the carbonyls with the α protons (Figure 3.2 and Figure 3.3). To normalize the signal of the carbonyls versus the amount of lignin we used the integral corresponding to the methoxy groups of the KL on the ^{1}H NMR and compared it with the residual signal of CHCl$_3$. As all the NMR solutions were prepared using the same source of CDCl$_3$, we could assume that the relative abundance of CHCl$_3$ and CDCl$_3$ was constant among the samples. Therefore, we used the signal on the ^{13}C spectrum corresponding to the CDCl$_3$ as a reference when integrating the signals generated by the labeled esters and compared them to the CHCl$_3$ from the ^{1}H. Assuming this, we could normalize the integrals on the ^{13}C spectrum to the amount of lignin measured on the ^{1}H spectrum.
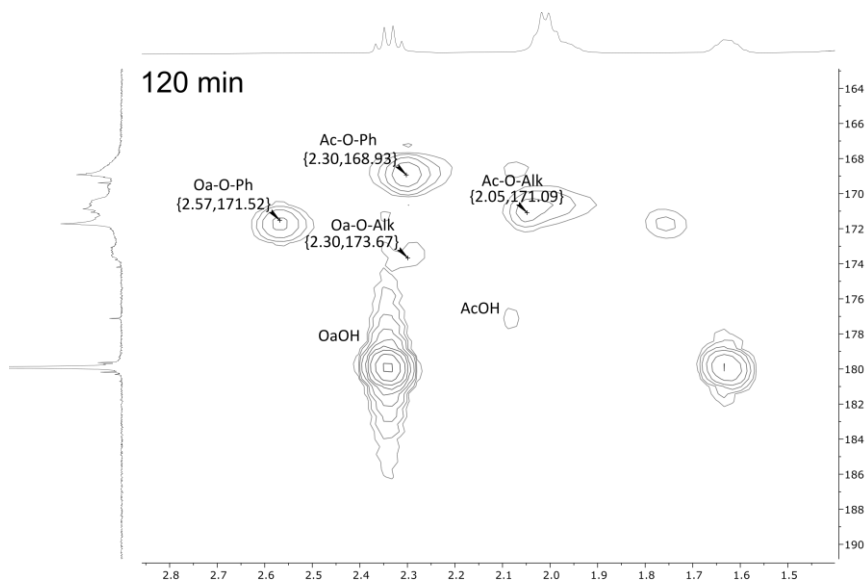
Figure 3.2 HMBC spectrum of the sample corresponding to reaction time 120 min.
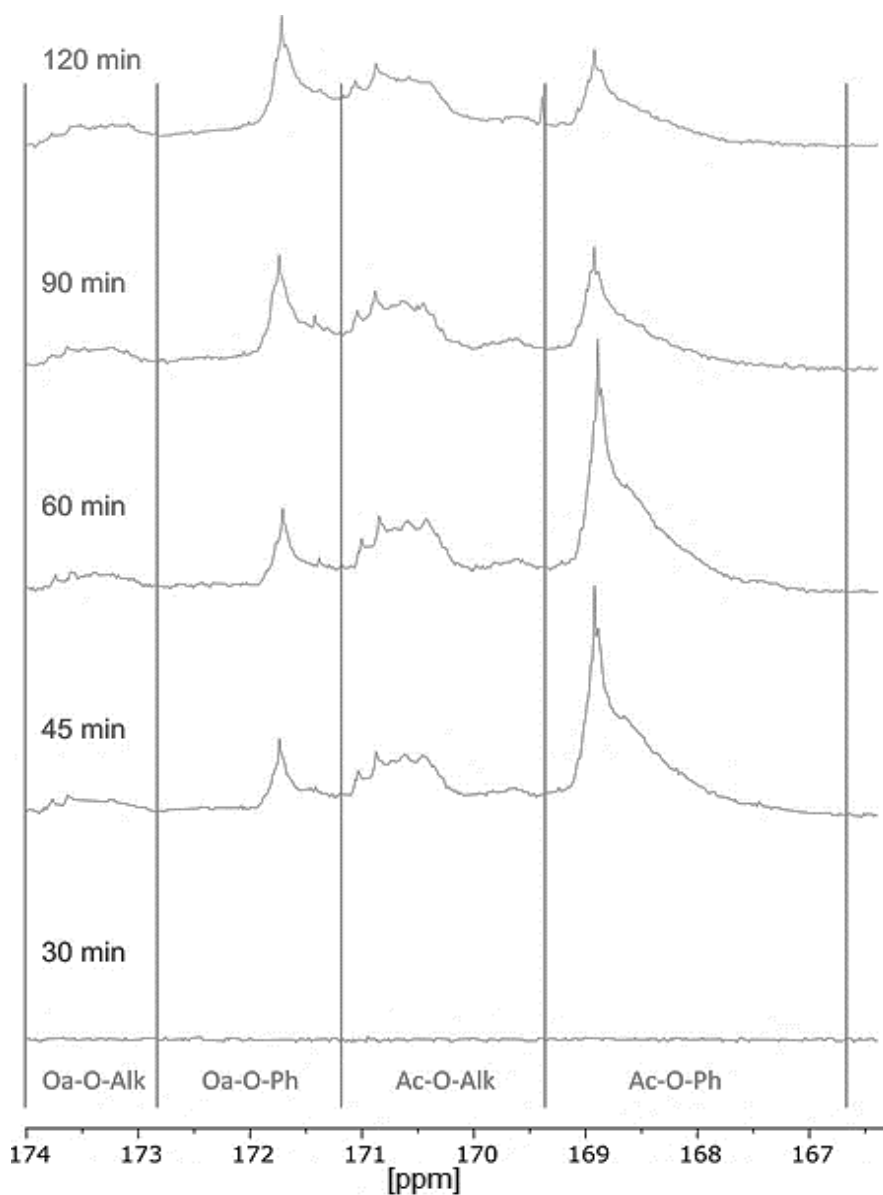
Figure 3.3 ^{13}C NMR spectra of ^{13}C labeling real-time study.

