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VTT
http://www.vtt.fi
P.O. box 1000FI-02044 VTT
Finland

**RESEARCH REPORT**

VTT-R-01428-20

# Hydrothermal and fast pyrolysis processes of biomass for valorization of lignin streams

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| Authors: | VTT: Marc Borrega, Taina Ohra-aho, Tiina Liitiä, Juha Lehtonen, Tarja Tamminen<br>Åbo Akademi: Ekaterina Kholkina, Narendra Kumar, Dmitry Murzin<br>VITO: Kristien De Sitter, Kelly Servaes |

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**Summary**

The LF4Value project investigated the application of the *Lignin First* philosophy to create the maximum value to lignin-based streams. The *Lignin First* philosophy, which considers lignin as the main biomass component to be valorized, was implemented by using chemical additives for reactive protection of lignin in two established thermal treatments of biomass: hydrothermal pre-treatments for saccharification, and fast pyrolysis processes.

The addition of 2-naphthol to the hydrothermal pre-treatment of pine wood improved its saccharification by two-fold, presumably because lignin condensation during the pre-treatment was minimized. On the other hand, chemical additives in the pre-treatment of birch and willow wood were not needed to achieve almost quantitative saccharification. The analyses of hydrolysis lignins from birch revealed differences in their composition and structure by the use of 1- and 2-naphthol, consistent with a lower extent of lignin condensation. Selected hydrolysis lignins from pine, birch and willow were successfully used as filler in PLA-based composites at 20% lignin loading. The addition of lignin slightly decreased the tensile strength and strain of PLA without significant increase in tensile stiffness. However, the different PLA/lignin composites exhibited a similar mechanical performance, which seemed to indicate that differences in lignin structure were not relevant.

The addition of chemical additives to fast pyrolysis of wood did not change the distribution of lignin- and carbohydrate-derived degradation products, probably because the reaction times were too short for the additives to react. The addition of 2-naphthol, however, slightly enhanced the stability of the fast pyrolysis bio-oils in long-term storage. The use of slag-based catalysts in fast pyrolysis demonstrated that the catalysts changed the product distribution and the yield of degradation products. However, the catalysts did not appear to prevent the recondensation of lignin pyrolysis products and consequently the yield losses in bio-oil. Both analytical and bench scale pyrolysis trials produced similar trends in product composition, even if the actual values differed, and thus analytical pyrolysis could be used for screening purposes.

The complex composition of the synthesized slag catalysts and the biomass feedstocks challenged the analysis of catalytic trends and structure-performance relationships. Therefore, the slag catalysts were tested in a model chemical reaction to assess their catalytic activity. Such model reaction was the carboxymethylation of cinnamyl alcohol with dimethyl carbonate to produce cinnamyl methyl carbonate. The use of catalysts resulted not only in high conversion and selectivity to the desired product, but also illustrated the dependence of the conversion on the basicity and surface area of the catalysts.

The biochars obtained in bench scale pyrolysis of wood were activated and acid washed prior to their use as catalyst for the post-treatment of degradation vapors in analytical pyrolysis of pine wood. The activated biochars reduced the oxygen content of the pyrolysis degradation products, particularly in those compounds derived from polysaccharides. The most promising catalyst for vapor upgrading was unwashed activated carbon from willow, having high surface area and pore volume together with high mineral contents (due to the presence of bark).

The lignin fraction in the bio-oils from bench scale pyrolysis of wood was precipitated by addition of water, but the membrane fractionation of a reference bio-oil was also investigated. The results from membrane nanofiltration showed that a compromise had to be found with respect to lignin yield in the permeate, permeate purity, and purity of the high MW fraction in the retentate.

The pyrolysis lignins obtained by addition of water to the bio-oils were tested for substitution of phenol in the synthesis of phenol-formaldehyde resins. The lignins were found to be highly reactive and prone for condensation reactions already during the dissolution phase in alkali. Oxidation of catechols appeared to enhance the attachment of phenol into birch pyrolysis lignin, preventing self-condensation and increasing the number of reactive sites for formaldehyde. With the more reactive pine pyrolysis lignin, the oxidation further enhanced the self-condensation, and crosslinking of phenol in general was lower.

Finally, the direct upgrade of fast pyrolysis bio-oil into transportation fuels by catalytic HDO was investigated. The carbonyl content decreased with increasing treatment temperature, indicating improved stability of the bio-oil. However, the water content also increased, indicating that considerable amounts of carbon were either cracked to gases or remained in the reactor as coke. This was further supported by the low yields of liquid product. The bio-oil was a very challenging feedstock for upgrading by HDO due to its high oxygen content, with highly reactive oxygenates.

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| **Written by** | **Reviewed by** | **Accepted by** |
|---|---|---|
| Marc Borrega | Tarja Tamminen | Kristian Salminen |
| Senior Scientist | Principal Scientist | Vice-President |

**VTT's contact address**

Tietotie 2, Espoo, P.O. Box 1000, FI-02044 VTT, Finland

**Distribution**

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# Preface

This report summarizes the work done within the LF4Value project, funded by Business Finland from September 2017 to August 2020. The research partners were **VTT Technical Research Centre of Finland Ltd** (coordinator), **Åbo Akademi,** and **VITO** (Flemish Institute for Technological Research), which participated with own funding as external collaborator. The project was also financially supported by the following industrial partners: **Stora Enso Oy, St1 Oy, Hexion, Raumaster, and Carbons Finland Oy.**

Several scientists and lab technicians in the research groups have contributed to the project, and their skillful contribution is gratefully acknowledged.

Espoo 24.11.2020

Marc Borrega

# Contents

# 1. Introduction

Lignocellulosic biomass is an abundant and renewable raw material that is becoming increasingly important as a source of precursors for chemicals, materials and fuels. Traditional thermochemical processes (such as pulping) for conversion of lignocellulosic biomass have focused on the exploitation of the carbohydrate fraction, primarily cellulose, and have neglected the potential of lignin as raw material. Lignin is an aromatic polymer that accounts for 20-32% of the dry biomass, depending on plant species. The lignin in the side-streams from pulping and other biorefinery processes is completely different in terms of structure and properties from the native lignin in the original biomass. Loss of the distinctive beta-ether structures of lignin, followed by condensation reactions and formation of C-C bonds, which are difficult to cleave, are typical phenomena in all types of biomass processing. Even if such technical lignins find value in various applications, their valorization potential may be significantly limited. Therefore, the only way to exploit the full potential of lignin is to consider it as the primary biomass component for valorization. This *Lignin First* approach can be applied by reactive protection of lignin during biomass processing in established thermal processes such as hydrothermal treatments (as pre-treatment for saccharification) and fast pyrolysis.

# 2. Background

## 2.1 Hydrothermal treatments

Hydrothermal treatments are a key pre-treatment step in the biochemical processing of lignocellulosic biomass to platform sugars. The pre-treatment renders the carbohydrates in biomass accessible for enzymatic saccharification, and the released sugars are then fermented or upgraded catalytically to desired fuels and chemicals. Hydrolysis lignin is a major co-product of the process, and thus finding high value applications for these lignins would have a great impact on the economic viability of fuel production from woody feedstocks.

Hydrothermal pre-treatments introduce drastic changes to the chemical structure of lignin. The major chemical changes involve depolymerization through cleavage of β-O-4 bonds, followed by repolymerization through the formation of C-C condensed linkages (Shevchenko et al., 1999). Radical species in lignin formed at high temperature and under acidic conditions are responsible for condensation reactions. Low molecular-weight compounds can be used to scavenge carbocations and radical species, and thus control the extent of condensation reactions taking place in the native lignin (Wayman and Lora, 1978). Recently, the addition of the phenolic compound 2-naphthol to the hydrothermal pre-treatment was shown to improve enzymatic saccharification of spruce wood, and this effect was ascribed to a reduction in lignin condensation as well as in unproductive enzyme binding (Pielhop et al., 2015). Formaldehyde has also been shown to prevent lignin condensation in wood during pre-treatment (Shuai et al., 2016). Lignin modification and prevention of condensation reactions during hydrothermal pre-treatment is likely to improve the enzymatic hydrolysis of cellulose and hemicellulosic sugars, and it may also enhance the application potential of hydrolysis lignins.

## 2.2 Fast pyrolysis processes

Wood-based fast pyrolysis bio-oil is presently entering into the heating oil market to replace fossil fuel oils and natural gas in boilers. The first commercial size pyrolysis plants are operational in Finland, in the Netherlands and in Canada. The composition and properties of bio-oil is completely different from conventional fossil liquid fuels or other bio-oils in the market. In addition to direct use as fuel in boilers, bio-oil has also potential for further upgrading to transportation fuels via fractionation and hydrodeoxygenation (HDO) processes. However, the instability of bio-oil is a bottleneck that limits its application potential. Secondary reactions of lignin during pyrolysis leading to condensation are expected to be the main phenomenon behind the instability of bio-oils, even if the specific reaction mechanisms are not well understood.

Hydrogen deficiency during depolymerization is one cause for condensation via radical coupling. This problem is especially severe in the absence of potential hydrogen donors, which is the case when pyrolyzing isolated lignin compared to the whole biomass, in which polysaccharides may act as reducing agents. In addition to the radical coupling route, ionic reactions via the alfa-carbocation may also take place as secondary reactions as described for the hydrothermal route. Therefore, the same chemical additives that prevent lignin condensation in hydrothermal pre-treatments may also act as stabilizing agents in fast pyrolysis processes. The expected benefits are increased stability of the bio-oil to be used either as fuel, as feed for conversion into traffic fuel, or alternatively as raw material for biomaterials such as resins. Lignin conversion in fast pyrolysis can be further boosted by the use of catalysts.

## 2.3 Slag catalysts

Recycling of slags from pyrometallurgical processing of natural ores has attracted much attention due to the possibility of converting slags into value-added products while diminishing waste (Dhoble and Ahmed, 2018). Ferrous slag is a by-product mostly produced during recovery of iron from the ores in the process of steel manufacturing (Piatak et al., 2015). The composition of ferrous slags is dominated by calcium (Ca) and silica (Si), with variable amounts of aluminum (Al), iron (Fe), magnesium (Mg) and other elements (Yildirim and Prezzi, 2011; Veselská and Majzlan, 2016). Slags can be applied in specialized market sectors, mainly road construction (Bocci, 2018) and cement production (Liu et al. 2017), but about ca 70% of the slags are still disposed of by landfilling (EUROSLAG, 2012; Dhoble and Ahmed, 2018). One option to lower the environmental impact and to enhance resource conservation is related to the application of slags in catalysis, benefitting from the unique properties of the slags. In particular, their elemental composition comprising a range of basic oxides along with oxides exhibiting acidic properties allows the synthesis of efficient, low-cost and environmentally friendly catalytic materials. Several research groups have successfully utilized steel slags in the synthesis of zeolite A, ZSM-5, and hydroxyapatite–zeolite composite materials (Sugano et al., 2005; Anuwattana et al., 2008; Kuwahara et al., 2009). Other studies are dedicated to the application of slags as catalytic supports (Dimitrova et al., 2004; Yu et al., 2017), or as catalysts per se (Kar and Gürbüz, 2016). Therefore, low-cost materials synthesized from steel slags may be utilized in catalytic fast pyrolysis of biomass or in other catalytic applications.

## 3. Objectives

The main objective of this project was to develop technologies to create a maximum added value to lignin-based biomass streams by applying the *Lignin First* philosophy. This goal was pursued by reactive protection of lignin during biomass processing in two established thermal processes: hydrothermal pre-treatments (for saccharification) and fast pyrolysis.

The project aimed at providing tools to control the lignin condensation reactions that take place during hydrothermal pre-treatment and fast pyrolysis of wood. For the hydrothermal route, the goal was to obtain a lignin residue (after saccharification) with application as biopolymer in materials requiring thermoplastic properties. For the pyrolysis route, the goal was to obtain a stable bio-oil of good quality and in high yield, with application in resin formulations or for upgrading into fuels via the hydrodeoxygenation (HDO) process.

Finally, the project also aimed at developing novel catalysts based on waste material from the metal industry (slag) or biochars from biomass waste. The potential of willow as biomass raw material was also to be demonstrated, which could create business for the forestry sector and machinery manufacturers (e.g. debarking).

## 4. Biomass raw materials

Pine, birch and willow wood were used as raw materials for the hydrothermal pre-treatments and fast pyrolysis experiments. Industrial pine and birch chips were delivered by Stora Enso, and 2-year old willow stems were provided by Carbons Finland. The willow wood contained bark because the small diameter of the stems hinders the use of conventional debarking equipment. However, for experimental purposes, a few willow stems were manually debarked with a knife. The wood materials were ground to a particle size of 0.5 – 1 mm (<0.5 mm for debarked willow wood) prior to their utilization in the hydrothermal and pyrolysis processes. Softwood hydrolysis lignin from bioethanol production, provided by St1, was also used as raw material in fast pyrolysis experiments. The raw materials are shown in Figure 1, and their chemical composition is listed in Table 1.

**Figure 1.** *From left to right: pine chips, birch chips, willow stems, hydrolysis lignin.*

***Table 1.*** *Identified chemical composition of the raw materials, shown as % on initial dry mass.*

| | Pine | Birch | Willow (no bark) | Willow (with bark) | Hydrolysis lignin |
|---|---|---|---|---|---|
| Extractives | 1.9 | 0.8 | 1.h4 | 0.8 | 4.5 |
| Glucose | 40.0 | 35.1 | 34.7 | 34.0 | 24.2 |
| Mannose | 11.5 | 1.7 | 1.6 | 1.7 | 1.4 |
| Xylose | 4.2 | 18.6 | 14.7 | 12.6 | 0.1 |
| Galactose | 1.7 | 0.7 | 0.6 | 0.9 | 0.3 |
| Arabinose | 1.4 | 0.4 | 0.4 | 0.7 | 0.2 |
| Rhamnose | 0.1 | 0.4 | - | - | - |
| *Subtotal sugars* | *58.9* | *56.9* | *52.0* | *49.9* | *26.2* |
| Acetate | 1.3 | 2.8 | 3.2 | 2.7 | nd |
| Klason lignin | 27.3 | 20.5 | 23.0 | 27.7 | 60.2 |
| Acid soluble lignin (ASL) | 0.2 | 2.3 | 2.5 | 2.4 | 1.2 |
| *Subtotal lignin* | *27.5* | *22.8* | *25.5* | *30.1* | *61.4* |
| Ash | 0.3 | 0.3 | 0.6 | 1.2 | 0.3 |
| Total | 89.9 | 83.6 | 82.7 | 84.7 | 92.4 |

Nd – not determined; carbohydrates are shown as polymeric sugars; the values are not corrected for losses in the acid hydrolysis stage during compositional analyses.

### 4.1 Lignin pelletizing

A protocol for pelletizing hydrolysis lignin was developed at VTT to improve the feeding of lignin into the reactor in fast pyrolysis processes. The protocol included screening and drying of the lignin, pelletizing, and final drying of the pellets. Drying of lignin was a slow and energy-intensive process, and thus pelletizing of wet lignin would be preferred. Nonetheless, the preparation of lignin pellets could be demonstrated, as seen in Figure 2.

***Figure 2****. Pellets of hydrolysis lignin.*

## 5. Catalyst development

### 5.1 Slag catalysts

#### 5.1.1 Synthesis and characterization of slag-based catalysts

Industrial desulfurization slag provided by SSAB (Finland) was used as a starting material for the catalyst synthesis. The slag, containing $SiO_2$, $Al_2O_3$, FeO, $Ca(OH)_2$, $CaCO_3$ and other minor components, was first crushed by ball milling and sieved to a particle size below 90 µm. The catalytic materials were synthesized by applying different procedures (Figure 3). Application of ultrasound (US) as an additional intensification tool involved a two-step synthesis, including pre-treatment with US and post-treatment at ambient or hydrothermal conditions. Some slag catalysts were also obtained without the US step, by stirring at ambient conditions or by hydrothermal synthesis in autoclaves operated in rotation mode. The catalytic materials were synthesized upon variation of the treating agent type (distilled water, 0.6M NaOH, 0.6M HCl solution, 0.6M ethylenediaminetetraacetic acid (EDTA) – 0.6M NaOH mixture, 0.1M tetraethyl ammonium hydroxide (TEAH) – 0.6M NaOH mixture), synthesis temperature (25˚C or 150˚C) and time (4h, 24h or 48h), US power (50, 80 or 100W) and US time (4h or 8h). Another approach based on a published procedure (see Kuwahara et al., 2009) comprised a multi-step treatment with 1M $H_3PO_4$ and 3M NaOH.

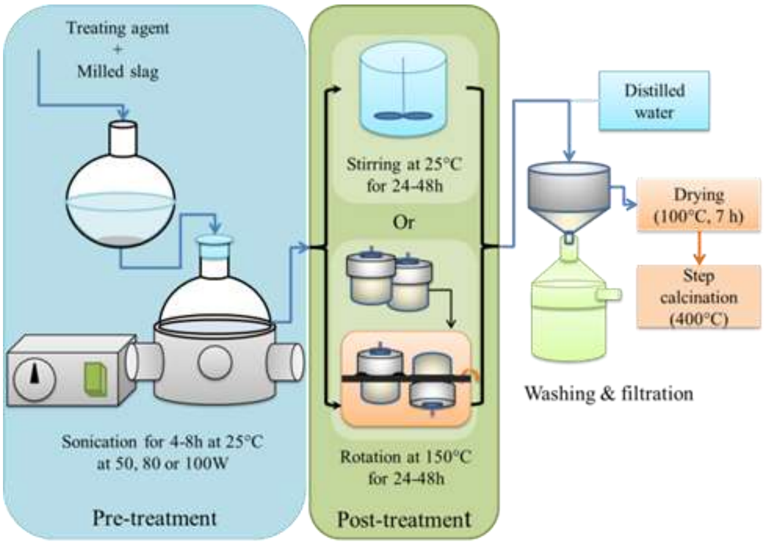

***Figure 3**. Scheme of the synthesis of slag catalysts.*

After synthesis, all samples were filtered, washed with distilled water, dried at 100˚C for 7h, and further calcined at 400°C. The synthesized materials were characterized by several analytical techniques including: nitrogen physisorption for determination of specific surface area and pore volume, scanning electron microscopy to study the crystals morphology (i.e. shape and size), transmission electron microscopy for investigation of the structure, porosity, metal particle size and channel systems, X-ray powder diffraction analysis to study the phase composition and purity, and temperature-programmed desorption of $NH_3$ and $CO_2$ to determine the amount and strength of acid and basic sites. More detailed information about the synthesis of slag-based catalysts and their characterization is presented in Kholkina et al. (2019a,b).