Once the methodology was established, a real-time study was performed to estimate the evolution of the acyl and the acetyl esters over time by separately integrating phenolic acetates (Ac-O-Ph), alkyl acetates (Ac-O-Alk), phenolic oleates (Oa-O-Ph), and alkyl oleates (Oa-O-Alk). As no free hydroxyl group was left at the end of the reaction (see ESI Paper II), we set the total amount of esters to 100% for the sample at 120 min which corresponds to the final product.
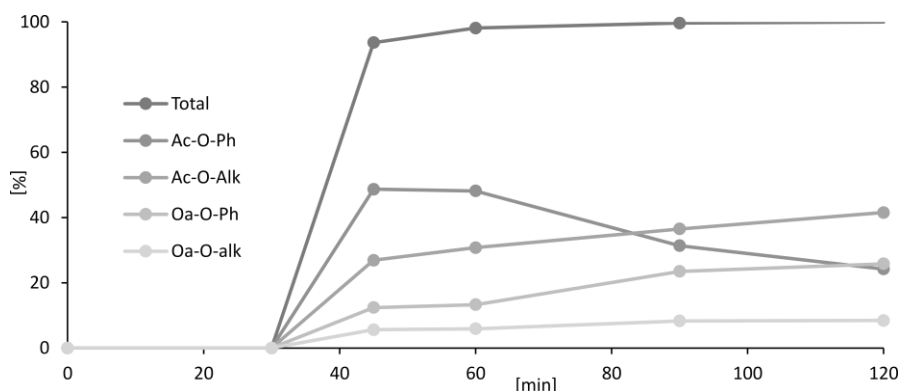
Figure 3.4 Esterification of KL with ^{13}C labeled oleic acid and acetic anhydride over time. Aromatic acetates (Ac-O-Ph), aliphatic acetates (Ac-O-Alk), aromatic oleates (Oa-O-Ph), and aliphatic oleates (Oa-O-Alk) relative abundance is described. Ac_2O was added after 30 min.

Plotting the results clearly showed how the acetylation is immediately occurring in the reaction medium after the addition of the acetic anhydride, and how prolonging the reaction and removing the acetic acid under vacuum promotes the conversion of phenolic acetates into phenolic oleates (Figure 3.4). Interestingly, under the reported reaction conditions, no transesterification of the aliphatic esters of lignin was observed.

3.3 Summary

The proposed methodology was able to steer the solubility properties of LignoBoost kraft lignin, achieving a lignin oil that could be blended with a common carrier liquid used in an oil refinery, to achieve drop-in quality fuels after a hydrotreatment step. In this work, the whole process from tree to gasoline station is described in more detail. The esterification methodology has been improved from our previous report, overcoming the need for catalytic pretreatment and utilizing a more easily recoverable organocatalyst such as pyridine. The esterification mechanism was further elucidated by performing a mechanistic study as well as by running a real-time study with ^{13}C labeled reactants. The results strongly suggested a reaction mechanism where the lignin acetates are formed first and subsequently in part converted into fatty esters, disproving the previous proposal which exclusively involved the reaction of fatty anhydrides generated in situ.

4 Lignin valorization by cobalt-catalyzed fractionation of lignocellulose to yield monophenolic compounds (Paper III)

4.1 Background

As mentioned in Chapter 1, exploitation of biomass, and more specifically lignocellulosic biomass as a replacement for fossil raw materials, is of great interest from both an environmental and an economical point of view. The complex composition of this feedstock has already been discussed, and the heterogeneous nature of lignocellulose forces the separation into its components to achieve full valorization. Its large availability and the demand for a sustainable and renewable resource, have recently boosted the attention of researchers on this well-known but recalcitrant material. Lignocellulose fractionation is nowadays an emerging research field and counts dozens of different approaches such as enzymatic treatment, steam explosion of woody biomass, and mechanochemical processes.[109–113]

Among the components of lignocellulose, lignin is the most complex in terms of chemical structure and reactivity. Even when separated from the matrix by depolymerization, lignin fragments remain extremely reactive and tend to re-condensate.[50,54] Therefore, except for lignosulfonates, there are no industrial applications for lignin. RCF allows to separate and chemically stabilize the most reactive components with one single procedure.[64] Our group has developed a system based on heterogeneous catalytic stabilization of the organosolv mixture yielding up to 40% of monophenolic compounds using a flow reactor involving Pd/C.[73,114] Rinaldi and co-workers have developed a cheaper catalytic system based on Raney nickel that allows magnetic separation of the catalyst. However, an over-stoichiometric amount of catalyst was required.[69]

In this chapter, we investigate a *lignin-first* approach based on a batch organosolv system employing a cobalt-based catalyst supported on nitrogen-doped carbon. The catalyst follows Beller's idea of creating nitrogen-enriched carbonaceous support on which the active metal is dispersed. The pre-catalyst nature controls the size and the formation of the metal particles, modifying the surrounding electron density and consequently increasing the activity of the metal center of the catalyst.[115]