Slag processing resulted in significant changes in the textural and structural properties of the material (Figure 4). The formation of crystals, their size and shape was directly related to the synthesis conditions and to the chemical nature of the treating agent. During treatment, the slag material underwent dissolution with formation of a gel and subsequent recrystallization into new phases. Ambient synthesis conditions resulted in the formation of needle shape crystals (Figure 4a), while application of high synthesis temperature resulted in crystallization of the slag phases into round shapes (Figure 4b). The major changes in the crystal shape and size occurred in those slags in which calcium was the main component.

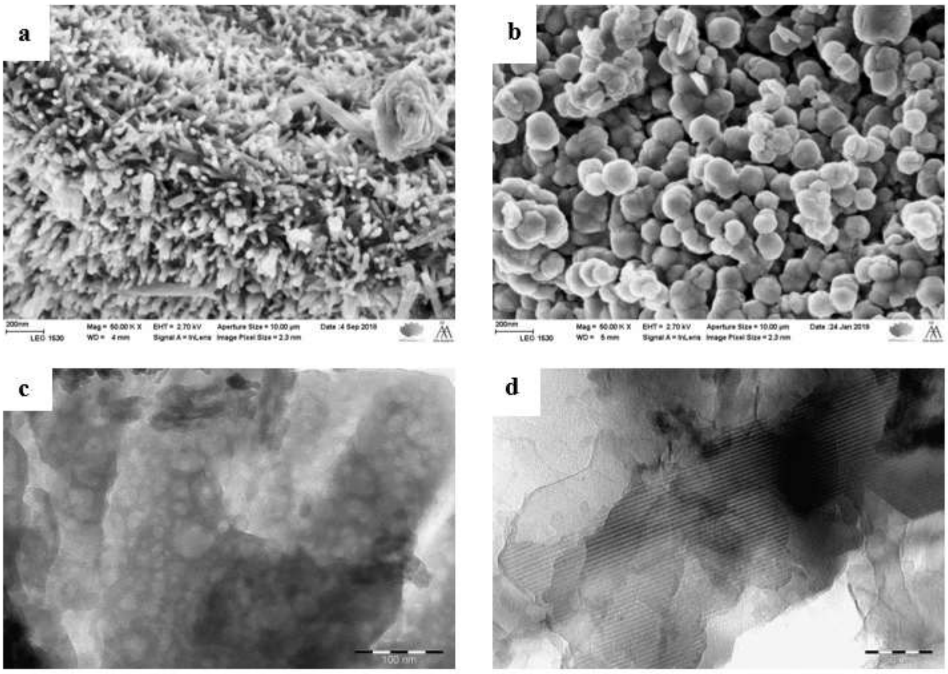

***Figure 4**. Scanning (a, b) and transmission (c, d) electron micrographs of the slag catalysts. Synthesis conditions were: a) $H_2O$ st 48h; b) H2O US (50W, 4h) rot 48h 150˚C; c) $H_2O$ st 48h; d) TEAH EDTA US (50W, 4h).*

Utilization of some treating agents (i.e. HCl, $H_3PO_4$ and EDTA) led to materials without specific morphologies, due to high leaching of calcium and its poor precipitation. At the same time, calcium dissolution resulted in the formation of pores (Figure 4c) and internal channels (Figure 4d) that enhanced the surface area. In most cases, treatment of the slag increased the surface area and pore volume of the synthesized materials in comparison with the initial slag (6 $m^2$/g). The highest surface area (64 $m^2$/g) was obtained for the catalyst prepared by a multi-step procedure with $H_3PO_4$ and NaOH. The XRD analysis showed that the industrial slag and the synthesized catalysts exhibited highly crystalline phases containing $CaCO_3$, $Ca(OH)_2$, $SiO_2$, $Al_2O_3$, $Fe_2O_3$ and $TiO_2$. The basicity of the synthesized catalysts had a strong dependence on the calcium content regulated by the leaching ability of the applied chemical agents, and on the synthesis and sonication conditions. Utilization of the US step generally showed a positive effect on the concentration of basic sites after the treatment.

### 5.1.2 Catalyst evaluation in analytical fast pyrolysis of woody biomass

The catalytic properties of the synthesized slag-based materials were evaluated in analytical fast pyrolysis of pine wood at VTT, with the aim of replacing acid zeolites, which are well-known pyrolysis catalysts. In particular, the slag-based catalysts were tested to investigate the influence of basicity on the yield and distribution of degradation products. Details of the testing procedure are described in Kholkina et al. (2019a,b). The catalytic results were dependent on the slag treatment and on the properties of the catalysts. It can be seen in Figure 5 that the slag materials significantly decreased the yield of degradation products, indicating their cracking ability, and resulted in high char formation. The highest yield was achieved with the catalyst containing the highest amount of basic sites. The catalytic pyrolysis of pine wood also demonstrated that the synthesized slag catalysts changed the distribution of degradation products, in comparison with thermal pyrolysis or with application of an unmodified industrial slag. The utilization of the slag-based materials reduced the oxygen content in the side chains structures of phenolic products, improving the properties of the produced bio oil. However, the complexity of the slag composition and the biomass feedstock made the analysis of catalytic trends relating structure with performance much more challenging.

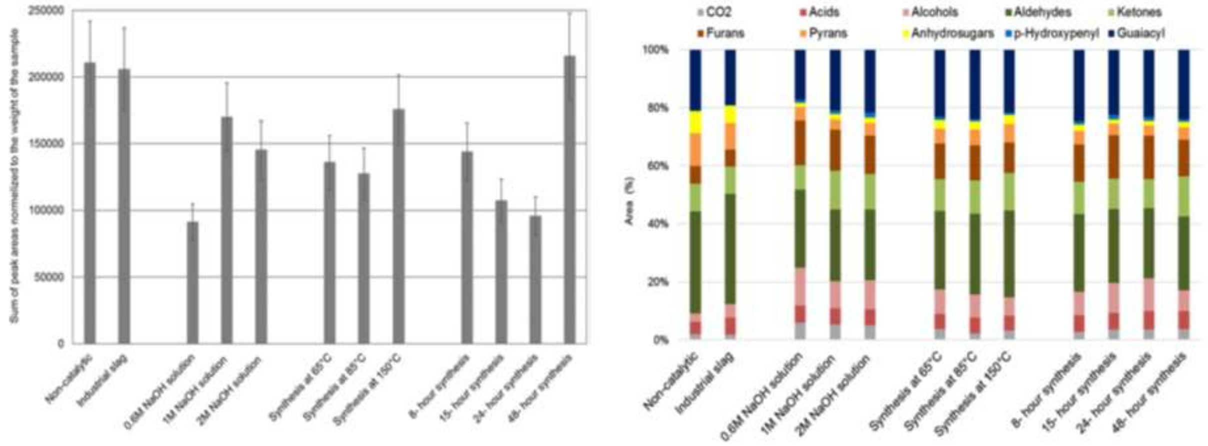

*__Figure 5__. The yield of degradation products (left) and their distribution (right) by analytical pyrolysis of pine wood with alkaline-treated slags.*

### 5.1.3 Catalyst evaluation in carboxymethylation reaction

The complexity of the elemental composition of the slag required its catalytic activity to be evaluated in a simple model reaction for a clear understanding of the influence of the material properties. Such suitable model reaction was the base-catalyzed carboxymethylation of cinnamyl alcohol (CA) with dimethyl carbonate (DMC), resulting in the formation of cinnamyl methyl carbonate (product I, Figure 6). Cinnamyl methyl carbonate is a valuable organic compound with application as an allylic electrophile in asymmetric allylic substitution (Cheng et al., 2019), and in synthesis of biologically active compounds (Gao et al, 2012; Tundo et al., 2018). At the same time, this reaction meets the requirements of Green Chemistry by using a green solvent (DMC) and a reactant produced from renewables (CA).

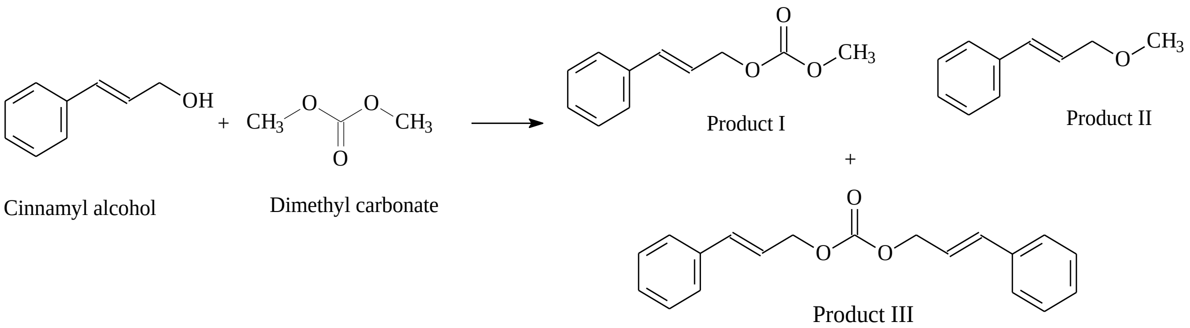

*__Figure 6__. Carboxymethylation of cinnamyl alcohol (CA) with dimethyl carbonate (DMC).*

Experiments were carried out at 150°C in a batch reactor with the slag catalysts and, for comparison, with commercial materials: $K_2CO_3$, hydrotalcite, MgO, $NaAlO_2$ and NaY zeolite. The results in Figure 7 showed that treatment of the slag was beneficial for the catalytic activity, indicated as increased conversion of CA in comparison with the untreated slag or with a blank experiment. The application of a US pre-treatment step in the synthesis of the slag-based materials allowed a higher conversion in comparison with the catalysts synthesized without the US step. The comparison of the commercial catalytic materials with the slag catalysts further confirmed the competitiveness of the latter, especially because of a higher stability to leaching in the reaction media. The utilization of low-cost slag materials allowed achieving high conversion levels (up to 85%) with ca. 89% of selectivity to the desired product (at 60% of CA conversion), making them potentially applicable in various base-catalyzed reactions.

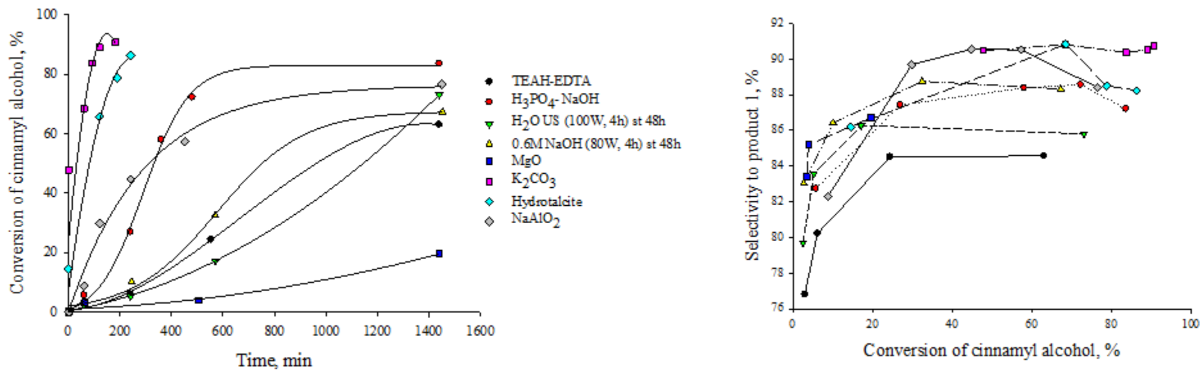

***Figure 7.*** *Conversion of cinnamyl alcohol (CA) as a function of time (left), and selectivity to the product I (see Figure 6) as a function of CA conversion (right).*

## 5.2 Biochar catalysts

### 5.2.1 Preparation and characterization of activated carbons

Biochars (BCs) produced by fast pyrolysis of pine, birch and willow (with bark) wood (see Section 6.2) were activated with steam and analyzed for their elemental composition, surface oxygen groups, surface area, and porosity. In addition, the willow BC and steam-activated willow were chemically activated by sulfonation. The sulfur-activated carbons (ACs) were analyzed similarly to the steam-activated ACs (Figure 8).

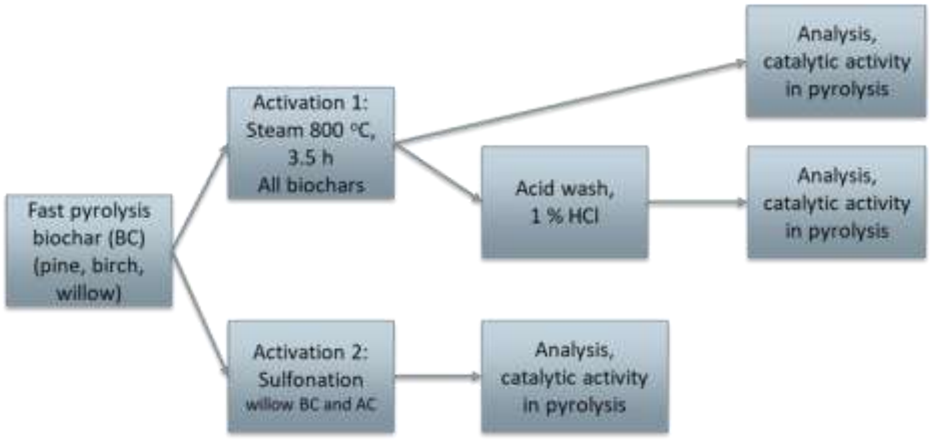

***Figure 8.*** *Activation scheme of biochars produced by fast pyrolysis of pine, birch and willow (with bark) wood.*

All the BCs had a high carbon content, which increased further by the steam activation treatment (Table 2). The BCs had approximately the same distribution of oxygen, hydrogen and sulfur, while the nitrogen content was the highest for the willow BC. The nitrogen content in willow was also the highest among the ACs. Because of the bark, the willow BC had a higher ash content than the other BCs. Based on the contents of nitrogen (N) and oxygen (O), willow was found to be the most promising candidate for catalytic pyrolysis experiments and thus selected for the sulfonation treatment, as both N and O have been found to increase the catalytic performance. The sulfonation treatment slightly increased the amount of sulphur (S), indicating successful addition of sulphur-containing groups to the surface of willow BC and AC.

***Table 2**. Elemental and ash content of the biochars (BCs) and activated carbons (ACs).*

| Sample | | C, wt-% | H, wt-% | N, wt-% | S, wt-% | O, wt-% | Ash, wt-% |
|---|---|---|---|---|---|---|---|
| Willow | BC | 76.2 | 3.5 | 0.9 | 0.019 | 19.1 | 7.4 |
| | AC | 87.4 | 0.6 | 0.8 | 0.06 | 6.3 | 8.6 |
| Willow, sulfonated | BC | 72.5 | 3.3 | 0.9 | 0.08 | 18.7 | nd |
| | AC | 89.6 | 0.8 | 1.0 | 0.06 | 6.3 | nd |
| Birch | BC | 76.7 | 3.5 | 0.3 | 0.016 | 18.8 | 2.2 |
| | AC | 93.7 | 0.6 | 0.5 | 0.02 | 3.8 | 3.1 |
| Pine | BC | 77.7 | 3.7 | 0.1 | 0.01 | 18.1 | 1.5 |
| | AC | 94.6 | 0.6 | 0.4 | <0.02 | 2.7 | 2.3 |

The BET surface area of the unwashed carbons could not be determined, probably due to the high ash content which caused pore clogging. Therefore, the results in Table 3 correspond to the BCs and ACs after acid washing. The surface area and porosity of the BCs were significantly increased by the steam activation treatment, in agreement with literature reports for different types of BCs. Sulfonation of the willow BC and AC further increased the surface area and pore volume. Originally, the BCs were mostly mesoporous with small amounts of macropores, but the steam activation increased the micropore volume. Sulfonation predominantly increased the amount of mesopores in the willow AC.

***Table 3**. Surface area, porosity, and oxygen group content of the biochars (BCs) and activated carbons (ACs) after acid washing (AW).*

| Treatment | | BET surf. area | Total pore volume, $cm^3/g$ | Micro-pores, <2 nm | Meso-pores, 2-50 nm | Macro-pores, >50 nm) | Carbox. groups, % | Lact. groups, % | Phen. groups, % | Total acidity, mmol/g |
|---|---|---|---|---|---|---|---|---|---|---|
| AW Willow | BC | 5 | <0.01 | 10 % | 76 % | 13 % | 16 | 39 | 45 | 1.02 |
| | AC | 295 | 0.13 | 88 % | 12 % | 0.5 % | 18 | 16 | 66 | 0.10 |
| AW Willow, sulfonated | BC | 23 | 0.03 | 0 % | 87 % | 13 % | 28 | 32 | 41 | 1.40 |
| | AC | 382 | 0.18 | 64 % | 34 % | 2 % | 41 | 24 | 35 | 0.34 |
| AW Birch | BC | 24 | 0.03 | 0 % | 96 % | 4 % | 11 | 35 | 54 | 1.01 |
| | AC | 329 | 0.13 | 87 % | 12 % | 0.2 % | 58 | 15 | 27 | 0.20 |
| AW Pine | BC | 26 | 0.03 | 0 % | 97 % | 3 % | 10 | 35 | 55 | 0.58 |
| | AC | 340 | 0.15 | 84 % | 16 % | 0.1 % | 68 | 10 | 22 | 0.13 |

Since surface oxygen groups are important in determining catalytic activity, Boehm titration was conducted on the biochars and ACs to quantify their carboxylic, lactonic and phenolic surface groups. The results in Table 3 show that the steam activation treatment reduced the amount of acidic groups on the carbon surfaces. The decrease of acidic surface groups can be related to the general decrease of oxygen and hydrogen content, which occurs during steam activation treatments. Prior to the steam activation, all biochars had a similar functional group composition, consisting mostly of phenolic groups. The steam treatment reduced the amount of phenolic groups and increased the amount of carboxylic groups in pine and birch, but not in willow. In willow, the amount of phenolic groups was further enhanced by the activation treatment, while the carboxylic groups remained at the same level as in the biochar. The amount of lactonic groups decreased in all activated carbons. Sulfonation increased the total acidity of both willow biochar and AC, and changed the group composition to resemble that of pine and birch AC, in which the carboxylic group was the most dominant.