4.2 Catalyst preparation

To create the nitrogen-enriched carbonaceous support, we started by synthetizing the phenanthroline-cobalt complex following a slightly modified reported procedure.[116] Co(OAc)$_2$ was selected as the metal source. The resulting solution was adsorbed on activated carbon and then pyrolyzed under Ar at 800 °C (Scheme 4.1).[115] The obtained material showed a metal loading of 0.45 wt% Co measured by ICP. Both pyridinic and pyrrolic moieties were detected during XPS analysis as well as N-graphitic and N-pyridine oxide species (ESI Paper III).
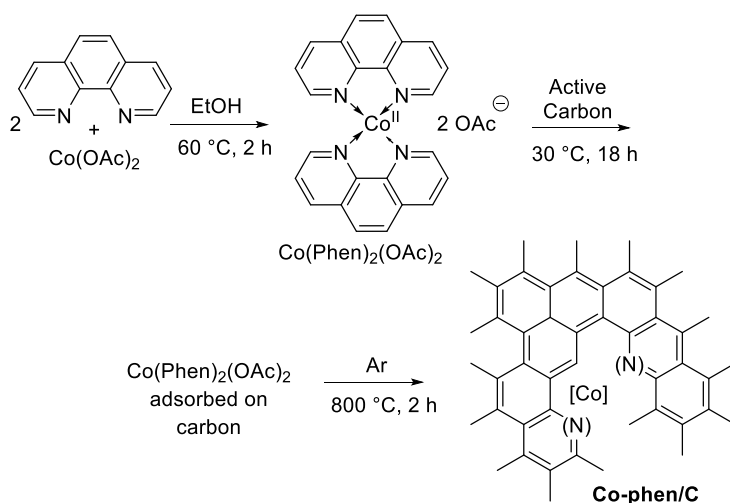
Scheme 4.1 Synthesis of Co-phen/C. The structure of the nitrogen-doped support has not been determined.

4.3 Catalytic fractionation of birch wood
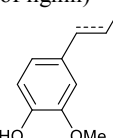
Birch was chosen as the lignocellulosic feedstock due to its high content of β–O–4' inter-unit motif, which is considered the target of the depolymerization and the high amount of S-units that generates more stable syringyl monophenolic compounds after depolymerization (Scheme 4.2).
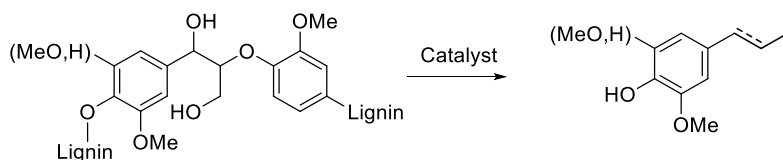
Scheme 4.2 β–O–4' unit catalytic depolymerization scheme.

The organosolv system was the same as the one developed in our group's previous work, *i.e.* a 1:1 v/v mixture of EtOH and water. Blank reactions gave yields lower than 6% of monophenolic products (Table 4.1, entries 1-3). When HCO$_2$H was used as the exclusive H$_2$ source, 17% of target products were detected and a scarce 29% of solid residue was obtained, due to the partial depolymerization of cellulose and high re-condensation of monophenolic compounds promoted by the acidic conditions (Table 4.1, entry 4). While using HCO$_2$Na as the hydrogen donor, 63% of solid residue was recovered and a mere 18% yield of monophenols was observed (Table 4.1, entry 5). The pulp yield (solid residue) was much higher than the target value of 38%, corresponding to the amount of cellulose present in the substrate, due to the presence of intact LCCs in the solid fraction. The optimized amount of hydrogen donor was 5 equiv of HCO$_2$H combined with 5 equiv of HCO$_2$Na, where 34% (76% of the theoretical yield, ESI Paper III 5.3) of monophenolic compounds were obtained in addition to 32% of solid residue (Table 4.1, entry 6). HCO$_2$H is contributing to the decomposition of hemicellulose that leads to a better delignification. Meanwhile, the HCO$_2$H/HCO$_2$Na mixture shows the best yield of monophenolic products.

Table 4.1 Catalytic fractionation of birch.

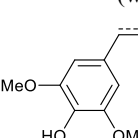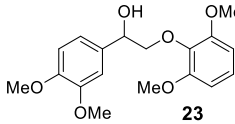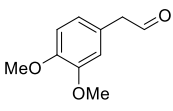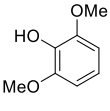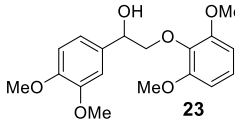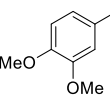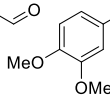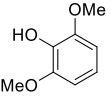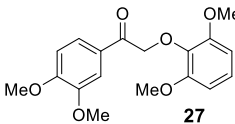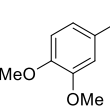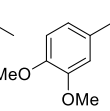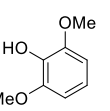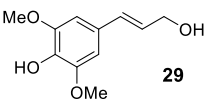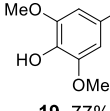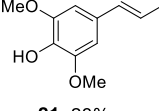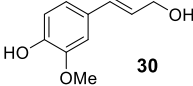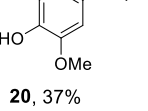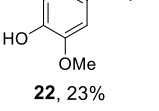| Entry	H-donor [equiv]	Pulp[a] [wt%]	MeO– structure	H structure	Other[b] [wt%]	Total [wt%]	pH[c]
1	-	33	1	1	3	**5**	3.6
2[d]	HCO$_2$H + HCO$_2$Na 5+5	38	1	1	4	**6**	4.1
3[d]	-	31	1	1	4	**6**	3.6
4	HCO$_2$H 10	29	7	4	6	**17**	3.1
5	HCO$_2$Na 10	63	8	3	7	**18**	6.7
6	HCO$_2$H + HCO$_2$Na 5+5	32	19	7	8	**34**	4.8

Reaction conditions: birch (200 mg), catalyst (30 mg, Co 1 mol%), EtOH/H$_2$O (6 mL 1:1 v/v), 200 °C, 4 h; [a] Ratio of dry pulp mass to the dry substrate. The cellulose content of the substrate is 38 wt%; [b] See ESI of paper III for details [c] pH measured after DCM-water extraction by diluting the aqueous phase to 25 mL; [d] No catalyst.

4.4 Mechanistic study on lignin model compounds

To investigate the role of the catalyst, we reacted model compounds varying the reaction conditions (Table 4.2). While reacting native β–O–4' model compound **23** in the absence of a catalyst, 59% of reactive aldehyde **24** and 90% of syringol (**25**) were formed, confirming that the acidity of formic acid is sufficient to cleave the β–O–4' bond. The lower yield of **24** in comparison with **25** depended on the re-condensation of the monolignols produced by acid-catalyzed cleavage (Table 4.2, entry 1). When using Co/phen on native β–O–4' model compound **23**, full conversion was observed.

Table 4.2 Study of lignin model compounds.

Entry	Substrate	H-donor [equiv]	Conv. [%]	Major products, selectivity [%]
1[a]	**23**	HCO$_2$H 3	95	**24**, 59% **25**, 90%
2	**23**	HCO$_2$H 3	>99	**24**, 63% **26**, 23% **25**, 97%
3	**27**	HCO$_2$H 3	>99	**28**, >99% **26**, trace **25**, 93%
4	**29**	HCO$_2$H + HCO$_2$Na 3+3	87	**19**, 77% **21**, 23%
5[b]	**30**	HCO$_2$H + HCO$_2$Na 3+3	>99	**20**, 37% **22**, 23%

Reaction conditions: substrate (0.18 mmol), Co-phen/C (20 mg 0.8 mol%), EtOH/H$_2$O (6 mL, 1:1 v/v), 200 °C, 2 h. [a] No catalyst used. [b] 39% dimers detected.

Moreover, 23% of the stabilized product **26** was detected and an increased yield (86%) of monolignols (**24** + **26**) was observed (Table 4.2, entry 2). Furthermore, we investigated the reaction with a β–O–4' model (**27**) that is unable to undergo acid-catalyzed cleavage. The reaction with the oxidized model **27** gave only the ketone **28** as a monolignol derivative, suggesting that the cleavage occurred through hydrogenation/hydrogenolysis (Table 4.2, entry 3). The ability of the catalyst to stabilize reactive molecules generated by solvolysis was also tested by treating the reactive monomers (**29** and **30**) under optimized catalytic conditions. Good yields of HDO products were observed, confirming the role of the catalyst (Table 4.2, entries 4 and 5). As expected, the G-unit monomer **30** underwent partial condensation showing dimers among the products.

4.5 Summary

In conclusion, we were able to substitute noble metals with a first-row transition metal, such as cobalt, keeping comparable reactivity towards reductive catalytic fractionation of birch. However, to perform a hydrogenation/hydrogenolysis reaction, the catalytic system needed an external source of hydride. By this, we produced up to 34% of phenolic compounds from birch using a cobalt-based catalyst supported on nitrogen-doped carbon. By reacting different model compounds, the roles of the solvolysis and the heterogeneous catalyst have been elucidated. We found that the catalyst is both stabilizing the monolignols produced *in situ* by acid-catalyzed solvolysis and also reductively cleaving the β–O–4' inter-unit motifs through hydrogenation/hydrogenolysis. The mixture of HCO_2H/HCO_2Na acts both as hydrogen donor and as buffer providing the optimal pH for the biomass solvolysis. The yields of monophenolic compounds showed in this report are comparable with the ones reported by other catalytic systems based on noble metals, with a clear advantage in terms of catalyst availability and cost. However, catalytic systems based on noble metal do not need any external source of hydrogen since they can exploit hemicellulose as a reducing agent. Thus, our catalytic system fills a gap between the efficient noble-metal-based heterogeneous catalysis, such as Pd,[65] and Ru,[117,118] and the inexpensive, but less efficient, Raney Ni-based ones required in stoichiometric amounts.[119]

5 OrganoSoxhlet: a circular fractionation to produce pulp for textiles (Paper IV)

5.1 Background

The dissolving pulp used for the production of textile fibers is characterized by high purity: high glucan and α-cellulose content, specific intrinsic viscosity, and high brightness.[120,121] To achieve such a quality material from wood, lignin and hemicellulose have to be removed during the fractionation process without affecting the cellulose. In the *lignin-first* process described in chapter 4, the pulping was performed parallelly to lignin valorization, running the fractionation and the catalysis in the same reaction medium. A clear drawback of *lignin-first* approaches is the partial exploitation of the carbohydrate fraction. Indeed, in RCF the solid residues are always contaminated with the heterogeneous catalyst which would later need a higher solvent consumption for the extra purification step and catalysis recycling. Even though relatively high yields of monophenolic compounds can be produced, treating lignocellulose by *lignin-first* has been reported to yield mainly a low-quality pulp only suitable for enzymatic hydrolysis, further lowering the industrial appeal of the process. Because of this, *lignin-first* has been belittled into *lignin-only*. Several methods have been proposed to overcome the pulp contamination with the heterogeneous catalyst during RCF, ranging from the confinement of the catalyst into porous containers to the utilization of flow-through reactors or even use the same catalyst to further react the residual cellulosic material yielding liquid products.[56] However, every methodology proposed so far comes with major drawbacks. When confining a heterogeneous catalyst in a container metal leaching, clogging and the particle size of the catalyst support are limiting the process. For instance, common catalysts supported on activated charcoal would not fulfill the requirements. Flow-through systems generally use a large amount of solvents to perform the same reaction run in a batch hindering the industrialization of this procedure. Further utilizing the catalyst used for the RCF for a supplementary catalytic step would surely overcome the need for the separation of solids. However, the pulp is not the final product of this process. Therefore, the development of a pulping system able to reduce the consumption of solvents and perform the catalysis step without vitiating the final product is still of