### 5.2.2 Post-treatment of pyrolysis vapors

Selected BCs and ACs were used as catalyst in the post-treatment of vapors from analytical pyrolysis of pine wood. In the post-treatment, the vapors formed in pyrolysis at 500 °C passed through the catalyst (kept at 250 °C) and ended up in a gas chromatography and mass spectrometry (GC/MS) device for analysis. The catalytic activity of the BCs and ACs was assessed based on the vapor composition, and the results were compared to those from thermal pyrolysis using the same experimental set-up. In addition, two commercial ACs (palladium on activated carbon, Pd/C and Maxsorb) were also tested using a slightly different method, in which the catalysts were mixed with the biomass before pyrolysis (at the same temperature).

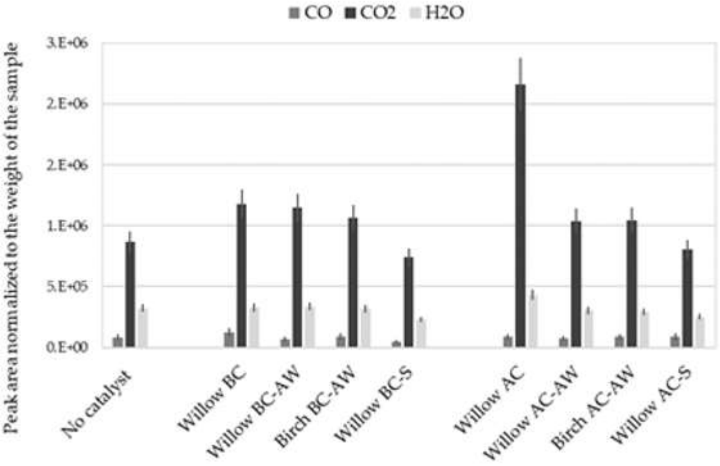

***Figure 9.*** *Gas and water release in thermal pyrolysis and after post-treatment. BC= biochar, AW=acid washed, S=sulfonated, AC=activated carbon.*

The post-treatment of pyrolysis vapors changed the formation of gas components and water compared to thermal pyrolysis (Figure 9). The BCs and ACs enhanced the formation of $CO_2$, while the sulphonated willow BC and AC slightly decreased it. The most significant increase in $CO_2$ formation was obtained with the unwashed willow AC, and was probably promoted by the high mineral content of the BC together with the increase in surface area and porosity after steam activation. On the contrary, leaching of minerals by acid washing led to a decrease in $CO_2$ formation. The formation of water followed the same trend as $CO_2$, being also the highest with the unwashed willow AC. A slight increase in formation of CO was observed with willow BC, but the other catalysts gave similar results as in thermal pyrolysis treatment (without catalyst).

A multivariate analysis using principal component analysis (PCA) was used to evaluate the differences in catalytic activity between char materials (Figure 10). Acid washing changed the activity of willow BC and AC. Moreover, after acid washing, the activation method had a higher effect than the feedstock type (birch, willow). Sulfonated BC showed similar activity as acid washed ACs, while sulfonated AC showed similar activity as acid washed BC. Finally, the commercial ACs had similar activity with respect to each other, but differed slightly from the char materials developed in this project (Figure 11). The commercial carbon materials altered similarly the lignin-derived products, while changes in carbohydrate derivatives were minor.

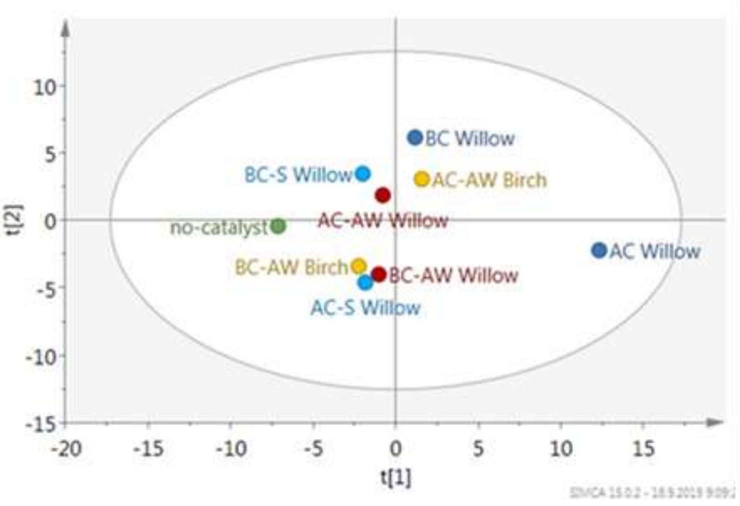

***Figure 10.*** *Differences in catalytic activity among post-treatments. BC= biochar, AW=acid washed, S=sulfonated, AC=activated carbon, B=birch, W=willow.*

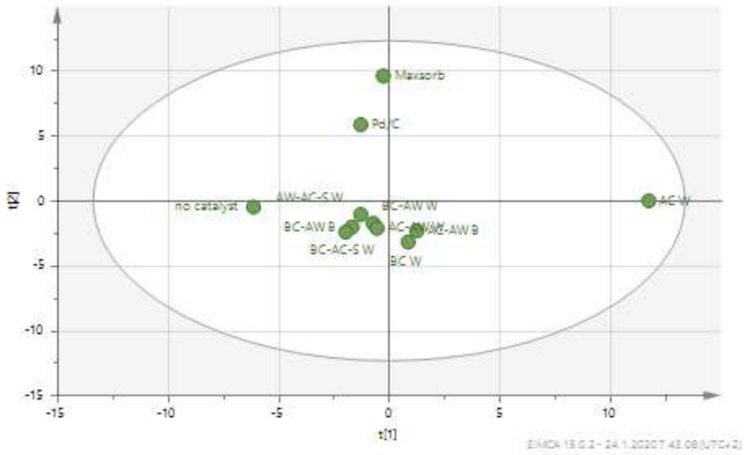

***Figure 11**. Differences in catalytic activity between char materials developed in the project and commercial activated carbon (Maxsorb) and carbon with palladium (Pd/C).*

## 5.3 HDO catalysts

Two catalyst samples (Pd-MgO and Pd-$SiO_2$) were prepared by Åbo Akademi to be tested at VTT in the HDO of fast pyrolysis bio-oil. MgO and $SiO_2$ were chosen as supports since they are present in steel slag materials. The evaporation impregnation method was chosen for the deposition of active metal Pd, and palladium nitrate was used as metal precursor. The synthesis of the catalysts was carried out in a rotator-evaporator for 24 h, followed by drying at 100 °C and calcination at 400 °C. Based on the transmission electron micrographs (Figure 12), better metal dispersion (Pd particle size 6-18 nm) was achieved by applying $SiO_2$ as a support, while somewhat larger Pd particles (16-74 nm) were observed on MgO.

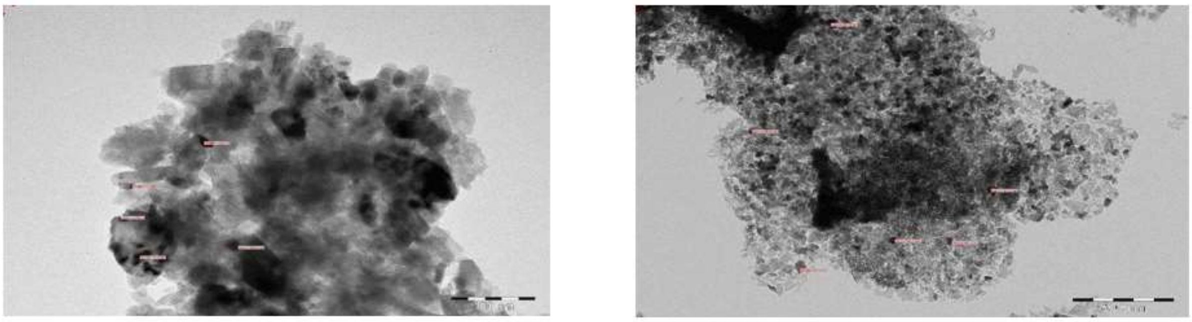

***Figure 12.*** *Transmission electron micrographs of Pd-$SiO_2$ (left) and Pd-MgO (right) catalysts.*

## 6. Fast pyrolysis processes

### 6.1 Selection of materials with analytical pyrolysis

Analytical pyrolysis was used to screen the effect of slag-based catalysts and chemical additives on the fast pyrolysis of wood (pine, birch and willow) and hydrolysis lignin samples, in order to find the best parameters for bench scale pyrolysis experiments. The combination of biomass feedstock, catalyst and chemical additive used in the analytical pyrolysis experiments is shown in Table 4. The analytical pyrolysis experiments were carried out at 500 °C, using a residence time of 4 seconds. The temperature selected was close to the temperature used in bench scale pyrolysis, but the residence time was a bit longer due to the different instrumentation.

***Table 4.*** *Combinations of biomass feedstock, catalyst and chemical additive tested in analytical fast pyrolysis. Data correspond to the biomass to additive ratio used in the experiments.*

| | No additive | Non-modified slag | Modified slags | 2-Naphthol | Formalin* | Calcium formate |
|---|---|---|---|---|---|---|
| Pine | 1:0 | 1:10 | 1:1, 1:5, 1:10 | 1:0.1, 1:0.05 | 1:0.1, 1:0.05 | 1:0.14; 0.28, 1:0.7; 1:1.4 |
| Birch | 1:0 | | 1:10 | | | 1:0.7; 1:1.4 |
| Willow (with bark) | 1:0 | | | | | |
| Willow (no bark) | 1:0 | | | | | |
| Willow bark | 1:0 | | | | | |
| Hydrolysis lignin | 1:0 | | 1:10 | | | 1:0.7; 1:1.4 |

*Formalin is a 37% aqueous (water) solution of formaldehyde with 10-15% methanol.

In analytical pyrolysis, the vapors from the degradation products formed are measured by GC/MS, while in bench scale pyrolysis, gas, liquid and char products are separately formed and collected. The pyrolysis degradation products in analytical pyrolysis represent the liquid product in bench scale pyrolysis, and hence can be used to study the depolymerisation performance of biomass samples.

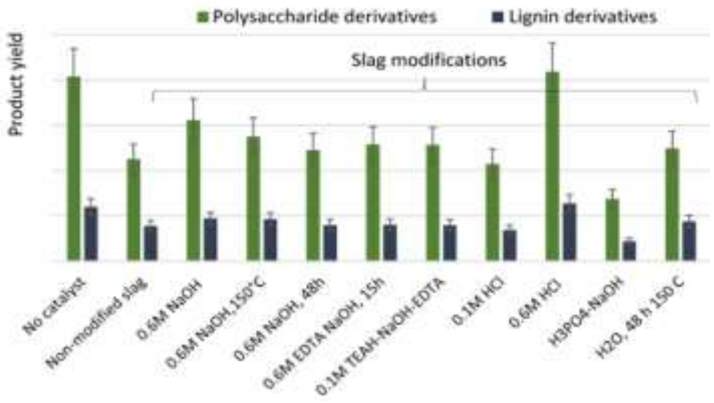

***Figure 13**. Changes in product yield in catalytic analytical pyrolysis of pine wood.*

The catalytic activity of the non-modified slag and slag-based catalysts was detected as a decrease in product yield and enhanced conversion of polysaccharides to low molecular weight compounds (Figure 13). The lignin was less altered than the carbohydrates, and the main change in lignin degradation products was a decrease in oxygen-containing functional groups (OH, C=O). The slag-based catalysts did not show any indication as potential hydrogen donors, which would prevent recondensation reactions of lignin pyrolysis products and consequently reduce yield losses. However, the release of reactive oxygen functional groups from the lignin side-chain might improve the stability of the bio-oil, even if yield losses occurred. The best catalyst with respect to the expected results, i.e. decrease in oxygen content and yield losses, was obtained with the non-modified slag, and therefore this material was selected for the bench scale pyrolysis experiments.

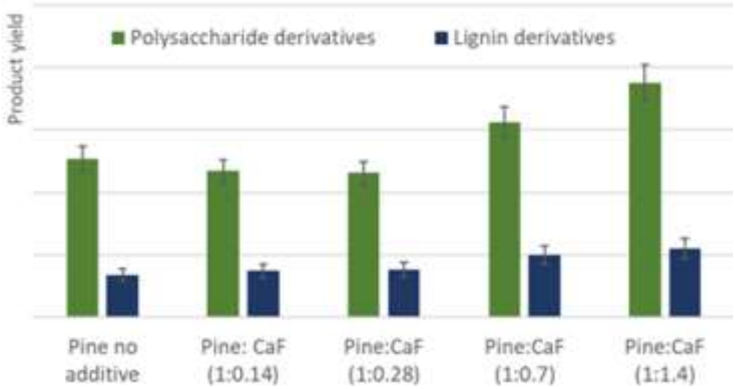

***Figure 14**. Changes in product yield in analytical pyrolysis of pine wood with calcium formate (CaF), with different biomass to additive ratios.*

The role of calcium formate as hydrogen donor in fast pyrolysis of pine wood was detected as enhanced depolymerisation of lignin and formation of more stable pyrolysis degradation products. The oxygen-containing functional groups in lignin decreased and the yield of lignin-derived products at high biomass-to-additive ratios (1:0.7 and 1:1.4) was increased (Figure 14). A similar effect was observed with the formation of polysaccharide derivatives. Calcium formate was not studied in bench scale because several other studies have already shown its effect on the composition of fast pyrolysis bio-oils.

The use of chemical additives such as 2-naphthol and formaldehyde in pyrolysis was motivated because the additives were expected to react with unstable lignin degradation products, thus preventing their repolymerisation in the bio-oil. However, such effect was not observed. Similar distribution of lignin and polysaccharide derived products was detected with and without additives (Figure 15). It was concluded that both 2-naphthol and formaldehyde were unable to prevent lignin condensation in fast pyrolysis as the reaction time was probably too short. Nonetheless, it was decided to test 2-naphthol in bench scale pyrolysis experiments to evaluate its effect on the formation of lignin derivatives in the bio-oil.

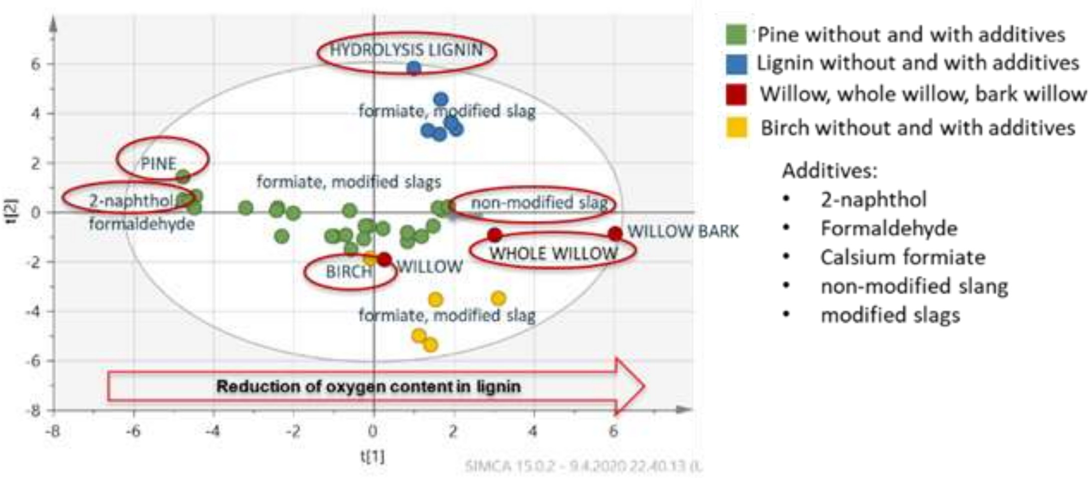

***Figure 15**. Principal component analysis of pyrolysis data from different biomass feedstocks with and without additives. The score plot of two principal components shows how pyrolysis experiments are related to each other based on the lignin degradation products. Materials, chemicals and catalysts selected for bench scale experiments are circled in red.*

## 6.2 Bench scale pyrolysis experiments

Bio-oil from different biomass feedstocks (pine, birch, willow and hydrolysis lignin) was produced in VTT's 1 kg/h bench scale unit, based on a bubbling fluidized-bed reactor in which aluminum oxide sand is used as fluidizing agent. The char left after pyrolysis was separated from the gases with two cyclones. After the cyclones, the hot vapors and gases were quenched rapidly and the bio-oil was condensed in the liquid recovery system by three coolers and one electrostatic precipitator (Figure 16). The composition of the non-condensable gases was analyzed by GC. In addition to the bio-oil, the biochar was also collected for utilization in the development of carbon-based catalysts (see Section 5.2).