great interest. The Soxhlet extractor is a common piece of laboratory glass-ware used in chemistry which use regenerated solvents to perform an inter-mittent flow of extracting solvents. It consists of a boiler and a reflux with the purpose of regenerating the solvents, a thimble which holds the solid sample and a syphon that periodically unloads the regenerated solvents back to the boiler. However, the temperature of extraction is limited by the boiling point of the chosen solvent mixture which refluxes. Therefore, when considering to perform pulping in a Soxhlet, the choice of solvents would be limited to high boiling ones, since most of the processes work in a range of temperature of 180-250 °C, further complicating the separation of the generated lignin oil.[64] High-pressure Soxhlet extractor overcomes this limitation as it is confined into an autoclave where the initial and the operating pressure can be controlled. It is currently used in few applications, mainly as a test device to check the solubility of solids in compressed gases, like refrigerating gases and low boiling point solvents such as ammonia.[122–124] In this work we investigated the possibility to perform RCF of poplar using a system based on a high-pressure Soxhlet extractor combined with EtOH:H_2O organosolv which we named OrganoSoxhlet.

5.2 Reactor design and operation

The reactor consists of a 600 mL autoclave equipped with a thermocouple, a gas valve, and a cooling coil (Figure 5.1). The gas valve allows the loading of the reactor with pressurized gas at room temperature. Inside the autoclave, two cups made of acid-proof stainless steel are positioned on top of each other: a collecting cup (CC) and on top of it, an extraction cup (EC) equipped with a siphon that unloads directly into the CC. The substrate, wrapped in a stainless-steel net with a mesh of 0.25 mm or in a cotton fabric cloth, is positioned in the EC just below the cooling coil to let the drops of freshly distilled solvent drip directly on it. The EC allows the thermocouple to pass through and measure the temperature of the liquid contained in the CC. During the loading operation, 200 mL of solvent is poured into the CC in contact with the heat source. The autoclave is sealed and the proper amount of gas is loaded. The positive pressure results in a higher boiling point of the solvent. The heat provided to the CC by a heating mantle creates the vapors which condense once in contact with the cooling coil. The role of the steam is both to supply fresh solvent for the pulping and to heat the EC. Once the level of the condensed solvent reaches the top of the siphon, it is discharged into the CC.
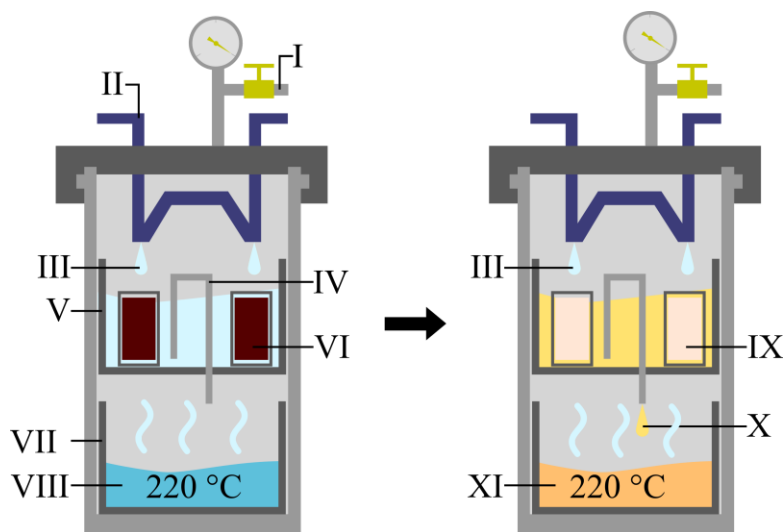
Figure 5.1 Schematic summary of the OrganoSoxhlet reactor. I: gas inlet, II: cooling coil, III: freshly distilled solvent enriched in EtOH, IV: siphon, V: extracting cup (EC), VI: substrate, VII: collecting cup (CP), VIII: EtOH:H_2O 1:3, IX: pulp, X: extraction liquor, XI: concentrated extraction liquors possibly containing a heterogeneous catalyst.

5.3   Substrate choice

As mentioned before, dissolving grade pulp derived from lignocellulose fractionation can be an alternative to cotton for the production of textiles.[30,49] Short rotation forestry has demonstrated the capability to supply the necessary amount of substrate, with an advantage in terms of soil and resource consumption. [125–127] For our study, we selected the genotype 23.4 of *Populus Trichocarpa* as the source of lignocellulosic biomass. The growth rate in cold climate regions of this clone has been recently investigated for the Baltic Sea Region, reporting an annual dry yield of 9.9 tons of biomass per hectare.[128] The composition of the poplar 23.4 wood meal consists of 43.2 wt% of glucans, 12.4 wt% of xylans, and 25.1 wt% of lignin (AIL+ASL) with an S:G ratio of 1.6 and a β–O–4' content of 51%. Extractives accounted for 4.4 wt% while ashes residues 0.6 wt%. Both sawdust and sticks were wrapped with a porous material, either stainless steel net or cotton fabric. The cotton fabric mass loss was used as an index of the degree of degradation of the glucan fraction in the substrate.

5.4 Organosolv optimization

Initial attempts were performed with 5 g of biomass and 200 mL of EtOH:H$_2$O mixture 1:1,[129–131] setting the temperature at 220 °C and the cooling flow rate at the maximum (1 L/min). Under these conditions, carbonization in EC and coke formation in CC were observed. By loading the liquors through the EC and soaking the substrate before the extraction the carbonization in the EC was prevented, yet coking in the CC was not eliminated. We proposed that this was because of the complete evaporation of the solvents in the CC at 13~15 barg and 220 °C, the operating conditions when the system was sealed at atmospheric pressure. It was possible to reach the operating pressure of approximately 25~30 barg at 220 °C with the addition of 8 barg of inert nitrogen gas at room temperature. Under these reaction conditions, H$_2$O is merely below its boiling point, obtaining more controlled evaporation of liquors which resulted in a severe reduction of coke formation in the EC and CC. Unfortunately, the weight loss of the substrate, measured after 4 h to evaluate the pulping efficiency, was a poor 37.3 wt% when the aimed value of *c.* 50 wt% (Table 5.1, entry 1). The chemical analysis of the solids gave 15 wt% of lignin and 10 wt% hemicellulose, indicating an incomplete pulping. It is known that acids promote the hydrolysis of the LCCs and the release of lignin.[132–136] The autoclave nature of the OrganoSoxhlet reactor gave us the possibility to load benign and easily recoverable carbon dioxide as both acid and initial positive pressure source. Changing the atmosphere into CO$_2$ resulted in a lower pH of the liquors.[137] The new conditions gave 54 wt% of mass loss associated with a high purity of the solid residue (Table 5.1, entry 2). The comparison of the different atmospheres confirms the beneficial effect of CO$_2$ on delignification and removal of hemicellulose.
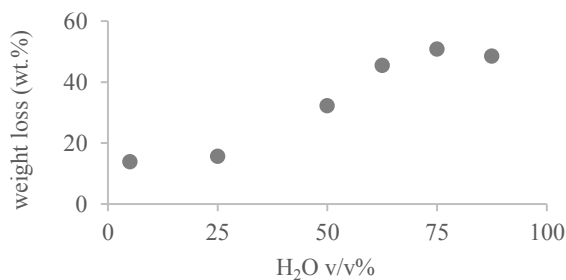
Figure 5.2 Weight loss versus solvent composition. Reaction conditions: of CO$_2$ (8 barg), poplar 23.4 sawdust (5 g) as substrate, total solvent volume 200 mL, reaction time 4 h.
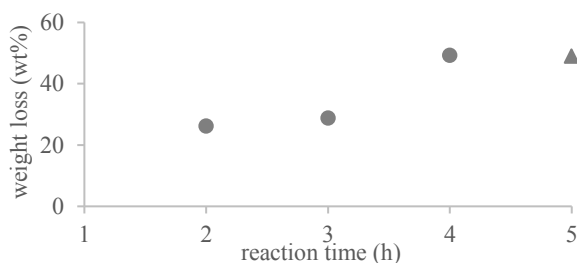
Figure 5.3 Weight loss versus reaction time. Reaction conditions: CO_2 8 barg, substrate (5 g), EtOH:H_2O (1:3 v/v, 200 mL). The triangular dot (5 h) represents a high degradation of fabric cloth (14 wt% mass loss).

The EtOH to H_2O ratio was investigated and the optimal solvent composition was found to be 25 v/v% of EtOH in H_2O (Figure 5.2). Our system needs a relatively low concentration of EtOH, 25 v/v% if compared to the previously reported EtOH:H_2O organosolv systems where the optimal concentration is usually ranging between 35-70 v/v%.[138–141] This is due to the maximum amount of solvent containable together with the substrate in the EC (approx. 100 mL). Thus, before being unloaded the liquor composition in the EC is enriched in EtOH, the solvent with the lower boiling point. Optimal results were achieved after 4 h (Figure 5.3). Prolonged reaction time resulted in an initial sugar degradation as shown by the mass loss of the fabric cloth (14 wt%). Lower cooling flow rates were investigated. A cooling rate flow of 0.5 L/min resulted in a slower condensation rate of the liquors and a consequent reduced pulping degree resulted in 31 wt% of mass loss (Table 5.1, entry 3). When no cooling flow was applied, both substrate and containers underwent carbonization (Table 5.1, entry 4). Therefore, 1 L/min was used as the optimal cooling flow rate. The pulping performance was independent of the mass of the substrate loaded in the reactor. The maximum biomass loading of the extracting cup reached 18.7 g of sawdust per batch, still run with 200 mL of EtOH:H_2O mixture 1:3 (Table 5.1, entry 5). This is due to the high dilution of the extracting solutions since the solvents that get in contact with the substrate are always freshly distilled.

Table 5.1 Pulping optimization.

Entry	Gas	Mass loss [wt%]	Lig [wt%]	Glu [wt%]	Xyl [wt%]
1	N_2	37.3	15	60	10
2	CO_2	54.0	2	94	2
3[a]	CO_2	31.0		-	-
4[b]	CO_2	58.7	-	-	-
5[c]	CO_2	54.8	4	90	3

Reaction conditions: gas (8 barg), substrate (5 g), EtOH:H_2O (200 mL, 1:3 v/v). Water flow 1 L/min. [a] No water flow, carbonized substrate, cloth bag mass loss 10 wt%. [b] Water flow 0.5 L/min. [c] Substrate 18.7 g.