The experimental conditions used in the bench scale pyrolysis experiments are shown in Table 5. Ethanol-impregnated pine was used as reference for the 2-naphthol case, which contained also small amounts of ethanol as needed for additive impregnation. The additive 1-naphthol was used because it was not expected to react with lignin similarly as 2-naphthol. In the in-situ catalytic pyrolysis experiment, aluminum oxide was replaced with the non-modified slag catalyst.

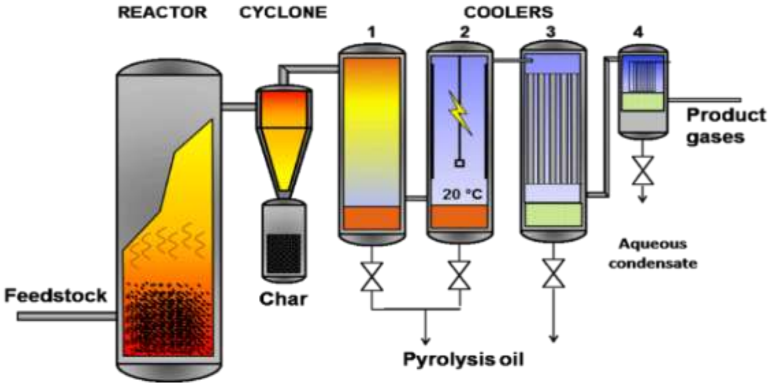

***Figure 16.*** *Schematic representation of VTT's bench scale fast pyrolysis unit.*

The fast pyrolysis of pine with the non-modified slag changed the proportions of product yields (Table 5), as due to the catalytic activity, more gas was formed together with char instead of liquid. Willow was pyrolysed with bark, which contained a high metal content. These metals acted as a catalyst enhancing gas formation similarly to the use of an external catalyst. The pyrolysis of hydrolysis lignin, containing more lignin and less sugars than the wood materials, resulted in the formation of more char and less liquid product. The increase of liquid yield with the use of naphthols was due to the added chemicals.

***Table 5.*** *Experimental conditions used in bench scale pyrolysis and yields of liquid, gas and biochar.*

| Feedstock | Pine | Pine | Pine | Pine | Pine | Birch | Whole Willow | Hydrolysis lignin |
|---|---|---|---|---|---|---|---|---|
| Additive | no | Non-modified slag | Ethanol | 1-naphthol | 2-naphtol | no | no | no |
| Ratio | | | | 1:0.05 | 1:0.05 | | | |
| Temperature, °C | 480 | 480 | 480 | 480 | 480 | 480 | 480 | 500 |
| Residence time, s | 0.8 | 1.0 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 1.1 |
| Cyclone char, wt-% | 13 | 17 | 13 | 12 | 11 | 11 | 19 | 29 |
| Gases, wt-% | 9 | 16 | 10 | 9 | 8 | 9 | 11 | 7 |
| Liquid, wt-% | 62 | 37 | 63 | 68 | 69 | 66 | 47 | 42 |
| Pyrolytic water, wt-% | 8 | 18 | 9 | 8 | 10 | 8 | 14 | 6 |

In general, the composition of the fast pyrolysis bio-oils (FPBOs) from different wood feedstocks was rather similar (Figure 17). Catalytic pyrolysis of pine with a non-modified slag enhanced the lignin yield in the FPBO and slightly reduced the oxygen content of the bio-oil, which was desirable for the subsequent upgrading of the bio-oil as fuel. The use of naphthols did not have significant effect on the composition of the FPBO, while ethanol used for additive impregnation slightly reduced the content of HMW lignin fraction since ethanol acted as hydrogen donor. The FPBO from hydrolysis lignin contained more lignin-derived compounds compared to the other FPBOs, obviously due to the higher lignin and lower carbohydrate content of the hydrolysis lignin feedstock. The results of bench scale and analytical pyrolysis showed similar trends in product composition, even if the actual values were not the same (Figure 18).

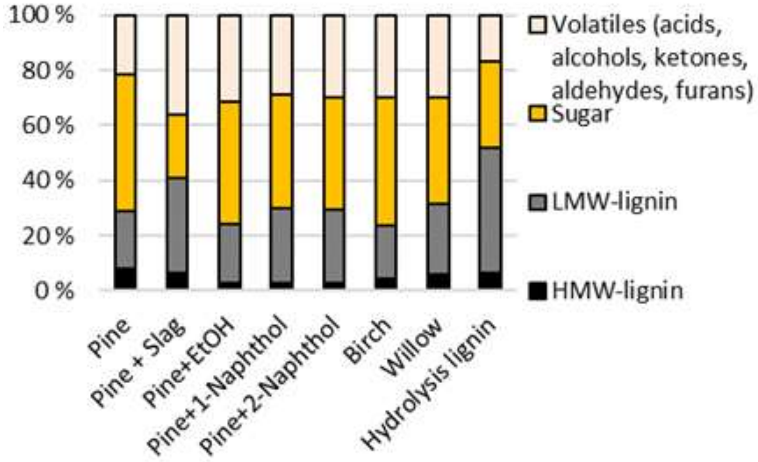

**Figure 17.** *Composition of fast pyrolysis bio-oils (FPBOs) determined as volatiles (sum of acids, alcohols, ketones, aldehydes and furans), sugars (polysaccharide derivatives), and low (LMW) and high molecular weight (HMW) lignin derivatives.*

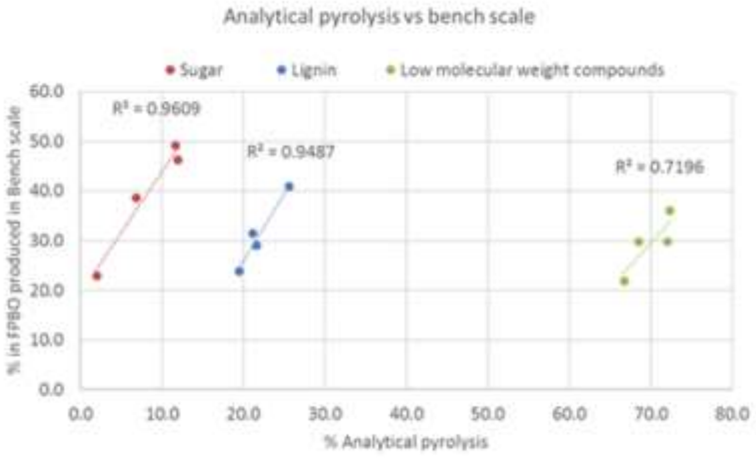

**Figure 18.** *Correlation between analytical and bench scale pyrolysis product (acids, alcohols, aldehydes, ketones, furans and phenols) yields obtained from pine, willow, birch, and catalytic pyrolysis of pine.*

Since the additive 2-naphthol in fast pyrolysis did not change the proportion of pyrolysis product yields (gas, liquid and char) nor the composition of the FPBO compared to reference experiments, additional tests were performed to evaluate the effect of additives on the stability of FPBOs. The stability test for FPBOs with and without additives was performed at 80 °C for 24 hours, which corresponds to the storage of FPBO at room temperature for one year and which generally increases the bio-oil viscosity i.e. molecular weight due to repolymerisation of bio-oil components. After the stability test, the water and acid content increased together with the molecular weight (Table 6), while the carbonyl content was decreased in all the FPBOs, indicating the occurrence of repolymerization reactions in the FPBOs during storage. However, based on microscopy images, phase separation did not take place, which suggested that the quality of all FPBOs was good. The increase in molecular weight was minor for the FPBO with 2-naphthol in comparison to the other FPBOs, thus indicating a slight improvement in stability. According to the results, it was concluded that the reaction time in pyrolysis was too short for the additives to react with lignin components, and therefore it would be recommended to mix the additives with the bio-oil after the pyrolysis.

***Table 6.*** *Molecular weight of FPBOs before and after stability test done at 80°C for 24 h.*

| | Mw (g/mol) before | Mw (g/mol) after | Mw increase, % |
|---|---|---|---|
| Pine | 790 | 1130 | 43 |
| Pine with EtOH | 760 | 1070 | 41 |
| Pine with 1-naphthol | 760 | 1050 | 38 |
| Pine with 2-naphthol | 760 | 920 | 21 |

## 6.3 Lignin fractionation from bio-oils

### 6.3.1 Solvent fractionation

Small scale solvent fractionation trials using the FPBOs from pine, birch, and willow (with bark) wood were performed at VTT to separate lignin-based components for application testing (section 8.2). A reference FPBO available at VTT, containing derivatives from lignin (22%), polysaccharides (34%), low molecular weight compounds (21%) and water (23%), was also used. In these trials, the lignin fraction (i.e. pyrolysis lignin) was precipitated by adding excess of water to the FPBO. After precipitation, the samples were centrifuged and the water soluble compounds were separated. Small amounts of phenolic compounds were found in the water soluble fraction. Since it was difficult to separate phenolic compounds from several other low molecular weight acids, alcohols, furans, aldehydes, ketones and sugar fragments, their type and concentration were determined by GC/MS.

***Table 7.*** *Lignin-derived components (wt-%) in FPBOs from pine, birch and willow wood, and average molecular weight (Mw) and content of hydroxyl groups and acids in the pyrolysis lignins.*

| | Pine | Birch | Willow | VTT's FPBO |
|---|---|---|---|---|
| Water soluble phenols*, wt-% | 2.5 | 3.1 | 3.8 | 1.6 |
| Pyrolysis lignin, wt-% | 17 | 16 | 24 | 22 |
| Mw, g/mol | 880 | 910 | 920 | n.m. |
| Phenolic OH, mmol/g | 3.6 | 3.9 | 4.1 | n.m. |
| Aliphatic OH, mmol/g | 1.2 | 1.3 | 1.6 | n.m. |
| COOH, mmol/g | 0.6 | 0.3 | 0.3 | n.m. |

* In pine, the main phenols were guaiacol, 4-methylguaiacol, vanillin and catechol. In birch and willow, the main phenols were syringol, 4-methylsyringol, catechol and syringaldehyde; n.m. = not measured

Based on the characterization results, all the pyrolysis lignins had similar average molecular weight (Table 7), even though they were obtained from different feedstocks having different lignin structure (hardwood vs softwood). Slightly more phenolic hydroxyls were present in the pyrolysis lignins from hardwoods (birch and willow), and somewhat more phenolic hydroxyls were present in the willow lignin compared to birch lignin. In willow, the bark may contain phenolic compounds that probably increased the yield of phenolic hydroxyls.

### 6.3.2 Fractionation by nanofiltration – screening of membranes

Fractionation of VTT's reference FPBO was performed at VITO using several nanofiltration membranes. For all fractionation trials, the FPBO was diluted in ethanol (10% feed and 90% ethanol). The membrane separation was carried out in a stainless steel high-pressure cross-flow filtration unit. The different polymeric and ceramic nanofiltration membranes used in the screening trials are listed in Table 8. A rectangular module (PS Prozesstechnik, Basel, Switzerland) with an active surface of approximately 0.01 m² was used for the polymeric flat sheet membranes. For the ceramic tubes, an in-house constructed cell with an active surface of approximately 0.0048 m² was used.

***Table 8.*** *Properties of the membranes used for screening trials at VITO.*

| Membrane code | Membrane type | MWCO (Da) | Membrane nature |
|---|---|---|---|
| LF4Value-1 | Polymeric flat sheet | 200 | Hydrophilic |
| LF4Value-2 | Polymeric flat sheet | 500 | Amphiphilic |
| LF4Value-3 | Polymeric flat sheet | 150 | Hydrophilic |
| LF4Value-4 | Polymeric flat sheet | 400 | Amphiphilic |
| LF4Value-5 | Polymeric flat sheet | 1000 | Hydrophobic |
| LF4Value-6 | Polymeric flat sheet | 500 | Hydrophobic |
| LF4Value-7 | Ceramic tube | 450 | Amphiphilic |

The results of the membrane filtration trials were evaluated using flux, UV and GPC measurements. The highest average fluxes were measured for the LF4Value-3 membrane at 15 bar and the LF4Value-2 and LF4Value-4 membranes at 35 bar (Figure 19), showing that the permeation flux was not only related to the membrane molecular weight cut off (MWCO) and pore size, but also to the interaction between membrane, solvent and solute. For all membranes, the flux increased significantly with applied pressure, and for most of the membranes, this increase was higher than expected based on the pressure increase, indicating swelling of the membranes. A difference in color was also observed, revealing a difference in separation efficiency (Figure 19). Whereas the permeate fractions of LF4Value-1, 2, 3 and 7 membranes were brown colored, a (slightly) yellow color was revealed for the permeate fractions of LF4Value-4, 5 and 6, indicating a lower concentration of lignin derivatives. These results were confirmed by UV measurements.

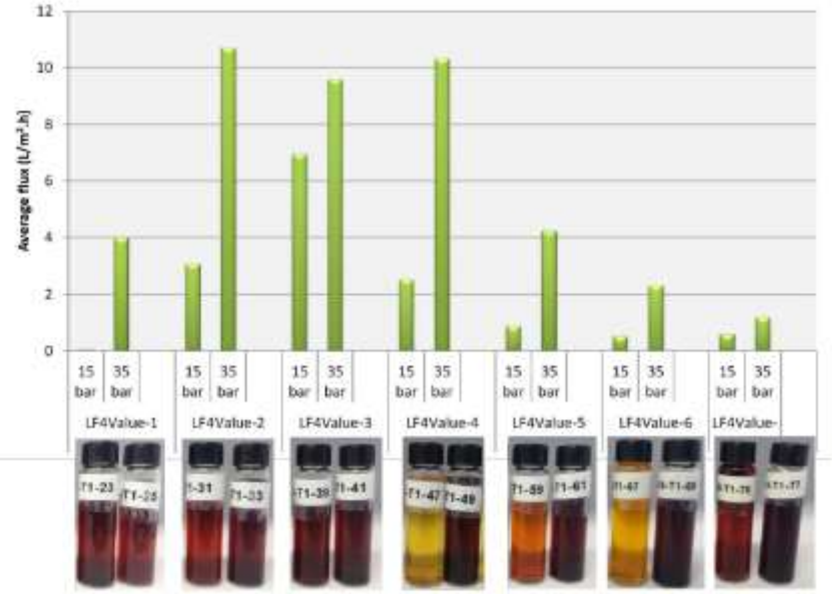

***Figure 19**. Average flux as a function of applied pressure and type of membrane at 25°C.*

GPC measurements were performed on all feed, retentate and permeate samples to evaluate the separation of different size components in these fractions. The composition of the feed, permeate and retentate samples collected for the different membranes at 15 bar is shown in Figure 20. Similar results were observed for the separation done at 35 bar. In both cases, a clear difference between permeate and retentate samples was observed for LF4Value-4, 5 and 6, which indicated that fractionation of the FPBO was feasible by using these membranes. More than 90% of the molecules present in the permeates of LF4Value-4 and 6 had a molecular weight below 700 Da. Since the highest retention and flux were measured for the LF4Value-4 membrane, this membrane was selected for the proof-of-concept trial.

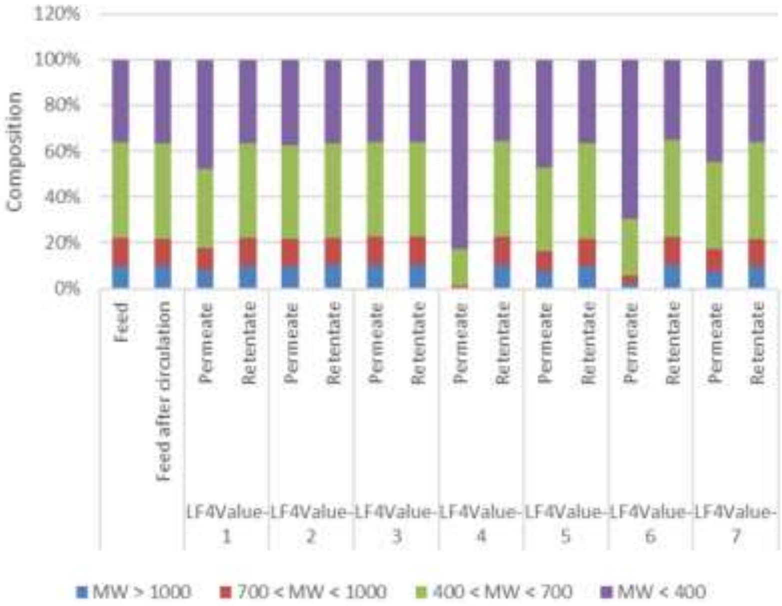

***Figure 20**. Composition of feed, permeate and retentate samples collected for the different membranes at 15 bar.*

### 6.3.3 Nanofiltration - proof-of-concept

Compared to the screening trials, a longer term fractionation trial was performed with the amphiphilic LF4Value-4 membrane, aiming at a proof-of-concept demonstration of membrane-based fractionation of pyrolysis bio-oil. The fractionation was done in diafiltration mode. After each diavolume, samples of retentate and permeate were taken, and these samples were analyzed with UV to determine their lignin content and the corresponding retention value. The retentions measured for each diavolume separately are presented in Figure 21. As can be seen, the retention drastically decreased for the 5th diavolume, indicating also that larger molecules were passing the membrane at this stage.

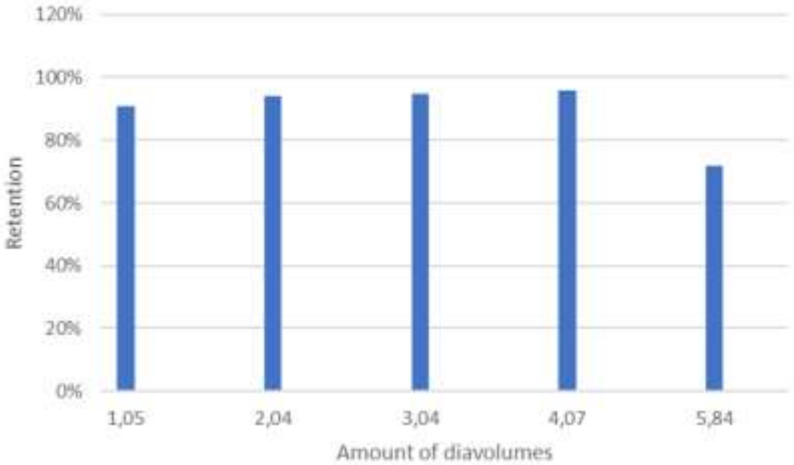

***Figure 21**. Lignin retention per diavolume (based on permeate point samples).*

Based on the lignin content in the feed and permeate samples, a cumulative yield of 22% was measured at the end of the diafiltration experiment. This means that 22% of the total amount of lignin was transferred towards the permeate. Since this value gave no information on the separation of the bio-oil in different molecular weight fractions, additional GPC measurements were performed, and based on the peak heights, the contribution of the different fractions towards feed, retentates and permeates were calculated.

As can be seen in Figure 22, after one diavolume, an enrichment of higher molecular weight fractions was observed in the retentate, while the permeate fraction only consisted of molecules with a molecular weight below 700 Da. With further addition of solvent during prolonged diafiltration, a portion of the higher molecular weight fractions (MW > 700 Da) started to permeate due to incomplete retention, thus resulting in a decreased purity of the permeate. On the other hand, the enrichment of higher molecular weight lignin derivatives in the retentate slightly increased with adding extra solvent. Therefore, according to these results, a compromise needs to be found with respect to:
- lignin yield in the permeate, which increased with increasing amount of diavolumes;
- permeate purity, which decreased with increasing amount of diavolumes;
- purity of the high MW fraction in the retentate, which increased with increasing amount of diavolumes.

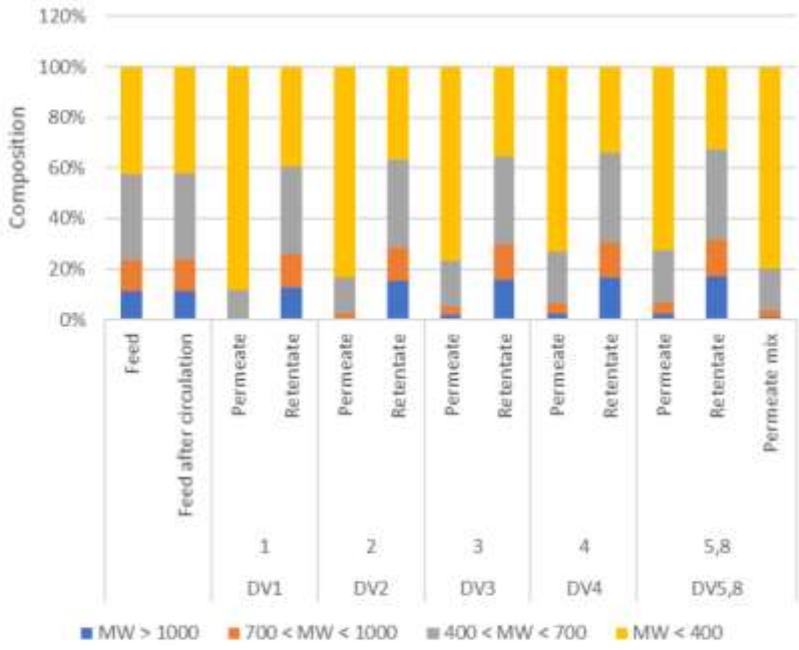

***Figure 22**. Composition of feed, permeate and retentate samples per diavolume.*

# 7. Hydrothermal pre-treatments and saccharification

## 7.1 Hydrolysis of pre-treated solids and sugar yields

Hydrothermal pre-treatments of pine, birch and willow (with and without bark) wood meal were performed in a rotating air-bath digester at 200 ºC temperature, with a liquid to wood ratio of 10:1 L/kg. The chemical additives 1-naphthol, 2-naphthol, or formaldehyde were added to prevent or minimize lignin condensation reactions. The charge of 1- and 2-naphthol was 4.7% on dry wood, while the charge of formaldehyde was 37% on dry wood. The reaction times ranged from 10 to 320 min, corresponding to pre-treatment severities *log $R_0$* 4.2 to 5.5. After the pre-treatment, the solid residues were recovered and thoroughly washed with water.

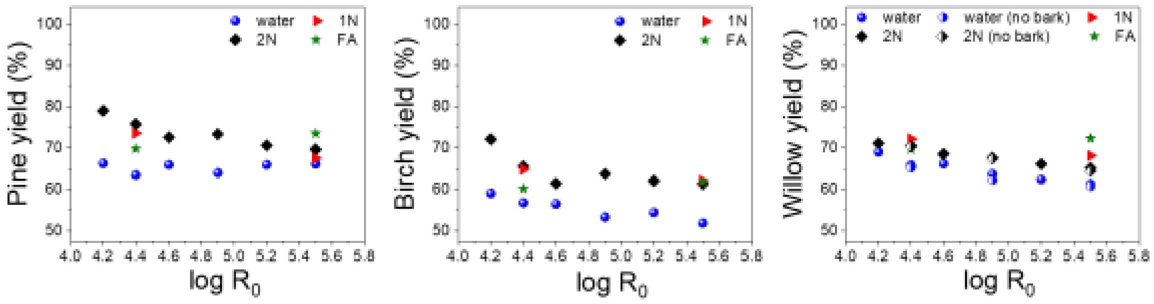

***Figure 23.** Solid yields after hydrothermal pre-treatment with/without chemical additives of a) pine, b) birch and c) willow milled wood. Water: water-only experiments; 1N: 1-naphthol; 2N: 2-naphthol; FA: formaldehyde. Willow wood was pre-treated with and without bark.*

The yields of pre-treated solid as a function of pre-treatment severity are shown in Figure 23. In the water-only experiments, the solid yield for pine and willow wood was between 60-70%, while the solid yield for birch was between 50-60%. The lower yield for birch wood may be partly explained by its higher hemicellulosic content compared to pine and willow wood (see Table 1), and particularly by the high xylan content, which is extensively removed during hydrothermal treatments at elevated temperatures (Borrega et al., 2011b). In willow, similar yields were obtained for wood meal with bark (particle size 0.5-1 mm) and without bark (particle size <0.5 mm). Compared to water-only experiments, the wood yields after hydrothermal pre-treatments with addition of chemical additives were about 5-10% higher for pine and birch, and about 5% higher for willow (Figure 23). The higher yields appear to indicate that the additives were incorporated to some extent into the wood structure.

The washed pre-treated wood solids were subjected to enzymatic saccharification in Erlenmeyer flasks with a consistency of 5%, in 50 mM Na-acetate buffer (pH 5) with a cellulase dosage of 20 mg of enzyme protein (Cellic CTec2, Novozymes) per dry gram of pre-treated solid. Na-azide was added to a concentration of 0.2 mg/ml in order to prevent microbial contamination. The flasks were incubated on a shaker (150 rpm) at 45 ºC for 72 h.

As shown in Figure 24, the sugar conversion was strongly dependent on the wood material as well as on the chemical additive used in the hydrothermal pre-treatment. In pine wood, only 20-25% of the carbohydrate fraction in the pre-treated solids could be hydrolysed after water-only experiments, but the addition of 2-naphthol increased the sugar conversion up to 50% (i.e. about 100% increase in saccharification) after 320 min of pre-treatment time ($log\ R_0$ 5.5). Pielhop et al. (2015) also reported an increase of up to 64% in saccharification of spruce wood by addition of 2-naphthol to the hydrothermal pre-treatment. Despite the significant increase in saccharification of pine, the overall sugar yield by addition of 2-nahpthol to the hydrothermal pre-treatment ($log\ R_0$ 5.5) was only 16% on initial dry wood. More severe pre-treatment conditions by addition of an acidic catalyst would probably be necessary for effective saccharification of pine wood (Galbe and Zacchi, 2002).

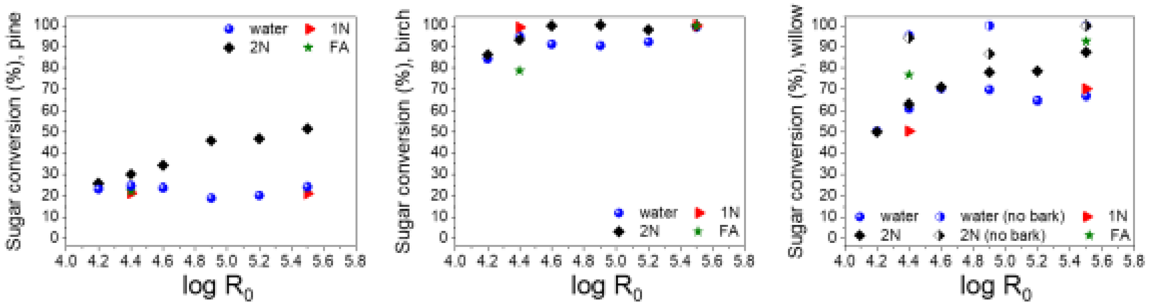

***Figure 24.*** *Enzymatic sugar conversion after hydrothermal pre-treatment with/without chemical additives of a) pine, b) birch and c) willow milled wood. Water: water-only experiments; 1N: 1-naphthol; 2N: 2-naphthol; FA: formaldehyde. Willow wood was pre-treated with and without bark.*

In birch and willow (without bark), almost quantitative (>90%) saccharification was obtained after a hydrothermal treatment with only water (no additives), and therefore the addition of additives did not bring about any additional benefits (Figure 24). In these two substrates, the total sugar yields were about 35-40% of the dry wood mass, indicating that nearly all the cellulose fraction was hydrolysed. In willow, the presence of bark clearly inhibited the saccharification, but the addition of 2-naphthol or formaldehyde increased the sugar conversion from 60-70% to about 90% at the highest pre-treatment severity ($log\ R_0$ 5.5). The results clearly indicate that if debarking methods could be developed, willow wood could be an alternative and suitable raw material for the sugar route. The use of 1-naphthol in hydrothermal pre-treatments did not have any effects on the sugar conversion compared to water-only experiments, regardless of the wood material.

## 7.2 Composition and structure of hydrolysis lignins

Most of the solid residues (hydrolysis lignins) left after enzymatic hydrolysis still contained a high amount of carbohydrates (up to 30-40% in the case of pine lignins), which hindered sample dissolution for the analytical determination of molar mass (by size exclusion chromatography) and lignin functionalities (by $^{31}$P-NMR). However, some hydrolysis lignins from birch had a lignin content above 85%, and thus these samples were selected for further analyses to evaluate any potential effects of the chemical additives on the lignin structure.

The birch hydrolysis lignins obtained from the experiments with 1- and 2-naphthol had a lower (10-15%) molar mass than the hydrolysis lignin from the water-only experiments (Table 9). The lower molar mass may be explained by the incorporation of the naphthols to the lignin structure during the hydrothermal pre-treatment, which prevented lignin re-polymerization by cross-linking (condensation) reactions. A similar effect has been reported by Pielhop et al. (2015) during hydrothermal pre-treatment of spruce wood with 2-naphthol. However, the more prominent effect of 1-naphtol on reducing the molar mass, compared to 2-naphthol, was somewhat surprising because 1-napthol was expected to allow partial re-polymerization of lignin through the additive (Wayman and Lora, 1978). Moreover, if the addition of 1-naphthol prevented (or minimized) the condensation of lignin during the pre-treatment, such effect was not apparently relevant for the enzymatic saccharification of the pre-treated wood.

***Table 9.*** *Chemical, molecular and structural properties of hydrolysis lignins from birch treated at 200 ºC for 20 min (log $R_0$ 4.4)*

| | **Only water** | **1-naphthol** | **2-naphthol** |
|---|---|---|---|
| Lignin (%) | 91.4 | 87.6 | 99.0 |
| Sugars (%) | 5.2 | 9.4 | 2.4 |
| Mw (g/mol) | 7 900 | 6 700 | 7 100 |
| Aliphatic OH (mmol/g) | 2.22 | 2.37 | 2.14 |
| COOH (mmol/g) | 0.14 | 0.08 | 0.16 |
| Phenolic OH (mmol/g) | 2.18 | 2.16 | 2.55 |
| Substituted C5 | 1.70 | 1.56 | 1.63 |
| Guaiacyl | 0.45 | 0.44 | 0.67 |
| p-OH-phenyl | 0.03 | 0.16 | 0.25 |
| Total OH (mmol/g) | 4.54 | 4.61 | 4.85 |

The lower extent of lignin condensation by the use of naphthols, as indicated by molar mass values, was also supported by the lower amount of substituted C5 units (Table 9). On the other hand, the use of 1-naphthol decreased the amount of carboxylic acid groups, while 2-naphthol clearly increased the amount of guaiacyl units. Signals from the naphthol attached to lignin may, however, partly overlap with the lignin guaiacyl units. The presence of free naphthol was also detected based on the sharp peaks in the p-hydroxyphenyl region, whose assignment was confirmed by model compounds.

## 7.3 Upscaled production of hydrolysis lignin

Selected pre-treatment and saccharification experiments were scaled up in a 30 L digester to produce hydrolysis lignins in large enough quantities for the preparation of PLA/lignin biocomposites. Based on the results obtained in the small scale trials, the pre-treatments selected for scaling up were those corresponding to the hydrothermal pre-treatment of pine without and with addition of 2-naphthol (*log* $R_0$ 5.5), birch without additives (*log* $R_0$ 4.4), and willow with bark and without additives (*log* $R_0$ 5.5). The yield of pre-treated solids was similar in the small and large scale trials, but the sugar yields after enzymatic hydrolysis were lower when the integrated pre-treatment and saccharification process was performed in large scale (Table 10). This effect was particularly evident for pine wood pre-treated with 2-naphthol and for willow wood (with bark). In pine wood, contrary to the small scale trials, the addition of 2-naphthol did not improve saccharification compared to water-only experiments. The lower sugar yields in the large scale trials may be explained by the higher consistency (10% instead of 5%) used in the saccharification step, as previously observed by other authors (Carrasco et al., 2010; Wang et al., 2012). The lower sugar yields obviously resulted in higher yields of hydrolysis lignins, with an actual lignin content between 55-75% (Table 11). The purity of the birch hydrolysis lignin was remarkably lower than in the small scale experiments.

***Table 10.*** *Yield of pre-treated solids and yield and composition of hydrolysis lignin from small and large scale trials.*

| | **Pine HL** | | **Pine HL (2N)** | | **Birch HL** | | **Willow HL** | |
|---|---|---|---|---|---|---|---|---|
| | Small | Large | Small | Large | Small | Large | Small | Large |
| Log $R_0$ | 5.5 | 5.5 | 5.5 | 5.5 | 4.4 | 4.4 | 5.5 | 5.5 |
| Additive | no | no | 2N | 2N | no | no | no | no |
| Yield of pre-treated solid (% on wood) | 66.2 | 64.7 | 69.7 | 65.8 | 56.8 | 57.7 | 61.3 | 60.3 |
| Yield of sugars (% on wood) | 7.6 | 4.8 | 16.2 | 5.2 | 35.6 | 31.8 | 19.2 | 7.9 |
| Yield of hydrolysis lignin (% on wood) | 58.6 | 59.9 | 53.6 | 60.6 | 21.2 | 25.9 | 42.1 | 52.4 |

# 8. Lignin applications

## 8.1 Composites

The performance of the hydrolysis lignins (HLs) produced in the project was tested at 20% loading in polylactic acid (PLA) composites. The aim was to use lignin as a low cost filler or even as a thermoplastic matrix polymer with acceptable mechanical properties. The tested hydrolysis lignins differed significantly in their carbohydrate content, and presumably also in their structure (Table 11). Due to their higher degree of methoxylation, hardwood lignins (birch, willow) were expected to have a less condensed and more flexible structure than softwood lignin (pine). The hardwood lignins also contained less polysaccharide residues. The carbohydrate content of the pine HL produced with 2-naphthol was somewhat lower than that of the pine HL without 2-naphthol, but still higher than that of the hardwood lignins. Unfortunately, the glass transition temperature (Tg) could be determined only for the birch HL, which had the lowest carbohydrate content. As expected, the Tg of birch HL was lower after the second heating than the Tg of a softwood HL (from St1).

***Table 11**. Composition and glass transition temperatures (Tg) of the studied hydrolysis lignins.*

| **Sample** | **Lignin content, %** | **Carbohydrate content, %** | **$Tg_1$, (°C)** | **$Tg_2$, (°C)** |
|---|---|---|---|---|
| Kraft lignin | >95 | < 3 | 142.0 | 151.3 |
| St1HL | 61.4 | 26 | 128.5 | 162.6 |
| Birch HL | 73.3 | 20.0 | 155.0 | 137.9 |
| Willow HL | 65.2 | 28.1 | nd | nd |
| Pine HL | 58.5 | 35.9 | nd | nd |
| Pine HL (2N) | 64.5 | 30.2 | nd | nd |

For the processing of lignin composites, injection molding grade PLA (3052D), a mini-scale compounder and injection molding equipment were used. Compounding was performed at 190°C with mixing at 100 RPM for 2 min. In injection molding, the temperature was 190°C in the cylinder and 40°C in the mold. Injection pressure of 450 bar (5s) and post pressure of 220 bar (10s) were used. In preliminary experiments, a lignin content of 30% resulted in brittle compounds, which were difficult to remove from the mold. Therefore, a lignin loading of 20% was used in all subsequent experiments.

The addition of 20% lignin resulted in somewhat reduced tensile strength and strain of PLA without any significant increase in tensile stiffness (Figure 25). The stiffness increase was more pronounced with co-addition of 15% chemithermomechanical pulp (CTMP) fibers. Lignin structure or purity had no significant effect on properties, as the variations between the different hydrolysis lignins were within the margin of error. Neither the naphthol nor the carbohydrate content had a clear effect on the HL performance. However, based on the slightly increasing tensile strength in going from hardwood to softwood, the high carbohydrate content might be beneficial rather than detrimental. The results of a reference kraft lignin were rather similar, further indicating that the differences in lignin structure did not play a significant role in the performance of the PLA/lignin composites.