5.5 Pulp quality optimization and solvent recycling

An attempt to produce dissolving grade pulp by using sawdust led to a low viscosity material, a sign of degraded cellulose. Aiming at a higher quality, the sawdust was substituted for wood sticks (approx. 35 x 2 x 2 mm) that underwent the same optimized treatment as for sawdust and yielded 51.7 wt% of dry substance. (Table 5.2, entry 1). Since the chemical composition of the solid residues was similar, we suggest that the lower mass loss observed when reacting wood sticks compared to sawdust is due to the lower amount of micro-particles of wood that are formed during the reaction and can pass through the porous containers. Our theory was supported by a lower coke formation observed in the CC when sticks were used. The lower density of the sticks compared to the sawdust resulted in a maximum loading of the reactor of approximately 10 g per run. To further optimize the solvent consumption, we performed a recycling study by running a series of subsequent reactions where the spent liquors were kept in the CC and new containers holding fresh substrate positioned in place of the reacted ones. Three cycles were investigated giving comparable results in terms of purity of the solid residues and yields (Table 5.2, entries 2–4). By this, up to 30.1 g of wood was fractionated using only 200 mL of solvent with a liquid to wood ratio of 6.6. If considering only the organic component of the liquors the ratio is reduced to 1.7 ethanol to wood ratio.

Table 5.2 Solvent recycling study.

Entry	Mass loss [wt%]	Lig [wt%]	Glu [wt%]	Xyl [wt%]	
1	48.3	3	94	3	Control
2	48.3	3	94	3	I cycle
3	49.1	4	92	3	II cycle
4	47.1	6	90	4	III cycle

Reaction conditions: 220 °C, 4 h, cooling flow 1 L/min, EtOH: H_2O (200 ml, 1:3 v/v), CO_2 (8 barg) at RT, poplar 23.4 sticks (10 g) as substrate.

5.6 Pulp disintegration and bleaching

To obtain dissolving grade pulp from the reacted biomass, the fibers stacked in the delignified wood needed to be liberated. With the help of an automatic disintegrator, unbleached pulp was achieved in 44 wt% yields versus initial wood (85 wt% from the previous step). Elemental chlorine-free (ECF) bleaching was applied, using sodium chlorite and NaOH:AcOH 1:1 buffer solution (see SI of paper IV) to obtain bleached pulp in 43 wt% versus initial

wood (98 wt% of unbleached pulp).[142] A slab made of bleached pulp was analyzed by the standard method ISO 2470-1 resulting in more than 91% of ISO-brightness. α-cellulose content was also analyzed and resulted in 90.6%. The bleached material was further tested for viscosity (442 mL/g) and DP (610) fulfilling the requirement for lyocell production.[143–145]

Material	A Raw sticks	B Treated sticks	C Pulp	D Bleached pulp
Klason lignin[wt%]	25	3	3	<1
Glucan [wt%]	42	94	94	98
Xylan [wt%]	12	3	3	2
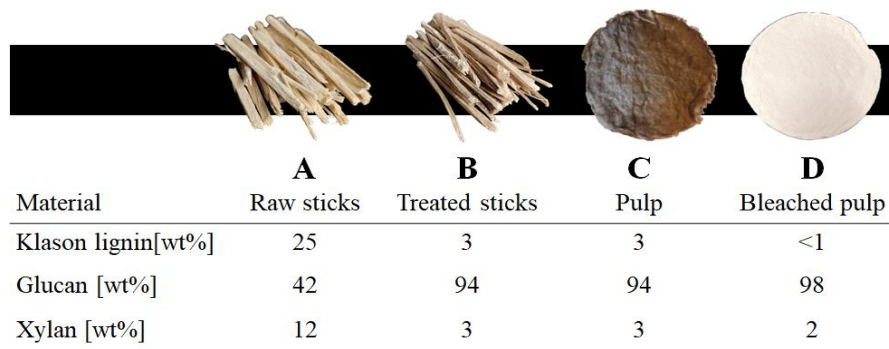
Figure 5.4 Poplar 23.4 composition over time, from sticks to bleached pulp.

5.7 Heterogeneous catalysis

To valorize the lignin fraction together with the cellulose according to RCF methodology, we needed to include a redox-active heterogeneous catalyst able to transform the molecules derived from lignin produced by solvolysis, as described in Section 1.4. The design of the reactor allowed us to involve a heterogeneous catalyst active towards the required chemical transformation of the compounds produced during the process avoiding its contact with the pulp (Figure 5.5).
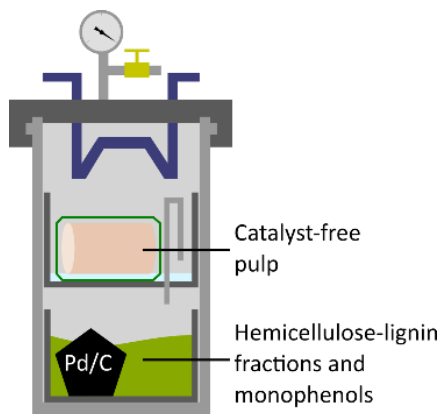
Figure 5.5 Catalytic Organosoxhlet.

Indeed, in most of the *lignin-first* approaches, it is extremely challenging to obtain a final product with proper ISO brightness since the heterogeneous catalyst, usually a dark powder, contaminates the treated biomass. In our version of RCF, the CC was used as a catalytic reactor while the pulping was run in the EC exploiting the same heat source. The organosolv liquors contain mono- and oligomeric fractions of lignin, highly reactive compounds prone to re-condensate. Including a heterogeneous catalyst under reducing conditions enabled the transformation of these fragments into stable and valuable compounds through hydrodeoxygenation/reduction.[146] Palladium has been reported to exploit sugars derived from hemicellulose as a hydride donor.[147] Thus, common Pd/C was chosen as the heterogeneous catalyst and no external source of hydrogen was involved. When using 4 mol% of Pd versus the initial amount of lignin monomers, 17 wt% of lignin oil in respect to the initial biomass was obtained, in accordance with our previously reported RCF on poplar.[147] The lignin oil was further analyzed by GC-MS/FID and 2 wt% of monophenolic compounds in respect to the biomass were detected while in the lignin oil collected in absence of the catalyst, (27 wt%), no monomers were detected demonstrating the activity of the catalyst. The reacted wood produced with Pd/C in the CC showed the same properties and composition as the one reacted without the catalyst. However, the monophenolic yield is low when compared to the previously reported in batch with the same catalyst. Therefore, further optimization is required to achieve optimal results of the catalysis performance.

5.8 Summary

In this chapter, we presented a pulping system able to achieve dissolving grade pulp with chemical-physical properties matching the requirements for lyocell production. The proposed methodology involved a high-pressure Soxhlet extractor coupled with ethanol/water organosolv without any acidic pretreatment on the biomass since gaseous carbon dioxide was used both to increase the initial pressure of the reactor and reduce the pH of the liquors. Up to 30.1 g of lignocellulosic biomass derived from short rotation forestry was treated with 200 mL of $EtOH:H_2O$ 1:3 v/v, achieving a promising liquid to wood ratio of 6.6 (1.7 considering only the organic fraction). The reactor design enabled the involvement of a heterogeneous catalyst, usually detrimental to the purity of the pulp, with no contamination. The utilization of 4 mol% of commercially available Pd/C produced monophenolic compounds and deoxygenated lignin oil when added to the CC.

Concluding remarks

The presented thesis dissertates four different approaches to valorize ligno-cellulosic biomass directly or its side streams.

In Chapter 2 we showed the ability to perform hydrodearomatization (HDA) on phenolic compounds derived from lignin thermal degradation *via* heterogeneous catalysis. By employing a commercially available catalyst (Pd/C) and an alternative hydrogen source (PMHS/water) HDA was achieved. Interestingly, we found that by slightly changing the amount of water in the reaction medium, the chemo-selectivity could be adjusted: either cyclohexanones or cyclohexanols could be selectively synthesized from a large scope of bio-oil model compounds. Commercial bio-oils such as bee-chwood tar creosote and cardanol were also fully transformed into more valuable products. Thus, we were able to reach high and ductile selectivity with small adjustments when transforming complex mixtures of bio-derived molecules.

In Chapter 3 a study on kraft lignin valorization via esterification was proposed. The presented strategy consisted of a 3-step procedure where kraft lignin was isolated, then transformed *via* esterification with fatty acids into a lignin-oil and later hydrotreated. The main focus was set on the elucidation of the reaction mechanism. By using ^{13}C labeled reactants, the mechanism concerning the esterification of kraft lignin with fatty acids catalyzed by pyridine was investigated. The resulting mechanistic proposal suggested initial acetylation with a consequent transesterification, mainly operated on the phenolic moieties, disproving a previous proposal.

Chapter 4 concerns the catalytic fractionation of birch wood sawdust in a one-pot batch reaction using a first-row transition metal as a reducing catalyst. We found that lignin got partially depolymerized by solvolysis, where formic acid plays a crucial role in the cleavage of LCCs. Studying the model compounds, we showed that the cobalt-based catalyst supported on nitrogen-doped carbon had different roles. A major role was to stabilize the reactive phenolic molecules by transforming them into prop(en)yl guaiacols and syringols. Moreover, the catalyst was contributing to the de-polymerization of the oligomers and thereby the final yield of monophenolic compounds. This study showed that precious metals previously used can be exchanged for a first-row transition metal, without reducing the efficiency of the catalytic system.

In Chapter 5, a holistic pulping strategy is introduced. Dissolving grade pulp was obtained from short rotation derived hardwood combining a high-pressure Soxhlet extractor with EtOH:H_2O based organosolv. CO_2 was found crucial for the LCCs cleavage since it lowers the liquor pH while being used to increase the pressure of the system. This system worked with a liquid to wood ratio of 6.6 obtaining a final product that matches the requirements for textile production. Parallelly, RCF was performed without contaminating the pulp nor needing a further washing step. Adding Pd/C to the system yielded a deoxygenated lignin oil containing monophenolic compounds, without affecting the pulping.

In conclusion, different contributions to the biomass valorization field have been proposed and discussed in this thesis which aims to inspire researchers to continue investigating selective transformations of complex mixtures of bio-derived molecules using alternative catalysts, reactants, and reactor design.

Appendix A: Contribution list

Author's contribution to each paper (referred to their roman numerals):

I.   Performed all the experimental work, the data analysis, wrote the manuscript and the supporting information.

II.   Conceived the mechanistic study, performed the mechanistic study, the data analysis, wrote the manuscript, and the supporting information. Elucidated the mass balance of the process (not included in the thesis).

III.   Contributed equally with Dr. Sari Rautiainen. Participated in catalyst synthesis, experimental work, and relative GC/MS analysis. Participated in the writing of the manuscript and supporting information.

IV.   Conceived the process, designed the reactor, performed the pulping and RCF reactions, wrote the manuscript, and contributed to the supporting information.

Appendix B: Reprint permissions

Reprint permissions were granted by the publishers for each publication (referred to their roman numerals):

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        Adv. Synth. Catal. **2018**, 360, 3924.
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II.   D. Di Francesco, C. Dahlstrand, J. Löfstedt, A. Orebom, J. Verendel, C. Carrick, Å. Håkansson, S. Eriksson, H. Rådberg, H. Wallmo, M. Wimby, F. Huber, C. Federsel, M. Backmark and J. S. M. Samec
        ChemSusChem **2021**.
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III.   S. Rautiainen,† D. Di Francesco,† S. N. Katea, G. Westin, D. N. Tungasmita, J. S. M. Samec
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        † Authors contributed equally
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