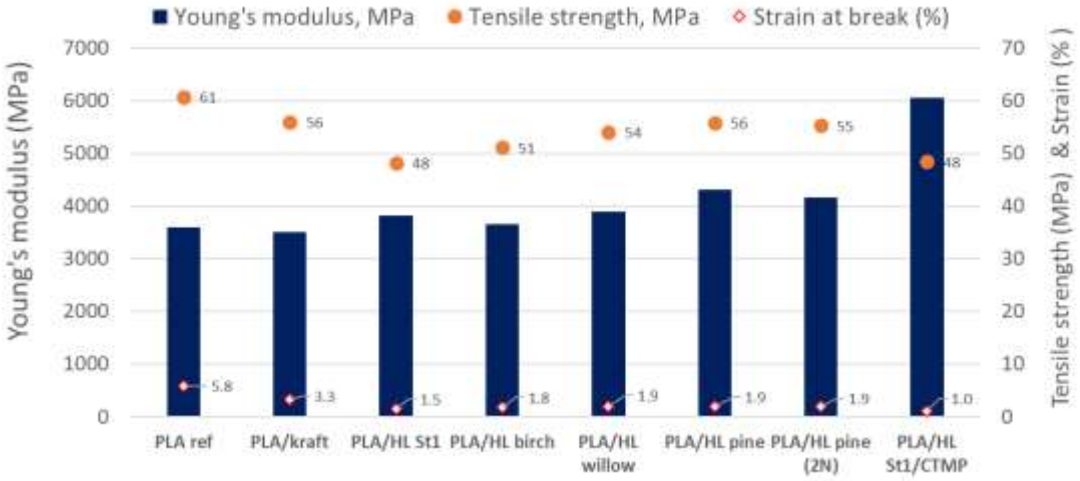

***Figure 25.*** *Effect of 20% lignin loading on mechanical properties of PLA. Young's modulus of PLA according to product specifications.*

It is typical for lignin-containing composites that tensile and impact strength are reduced with increasing lignin loading, resulting in very brittle composite materials. The low tensile and impact strength is assumed to be largely due to the poor compatibility of lignin with the more hydrophobic polymer matrix. The performance can be improved, e.g. by chemical modification, but this increases the production costs. Coupling agents, e.g. maleic acid grafted on polyolefins, have also been used in plastic composites to improve the connection between reinforcing fibers and polymer. Recently, epoxidised linseed oil (ELO) has been shown to improve the mechanical properties of PLA biocomposites through better connection with pulp fibers and nanocelluloses (Immonen, 2018). The connection is based on chemical reactions with the hydroxyl groups of the fibers and the interactions/reactions with PLA (Figure 26).

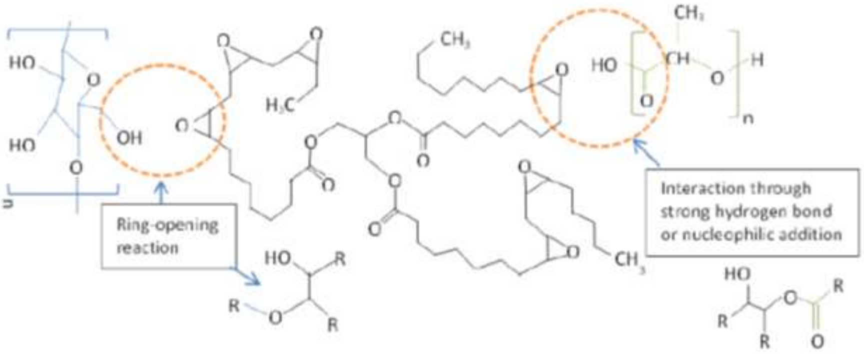

***Figure 26.*** *Suggested reaction scheme for coupling cellulose fibers and PLA with epoxidised linseed oil (ELO).*

In this project, the bio-based ELO was tested as a novel plasticizing coupling agent to improve the lignin processability and to chemically connect lignin to the PLA matrix. In addition, polyvinylacetate (PVAc) and silane-based additives were also tested (Figure 27). Vinnex is a PVAc-based compatibiliser/binder that should improve compatibility of hydrophilic fillers and

PLA. The improved performance is based on physical interactions, not chemical bonding. Dynasylan GLYMO is a silane-based compatibilizer with epoxy functionalities. Unlike ELO, it has only one epoxy group and it cannot link lignin to PLA chemically like ELO. By reacting with lignin, it should increase the hydrophobicity and thermoplasticity of lignin, and therefore improve the processability and compatibility with PLA.

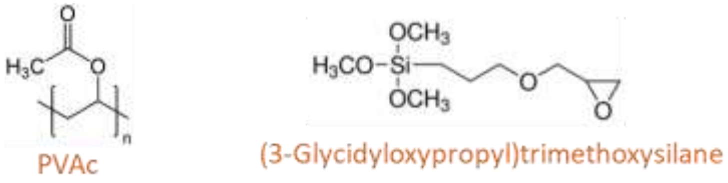

***Figure 27**. Chemical structure of PVAc and silane based compatilibizers, used in this study.*

In lignin/PLA composites, the epoxidised coupling agents had no beneficial effect on tensile strength nor on strain (typically correlating with the impact strength) (Figure 28). This was observed also when using kraft lignin, which had a higher content of phenolic units available for the coupling reactions. On the other hand, the small molecular coupling agents and compatibilizers plasticized both the lignin and PLA, which clearly improved the processability. The composites were easier to remove from the mold, and the post-cleaning was improved. However, due to the PLA plasticizing effect of epoxidised coupling agents, the tensile strength was even further reduced.

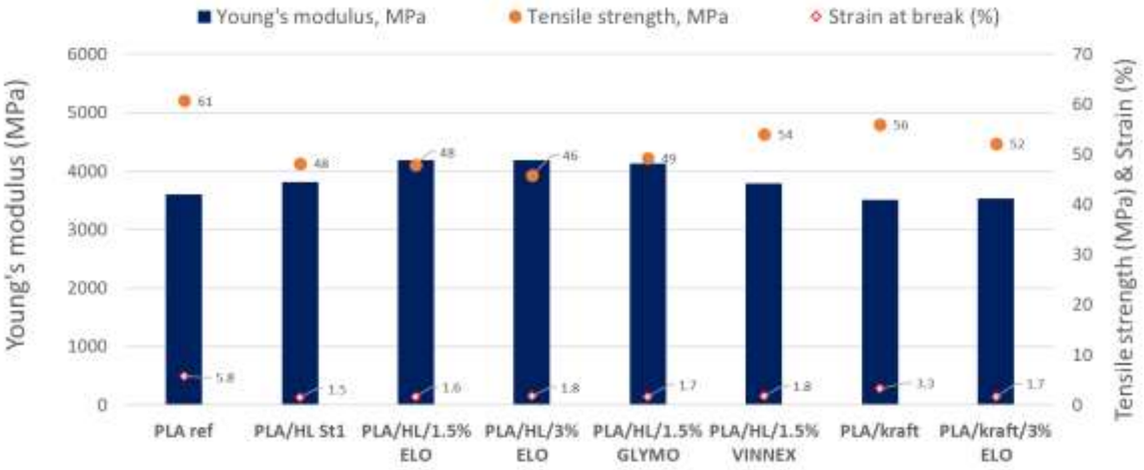

***Figure 28**. The effect of coupling agents and compatibilizers on mechanical properties of PLA composites at 20% lignin loading.*

Scanning electron microscope (SEM) images indicated that the more hydrophilic lignin (St1 HL) was not fully compatible with the PLA matrix. Phase separation and a clear discontinuity in the matrix could be seen between lignin and PLA (Figure 29, left). However, lignin compatibility with PLA matrix was clearly improved with increasing ELO dosage (Figure 29, right). It is evident that ELO performed as a plasticizer, improving miscibility and processability. In addition to lignin, it also plasticized PLA, as a clear reduction of the Tg of PLA from 58.6°C up to 53.6°C was detected with increasing the content of ELO. The crystallization temperature of PLA (119°C) increased with lignin (127°C) but decreased with ELO (116°C). Despite the results obtained here with ELO, various coupling agents in different ratios and dosing protocols should be still tested to ascertain first that they react with lignin, and the results should also be confirmed at a larger scale by impact strength measurements.

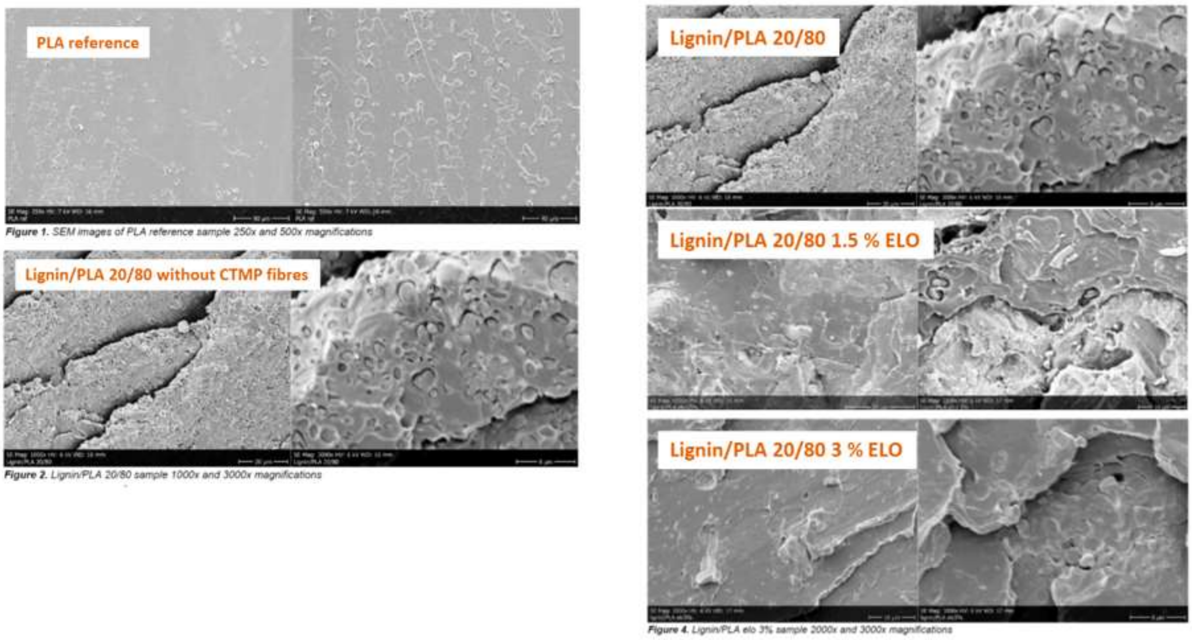

***Figure 29**. SEM images of neat PLA and lignin/PLA composites at 20% lignin content with and without ELO (at 1.5 and 3% loading).*

## 8.2 Resins

The lignin fractions obtained after fractionation of fast pyrolysis bio-oils from pine, birch and willow wood were here tested in the synthesis of phenol-formaldehyde (PF) resins for substitution of phenol. Only pyrolysis lignins were tested due to their higher phenol content and good solubility compared to the hydrolysis lignins. A reference pyrolysis lignin, separated from a previously produced bio-oil and available in larger quantities, was used for prescreening of resin synthesis protocols. This reference lignin originated from fast pyrolysis of a mixture of softwood and hardwood feedstocks.

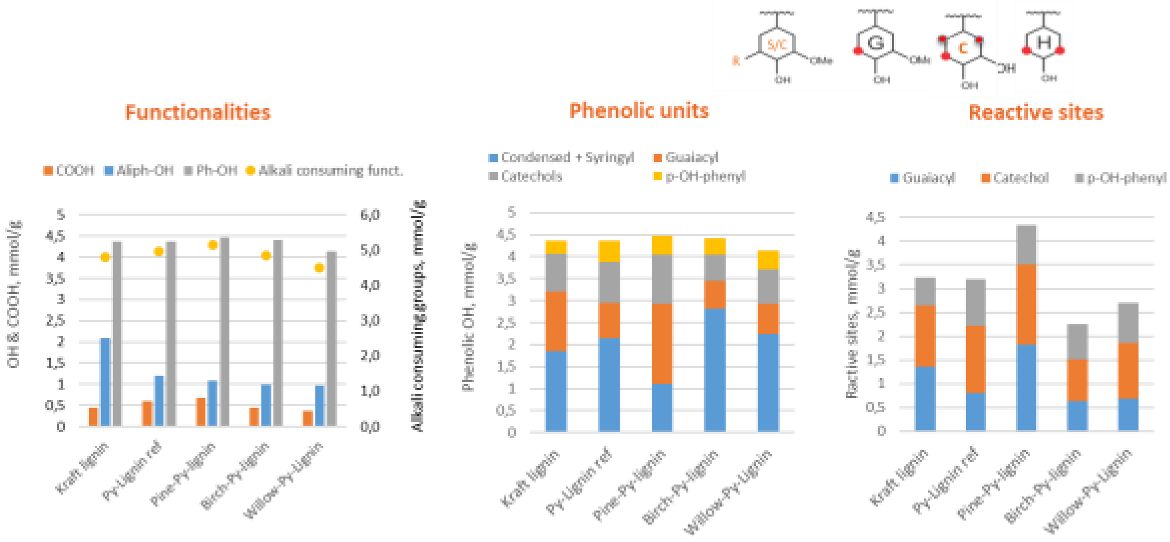

***Figure 30**. Chemical characteristics of the pyrolysis lignins used in this study.*

At first, the number of theoretically reactive sites for the crosslinking reactions with formaldehyde was determined for all pyrolysis lignins by means of $^{31}$P NMR (Figure 30). The pine pyrolysis lignin had the highest number of reactive sites, whereas the hardwood pyrolysis lignins, as expected, possessed less theoretically reactive sites. The number of theoretically reactive sites of the reference lignin was rather comparable with that of the commercial kraft lignin.

### 8.2.1 Hydroxymethylation to evaluate reactivity and chemical dosing

The reactivity of lignin with formaldehyde has typically been determined by hydroxymethylation experiments performed at a consistency of 10% at 60°C with excess formaldehyde. This provides the maximum formaldehyde consumption and the formaldehyde dosage for the actual resin synthesis. The actual reactivity and chemical dosing protocols were first tested with the reference pyrolysis lignin. Unlike any other lignin tested earlier, this pyrolysis lignin had a high tendency to condense in alkali, resulting in its precipitation during the experiments. The alkali demand was also higher than based on the alkali-consuming functionalities determined by $^{31}$P NMR. In earlier experiments with other types of lignins such as softwood kraft lignin, the alkali dosage was set at a molar fraction of 0.65 of the alkali-consuming functionalities of lignin. However, in a dissolution experiment with the pyrolysis lignin, the pH level could be maintained at the target level of ~10.5 only by using a very high alkali dosage of 5.5 mmol/g. This dose is 11% higher than the content of alkali-consuming phenolic hydroxyl and carboxyl functionalities (4.95 mmol/g) in the reference pyrolysis lignin as determined by $^{31}$P NMR.

A modified chemical dosing order together with a high alkali dosage prevented the excessive condensation and precipitation of the lignin. In this case, all components (NaOH, formaldehyde, water) were combined at the beginning (10 min mix), heated to 60°C, and maintained at this temperature for 3h. However, an unexpected high consumption of formaldehyde (6.2 mmol/g) compared to the theoretically reactive sites (3.2 mmol/g) was detected when using this method.

### 8.2.2 Resin synthesis at 50% phenol substitution

The first two PF resin syntheses were performed at 80°C using a phenol-to-lignin mass ratio of 50:50 (50% solids content) with a target viscosity of 3.5-4.5 cP. The same alkali dosage (5.5 mmol/g) was used as in the formaldehyde determination experiment. Two different formaldehyde dosages, either based on theoretical reactive sites (3.2 mmol/g calculated based on $^{31}$P NMR) or based on actual consumption (6.2 mmol/g), were used. In resin synthesis, no precipitation was observed. The residual formaldehyde was also at an acceptable level (<0.1%) after the synthesis. However, the residual phenol content was high (2-3%), indicating insufficient crosslinking that was further confirmed by molar mass measurements. Better results in resin synthesis were obtained when both alkali (using a 0.65 molar ratio of alkali to alkali-consuming functionalities) and formaldehyde were dosed according to the theoretically reactive sites. This dosing protocol was used for the testing of pyrolysis lignins from pine, birch and willow produced in this project. No precipitation was detected since phenol performed as a co-solvent, although alkali-induced condensation reactions may be expected during resin synthesis.

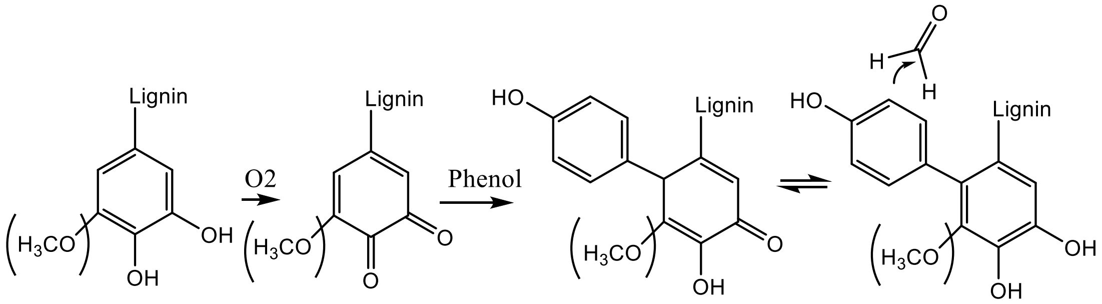

***Figure 31**. Hypothesis for the occurrence of condensation reactions with phenol via oxidation of catechol units of pyrolysis lignin.*

The reason for the unexpected condensation reactions of pyrolysis lignins is not known. However, it is possible that the condensation takes place via oxidation of catechol units to quinones, which tend to react with the phenolic units of pyrolysis lignin. Similar types of condensation reactions have been reported in literature for tannins. Based on this hypothesis (Figure 31), oxidation during chemical mixing was tested to prevent the uncontrolled condensation and to attach phenol to the pyrolysis lignin. It was assumed that phenol, as a small molecular compound, reacts with the quinone formed by oxidation faster than with the more bulky oligomeric phenolic units of pyrolysis lignin, and could thus control the self-condensation. Phenol attachment to pyrolysis lignin would increase its reactivity with formaldehyde, and would also prevent the phase separation of cross-linked phenol and pyrolysis lignin in the resin.

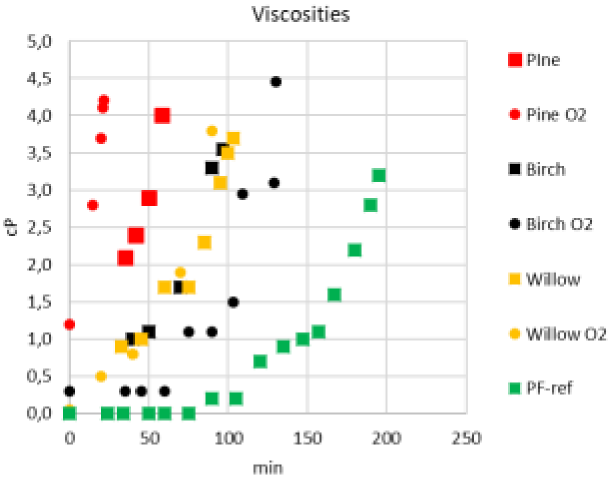

***Figure 32**. Viscosity development during resin synthesis with various pyrolysis lignins.*

The resin synthesis at 50 % phenol substitution and 50% solids content was performed to a target viscosity of 3.5-4.5 cP, using following procedures:

- **Normal case:** pyrolysis lignin and all chemicals were mixed for 10 min at room temperature, after which temperature was increased to 60°C and mixing was continued for 30 min. The actual condensation step was performed at 80 °C until the target viscosity was reached.
- **$O_2$ to enhance reactions with phenol:** pyrolysis lignin was mixed with alkali and phenol at room temperature for 40 min under $O_2$ bubbling. After this, formaldehyde was added slowly, and the temperature was increased to 60°C and the stirring continued for 30 min. The actual condensation step was performed at 80 °C until target viscosity was reached.

The viscosity development during the resin synthesis is shown in Figure 32. A faster viscosity increase was detected for the pine pyrolysis lignin using $O_2$ compared to the normal case. It is likely that the self-condensation was also enhanced by oxidation due to the high number of reactive sites and catechol units in the lignin. The initial viscosity was also higher than in the other samples, indicating that some condensation took place already during the $O_2$ bubbling pre-treatment. Unlike with pine, a slower viscosity increase was detected for the birch pyrolysis lignin using $O_2$. This was in line with the lower tendency to condense of the more methoxylated lignins, and it is likely that the oxidation enhanced more the reactions with the small molecular phenol. Finally, the oxidation had no effect on the willow pyrolysis lignin. Due to the bark residues giving a higher catechol content than in birch pyrolysis lignin, the willow pyrolysis lignin had features of both hardwood and softwood pyrolysis lignins. The oxidation also reduced the residual phenol content of birch and willow pyrolysis lignins more than that of the pine pyrolysis lignin (Figure 33). Phenol reacted especially with the hardwood pyrolysis lignins, which have lower catechol contents and lower tendency to condense compared to the pine pyrolysis lignin.

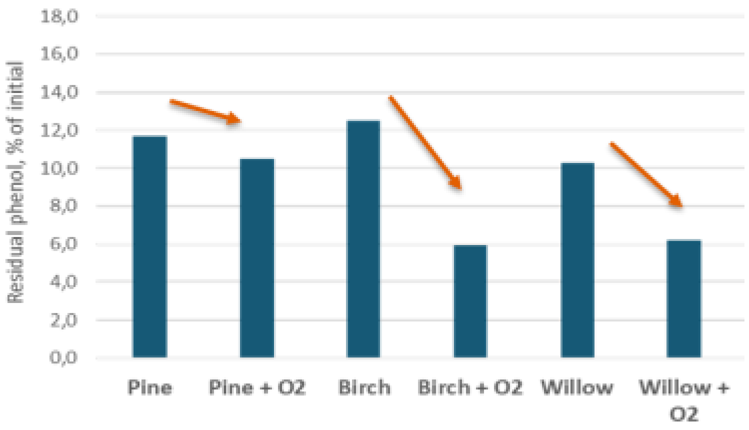

***Figure 33**. Residual phenol content of the pyrolysis lignin based resins*

A lower content of less cross-linked low-molecular weight material was detected in hardwood pyrolysis lignins compared to the pine pyrolysis lignin. The molar mass measurements indicated that phenol was better attached to the less reactive hardwood lignins (Figure 34), or the prolonged reaction time enabled the cross-linking of both phenol and lignin to a higher extent. With pine pyrolysis lignin, the fast self-condensation reactions led to a fast reaction time, which probably was too short even for the crosslinking of phenol with formaldehyde.

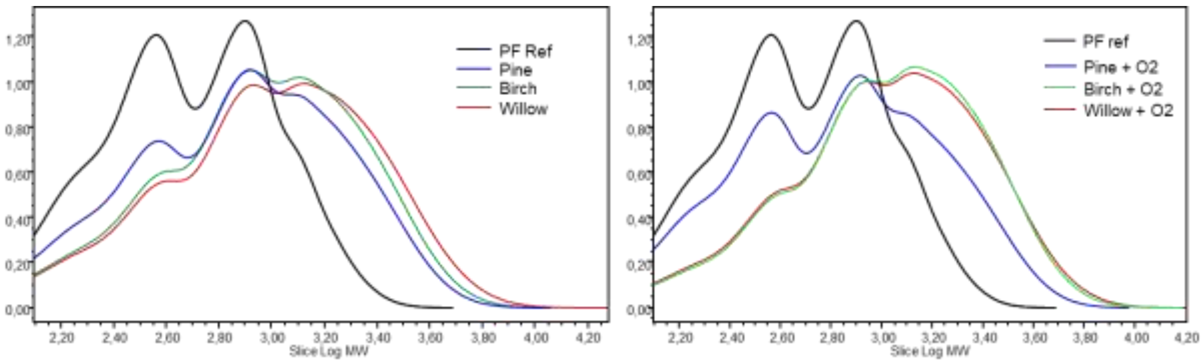

***Figure 34**. Molar mass distributions of the pyrolysis lignin based resins prepare without (left) and with (right) oxygen bubbling.*

## 8.3 Fuels

Upgrading of VTT's reference FPBO was studied by hydrodeoxygenation (HDO) in a high-pressure continuous plug flow reactor system (Figure 35). The main target was to study the stabilization of the bio-oil by mild HDO treatments (125 °C > T < 300 °C). The tests were performed with a 5% Ru/C catalyst obtained from Ranido, as well as with two catalysts (5% Pd-MgO and 5% Pd-SiO) provided by Åbo Akademi (see Section 5.3). Other experimental conditions were: pressure 80 bar, WHSV 1 1/h. The targeted and measured run parameters are reported in Table 12.

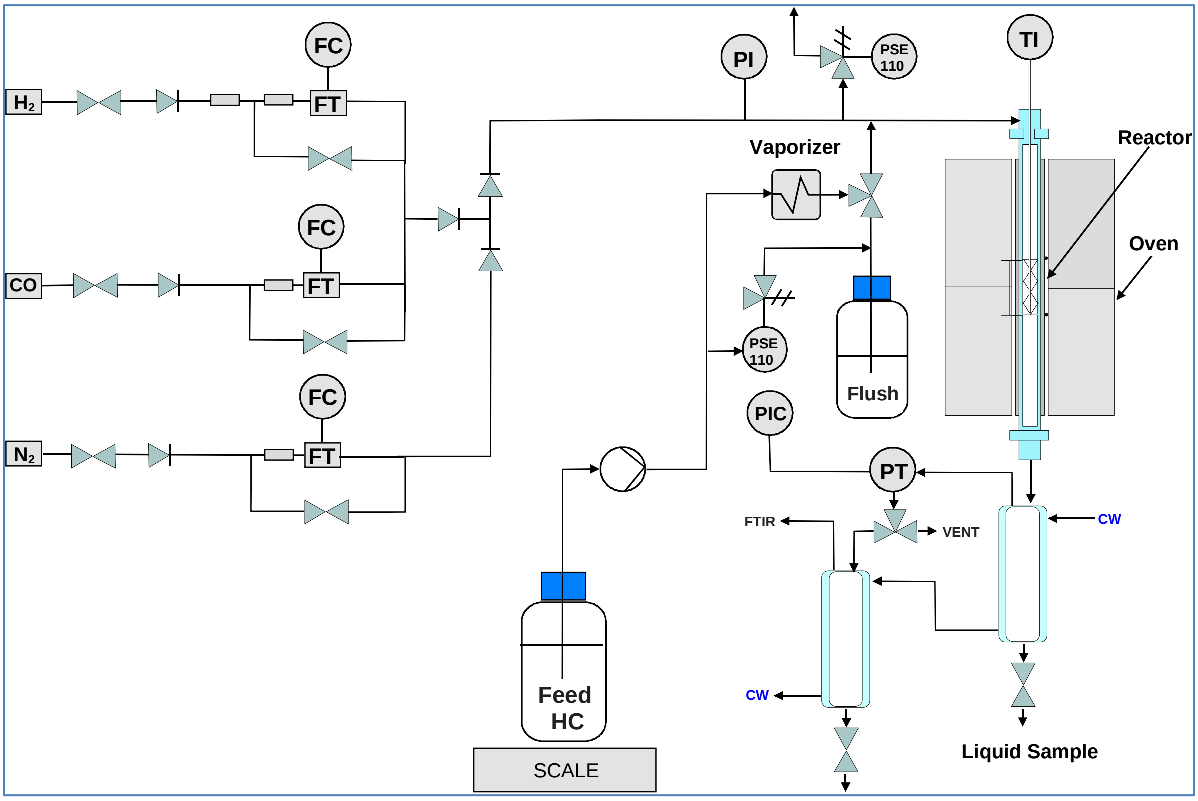

*Figure 35. VTT continuous high pressure reactor system.*

Due to the instability of the bio-oil, there were plugging problems of the reactor at temperatures of 150 °C and higher. Therefore, it was decided to limit the length of the run to one day. The problem was most serious at 200 °C, but above this temperature, the operation became somewhat easier.

***Table 12.*** *Run data of HDO experiments.*

| | | Targets parameters | | | | Reactor T | | | Reactor P | | | Feeds | | | | Outlets | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Run/sample | Catalyst | | WHSV | T | P | T380 | T350 | T average | upper | lower | Difference | H2 | N2 | liquid in | liquid in | liquid mass | collection time | liquid flow out | Liquid yield | WHSV from inlet |
| | | g | 1/h | C | bar | C | C | C | bar | bar | bar | l/h | l/h | g | g/h | g | h | g/h | % | 1/h |
| LF4V-HDO 1.0 | PD-SiO2-C | 2 | 1 | 150 | 80 | 156 | 157 | 156,33 | 79,8 | 79,4 | 0,37 | 3 | 0 | 329,8 | 14,40 | 302,0 | 22,9 | 13,19 | 91,6 % | 7,20 |
| LF4V-HDO 1.1 | PD-SiO2-C | 2 | 1 | 150 | 80 | 150 | 149 | 149,2 | 85,6 | 80,0 | 5,60 | 3 | 0 | 44,62 | 1,9 | 40,1 | 23,2 | 1,73 | 89,7 % | 0,97 |
| LF4V HDO2.0 | Ranido RCAT-8830 5%Ru/C | 2 | 1 | 100 | 80 | 98,9 | 100 | 99,60 | 80,9 | 80,2 | 0,71 | 3 | 0 | 45,4 | 2,25 | 15,9 | 20,2 | 0,79 | 35,0 % | 1,12 |
| LF4V HDO2.1 | Ranido RCAT-8830 5%Ru/C | 2 | 1 | 100 | 80 | 100 | 99 | 99,1 | 81,0 | 80,1 | 0,88 | 3 | 0 | 97,28 | 2,1 | 81,2 | 45,8 | 1,77 | 83,6 % | 1,06 |
| LF4V HDO2.2 | Ranido RCAT-8830 5%Ru/C | 2 | 1 | 100 | 80 | 99 | 100 | 99,4 | 81,3 | 80,6 | 0,70 | 3 | 0 | 45,76 | 2,0 | 35,5 | 23,4 | 1,52 | 77,6 % | 0,98 |
| LF4V HDO3.0 | Ranido RCAT-8830 5%Ru/C | 2 | 1 | 150 | 80 | 149 | 150 | 149,4 | 79,2 | 78,9 | 0,37 | 3 | 0 | 51,84 | 2,5 | 9,2 | 20,5 | 0,45 | 17,7 % | 1,26 |
| LF4V-HDO3.1 | Ranido RCAT-8830 5%Ru/C | 2 | 1 | 150 | 80 | 149 | 150 | 149,3 | 80,6 | 77,7 | 2,93 | 3 | 0 | 6,36 | 2,1 | 4,4 | 3,0 | 1,46 | 69,0 % | 1,06 |
| LF4V HDO4.0 | Ranido RCAT-8830 5%Ru/C | 2 | 1 | 200 | 80 | 204 | 204 | 204,0 | 84,0 | 77,1 | 6,92 | 3 | 0 | 33,57 | 1,8 | 9,2 | 18,2 | 0,50 | 27,3 % | 0,92 |
| LF4V HDO5.0 | Ranido RCAT-8830 5%Ru/C | 7,75 | 1 | 150 | 80 | 150 | 149 | 149,2 | 66,9 | 65,7 | 1,21 | 3 | 0 | 40,4 | 7,0 | 5,0 | 5,8 | 0,86 | 12,4 % | 0,90 |
| LF4V HDO5.1 | Ranido RCAT-8830 5%Ru/C | 7,75 | 1 | 150 | 80 | 149 | 148 | 148,6 | 79,5 | 78,2 | 1,38 | 8 | 0 | 4,9 | 3,5 | 2,0 | 1,4 | 1,43 | 40,8 % | 0,45 |
| LF4V HDO6.0 | Ranido RCAT-8830 5%Ru/C | 7,72 | 1 | 150 | 80 | 150 | 151 | 150,4 | 80,2 | 79,1 | 1,06 | 8 | 0 | 45,67 | 7,5 | 10,6 | 6,1 | 1,74 | 23,2 % | 0,97 |
| LF4V HDO6.1 | Ranido RCAT-8830 5%Ru/C | 7,72 | 1 | 150 | 80 | 149 | 149 | 149,0 | 79,1 | 77,9 | 1,20 | 8 | 0 | 19,02 | 7,6 | 19,0 | 2,5 | 7,60 | 99,9 % | 0,99 |
| LF4V HDO7.0 | Ranido RCAT-8830 5%Ru/C | 7,73 | 1 | 200 | 80 | 197 | 202 | 199,6 | 77,7 | 77,0 | 0,70 | 8 | 0 | 45,67 | 6,1 | 10,6 | 7,5 | 1,41 | 23,2 % | 0,79 |
| LF4V HDO8.0 | Ranido RCAT-8830 5%Ru/C | 7,72 | 1 | 250 | 80 | 251 | 256 | 253,4 | 84,7 | 79,4 | 5,28 | 8 | 0 | 37,5 | 7,4 | 8,1 | 5,1 | 1,59 | 21,6 % | 0,95 |
| LF4V HDO8.1 | Ranido RCAT-8830 5%Ru/C | 7,72 | 1 | 250 | 80 | 249 | 256 | 252,1 | 85,4 | 78,7 | 6,69 | 8 | 0 | 8,7 | 5,8 | 4,1 | 1,5 | 2,73 | 47,1 % | 0,75 |
| LF4V HDO9.0 | Ranido RCAT-8830 5%Ru/C | 7,74 | 1 | 300 | 80 | 314 | 319 | 316,0 | 83,9 | 81,3 | 2,60 | 8 | 0 | 28 | 6,8 | 6 | 4,1 | 1,46 | 21,4 % | 0,88 |
| LF4V HDO9.1 | Ranido RCAT-8830 5%Ru/C | 7,74 | 1 | 300 | 80 | 301 | 310 | 305,3 | 88,2 | 79,1 | 9,17 | 8 | 0 | 3,6 | 7,2 | 2,98 | 0,5 | 5,96 | 82,8 % | 0,93 |
| LF4V HDO10.0 | Pd-MgO-C | 5 | 1 | 300 | 80 | 315 | 310 | 312,3 | 85,1 | 79,4 | 5,75 | 8 | 0 | 26,1 | 5,8 | 2,4 | 4,5 | 0,53 | 9,2 % | 1,16 |
| LF4V HDO10.1 | Pd-MgO-C | 5 | 1 | 300 | 80 | 313 | 308 | 310,5 | 90,8 | 79,0 | 11,76 | 8 | 0 | 25,8 | 5,7 | 7,94 | 4,5 | 1,76 | 30,8 % | 1,15 |

The carbonyl content in the bio-oil decreased with increasing the reactor temperature (Figure 36, left), thus indicating improved stability of the bio-oil. On the other hand, the water content in the bio-oils produced at higher temperatures was very high (Figure 36, right), indicating that considerable amounts of carbon in the biomass feedstock was either cracked to gases or it remained in the reactor as coke. This was further supported by the low yields of liquid product at higher temperatures (Figure 4). However, the maximum formation of water and minimum yield of liquid product was observed at 200 °C, thus suggesting improved performance at higher temperature (250 °C). It was not possible to calculate to full mass balances for the runs due to lack of gas phase analyses and flow measurements.

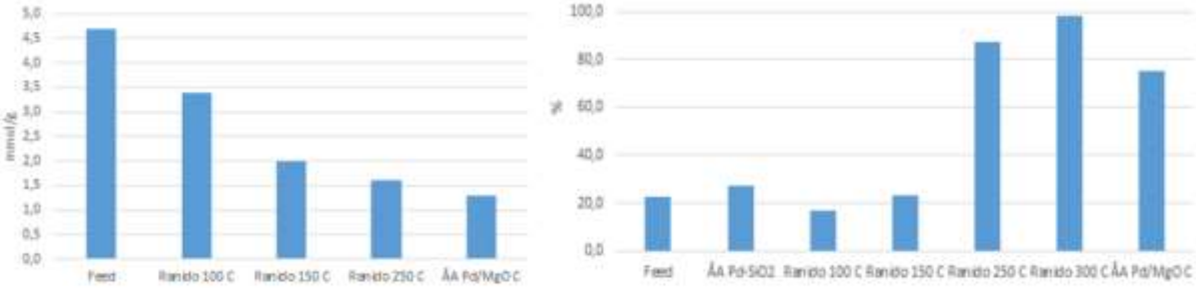

**Figure 36**. Carbonyl (left) and water content (right) in the bio-oils.

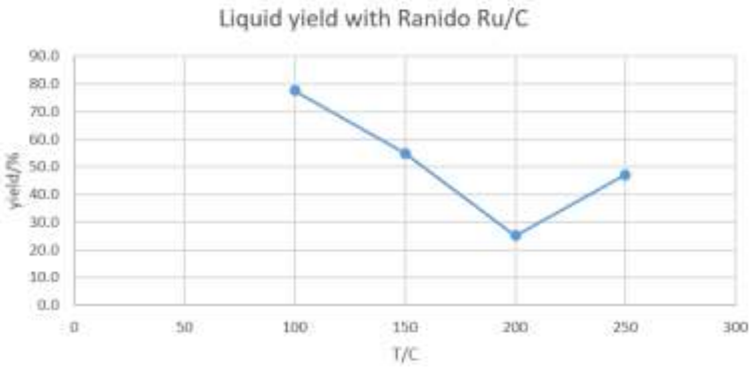

***Figure 37**. Liquid product yield as a function of reactor temperature with Ranido Ru/C catalyst.*

Catalyst deactivation and reactor plugging were the most serious problems observed in the upgrading of bio-oil by HDO. It is suggested that the HDO process should be carried out at least in three stages e.g. by applying the following temperature ranges: first stage at 100 – 150 ºC, second stage at 150 – 250 ºC, and third stage at temperatures beyond 300 ºC.

## 9. Conclusions

The addition of 2-naphthol to the hydrothermal pre-treatments clearly improved the saccharification of pine wood, resulting in up to 100% increase in sugar yield. In hardwoods (birch and willow without bark), the use of chemical additives in hydrothermal pre-treatments were not needed to reach quantitative cellulose conversion during enzymatic hydrolysis. The presence of bark in willow, however, partly inhibited the saccharification of the pre-treated wood material. Despite the remarkable improvement in the saccharification of pine wood by the use of 2-naphthol, the sugar yields were only about 16% on wood, considerably lower than the 35-40% obtained by saccharification of pre-treated birch and willow (without bark) wood. The use of an acidic catalyst is probably still needed in the pre-treatment of pine wood to open up the cell wall structure and facilitate the accessibility of carbohydrates to enzymes. The use of 1- and 2-naphthol in the pre-treatment of birch wood resulted in hydrolysis lignins with lower molar mass and distinct chemical functionalities, which appeared to suggest that the additives somewhat prevented the occurrence of lignin condensation reactions.

Selected hydrolysis lignins from pine, birch and willow (with bark) wood were used in the preparation of PLA composites. The addition of 20% lignin resulted in some reduction in tensile strength and strain of PLA without significant increase in tensile stiffness. The stiffness could be increased more efficiently with reinforcing fibres, such as CTMP fibers. Lignin structure or purity had no significant effect on the mechanical properties of PLA composites, and the results with kraft lignin (as reference) were very similar as with the hydrolysis lignins. However, hydrolysis lignins were clearly less odorous than kraft lignin, which could be a clear benefit for industrial application. The use of small molecular coupling agents and compatibilizers plasticized both lignin and PLA, which improved the processability and the compatibility of lignin with PLA. The compounds were easier to remove from the mould and the post-cleaning was improved, which in industrial processing can have an impact on production capacity. Unfortunately, the coupling agents did not improve the mechanical properties of lignin-PLA composites, but rather a further reduction in tensile strength was detected due to the plasticizing of PLA.

In analytical and bench scale fast pyrolysis of biomass, the addition of chemical additives (1- and 2-naphthol and formaldehyde) did not change the distribution of lignin and carbohydrate derived degradation products. It is likely that the reaction times (< 5 s) in fast pyrolysis were too short for the additives to react with the biomass feedstock. The addition of 2-naphthol, however, slightly enhanced the stability of the bio-oils in long-term storage, although this effect could probably be achieved by mixing the additive and the bio-oil after the pyrolysis process. The use of calcium formate did enhance the depolymerisation of lignin and the formation of more stable degradation products, due to the role of calcium formate as H-donor. In general, results from analytical and bench scale pyrolysis produced similar trends with respect to the analyses of degradation products, thus indicating that analytical fast pyrolysis is a useful and powerful tool for screening purposes.

The biochars formed in bench scale pyrolysis of birch, pine and willow wood (with bark) were used as raw material to produce carbon catalysts by steam activation and sulfonation. The activated carbon catalysts were then applied to the post-treatment of degradation vapors in analytical pyrolysis of pine wood. All catalytic materials changed the composition of pine pyrolysis derivatives, but the activated biochar from willow had clearly the highest impact on vapor composition. This effect was mainly due to its high alkaline metal content, which catalysed the degradation of polysaccharides into low molecular weight compounds and gas instead of anhydrosugars.

Catalytic fast pyrolysis of biomass was also performed with slag-based catalysts. These novel and low-cost catalytic materials were synthesized from steel slag by treatment with different chemical reagents and synthesis conditions (i.e. temperature, time, ultrasonication power), resulting in a broad range of catalysts with different morphological and structural properties, phase content and basicity. Evaluation of the synthesized materials in fast catalytic pyrolysis of woody biomass demonstrated that the slag catalysts changed the product distribution and the yield of the degradation products. However, the slag-based catalysts did not show any indication as potential hydrogen donors, which would prevent recondensation reactions of the lignin pyrolysis products and consequently reduce yield losses. Nonetheless, the release of reactive oxygen functional groups from the lignin side-chain might improve the stability of the bio-oil, even if yield losses occurred. The synthesized slag-based materials were further used in the carboxymethylation of cinnamyl alcohol with dimethyl carbonate to produce cinnamyl methyl carbonate, which is a valuable organic compound with various applications. The slag-based catalysts resulted not only in high conversion and selectivity to the desired product, but also illustrated the dependence of the catalytic results on basicity and surface area. Based on these results, waste slag materials have potential applicability as catalysts after certain treatment improving their properties.

The separation of lignin-based compounds from fast pyrolysis bio-oil was investigated with nanofiltration membranes. In general, the membrane fractionation of bio-oil indicated that a compromise needs to be found with respect to lignin yield in the permeate, permeate purity, and purity of the high MW fraction in the retentate. The separation of pyrolysis lignin from the bio-oils produced in bench scale pyrolysis of pine, birch and willow (with bark) wood was also performed by addition of water, which readily precipitated the pyrolysis lignin. These lignins were investigated as alternative for phenol substitution in PF resins. The pyrolysis lignins had good solubility and high reactivity towards formaldehyde. Moreover, these lignins also had a high tendency to condense in alkaline conditions, resulting in excess alkali consumption and even precipitation in the absence of phenol. The condensation reactions may take place via oxidation of catechol units to quinones that tend to react with the phenolic units of pyrolysis lignin. Therefore, oxidation during chemical mixing was tested to prevent the uncontrolled condensation and to attach phenol into pyrolysis lignin. The oxidative activation seemed to be more applicable to the less reactive hardwood pyrolysis lignins. Oxidation of catechols enhanced the attachment of phenol into birch pyrolysis lignin, preventing self-condensation and increasing the number of reactive sites for formaldehyde. With the more reactive pine pyrolysis lignin, the oxidation further enhanced the self-condensation, and the attachment or crosslinking of phenol was generally lower compared to birch.

In addition to bio-oil fractionation to separate the pyrolysis lignin, the direct upgrade of fast pyrolysis bio-oil into transportation fuels by catalytic HDO was also studied. Catalyst deactivation and reactor plugging were the most serious problems observed. The bio-oil was a very challenging feedstock for upgrading by HDO due to its high oxygen content, with highly reactive oxygenates in the oil (aldehydes, ketones, acids). The commercialization of bio-oil upgrading process needs significant further research, where the focus should be on real bio-oil feeds and first stage stabilizing treatment by mild HDO.

Finally, the suitability of willow wood (even with bark) as alternative wood raw material for hydrothermal and pyrolysis processes was demonstrated. However, debarking methods for willow should be sought prior to hydrothermal pre-treatment because the presence of bark clearly inhibits the enzymatic saccharification of this raw material. In any case, more analyses of the different lignin fractions obtained after hydrothermal and pyrolysis processes need to be conducted to evaluate the potential of willow compared to other wood species.

# 10. Future outlook

The observed improvement in saccharification of pine wood by addition of 2-naphthol to the hydrothermal pre-treatment was remarkable, but similar effects should be ideally sought with addition of bio-based phenolic compounds. With respect to the use of hydrolysis lignin in the preparation of PLA-based composites, other coupling agents and/or dosing protocols using different ratios should be still tested to ensure the reactions with lignin. The results of the PLA/lignin composites should also be confirmed at larger scale with more efficient mixing, and preferably also by impact strength measurements. Moreover, the effect of lignin as fire retardant and natural antioxidant could be evaluated to demonstrate the full potential of lignin for improving the properties of PLA-based composites.

Slags from the steel industry can be used to synthesize catalytic materials for different types of chemical reactions. Other waste materials and treatment methods will be still studied in the synthesis of novel catalysts with improved properties, and their catalytic activity in fast pyrolysis of biomass could be evaluated. In particular, the dependence of the catalytic activity on the basicity and surface area of the synthesized catalytic materials should be investigated.

The activation of the biochars obtained in fast pyrolysis of biomass can be investigated using different raw materials and/or activation methods, and the performance of the activated carbons can also be studied in several applications. On the other hand, the upgrading of the pyrolysis bio-oils into fuels by catalytic HDO will continue by enabling prolonged operation time for mild stabilizing HDO. The temperature of the first stage is not the only way to reach this, but the feeding system of the bio-oil should also be modified in order to minimize the time to which the bio-oil is exposed to heat before the catalyst bed. Pretreatment of the bio-oil before HDO could also be one way to improve the stability.

Membrane fractionation of fast pyrolysis bio-oil will continue to find the most suitable membranes for efficient and cost-effective separation of pyrolysis lignins. The use of these highly reactive lignins as alternative for phenol substitution in PF resins should be still studied, although proper resin synthesis protocols need to be yet developed. The effect of oxygen on condensation reactions will be studied further in detail to provide a better understanding on how to utilise this treatment in resin synthesis. The performance and reactivity of the pyrolysis lignins and the effect of oxygen should still be confirmed by ABES gluing trials.

# 11. Dissemination activities

## Peer-reviewed publications

1. Kholkina E, Kumar N, Ohra-aho T, Lehtonen J, Lindfors C, Perula M, Peltonen J, Salonen J, Murzin DY. 2019. Synthesis and characterization of catalytic materials using industrial slag: Influence of alkaline pretreatment, synthesis time and temperature. **Topics in Catalysis**, 62:738-751; doi: 10.1007/s11244-019-01162-5.

2. Kholkina E, Kumar N, Ohra-aho T, Lehtonen J, Lindfors C, Perula M, Peltonen J, Salonen J, Murzin DY. 2019. Transformation of industrial steel slag with different structure-modifying agents for synthesis of catalysts. **Catalysis Today** (in press); doi: 10.1016/j.cattod.2019.04.033

3. Ohra-aho T, Lindfors C, Lehtonen J, Tamminen T, Siipola V. 2020. Activated carbons from fast pyrolysis biochar as novel catalysts for the post-treatment of pyrolysis vapors, studied by analytical pyrolysis. **C—Journal of Carbon Research,** 6, 0065; doi:10.3390/c6040065

## Conference publications and presentations

4. Servaes, K. 2017. Lignin First Concept for High-Value Applications. 4th Biorizon annual event: from the lab to piloting, Antwerp, Belgium, 30th November 2017 (poster presentation).
5. Lehtonen J, Ohra-aho T, Lindfors C, Kholkina E, Kumar N, Murzin D, Oasmaa A. 2018. Application of steel industry slags as novel cost efficient catalysts in catalytic fast pyrolysis of biomass. 27th European Biomass Conference and Exhibition in Copenhagen, Denmark, 14-18th May 2018.
6. Ohra-aho T, Kumar N, Murzin D, Kholkina E, Lindfors C, Oasmaa A, Lehtonen J, Tamminen T. 2018. Steel industrial slags as novel catalysts for the conversion of biomass into bio-oil, evaluated by analytical pyrolysis. 22nd International Symposium on Analytical and Applied Pyrolysis in Kyoto, Japan, 3rd- 8th June 2018 (oral presentation)
7. Kholkina E, Kumar N, Lindfors C, Ohra-aho T, Lehtonen J, Perula M, Peltonen J, Salonen J, Murzin DY. 2018. Novel catalytic materials from industrial slags for application in catalytic fast pyrolysis of pine sawdust. 7th International Conference on Engineering for Waste and Biomass Valorisation, Prague, Czech Republic, 2-5th July 2018 (oral presentation)
8. Kholkina E, Kumar N, Ohra-aho T, Lehtonen J, Lindfors C, Perula M, Peltonen J, Salonen J, Murzin DY. 2018. Application of industrial wastes in creation of zeolitic materials: synthesis, characterization and evaluation. 18th Nordic Symposium on Catalysis, Copenhagen, Denmark, 26-28th August 2018.
9. Kholkina E, Kumar N, Ohra-aho T, Lehtonen J, Lindfors C, Perula M, Peltonen J, Salonen J, Murzin DY. 2018. Synthesis and characterization of novel catalytic materials from industrial slag: Information of treating agent, synthesis time and temperature. Annual Conference Johan Gadolin Process Chemistry Centre, Turku, Finland, 22nd November 2018 (flash oral and poster presentation).
10. Kholkina E, Kumar N, Ohra-aho T, Lehtonen J, Lindfors C, Perula M, Peltonen J, Salonen J, Murzin DY. 2019. Synthesis and characterization of catalytic materials from industrial slag: Influence of treating agent, synthesis time and temperature. Pecha Kucha oral presentation, Finnish Young Scientist Forum on Catalysis, Oulu, Finland, 5th April 2019.
11. Borrega M. 2019. Hydrothermal processing of biomass as integral part of biorefineries. 2nd International Workshop in Biorefinery of Lignocellulosic Materials, Córdoba, Spain, 4-7th June 2019 (invited lecture).
12. Lindfors C, Oasmaa A. 2019. IEA Bioenergy Task 34 Country report – Finland. IEA Bioenergy Task 34 meeting, Karlsruhe, Germany, 25-26th June 2019.
13. Kholkina E, Kumar N, Ohra-aho T, Lehtonen J, Lindfors C, Perula M, Peltonen J, Salonen J, Eränen K, Murzin DY. 2019. Physico-chemical and catalytic properties of industrial slag catalysts using different organic surfactants. 14th European Congress on Catalysis, Aachen, Germany, 18-23th August 2019 (poster presentation).
14. Borrega M, Pihlajaniemi V, Tamminen T. 2019. Chemical additives in hydrothermal treatments: effects on saccharification and on the properties of hydrolysis lignin from pine, birch and willow wood. 20th International Symposium on Wood, Fiber, and Pulping Chemistry, Tokyo, Japan, 9-11th September 2019 (oral presentation).
15. Kholkina E, Kumar N, Lehtonen J, Peurla M, Peltonen J, Salonen J, Murzin DY. 2019. Application of ultrasound irradiation for treatment of industrial steel slag in creation of slag-

based catalysts. 5th International Congress on Catalysis for Biorefineries, Turku, Finland, 23rd – 27th September 2019.

16. Lehtonen J, Siipola V, Ohra-aho T. Modified fast pyrolysis biochars as novel catalysts for biomass ex-situ catalytic fast pyrolysis. 5th International Congress on Catalysis for Biorefineries, Turku, Finland, 23rd – 27th September 2019.
17. Liitiä T, Borrega M, Pihlajaniemi V, Wikström L, Tamminen T. 2020. Hydrolysis lignins in PLA-based composites. Nordic Wood Biorefinery Conference, Online, 13th - 15th October 2020.

## Manuscripts submitted

18. Kholkina E et al. 2020. Ultrasound irradiation as an effective tool in synthesis of the slag-based catalysts for carboxymethylation. Part I: Synthesis and characterization. Submitted manuscript.
19. Kholkina E et al. 2020. Ultrasound irradiation as an effective tool in synthesis of the slag-based catalysts for carboxymethylation. Part II: Catalytic performance. Submitted manuscript.
20. Borrega M, Pihlajaniemi V, Liitiä T, Wikström L, Tamminen T. 2020. Evaluation of chemical additives in hydrothermal pre-treatment of wood for the integrated production of monosugars and hydrolysis lignins for PLA-based biocomposites. Manuscript in preparation.

* Manuscripts submitted by the end of 2020.

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