

# GREEN BIORAFF SOLUTIONS

POPULAR SCIENCE REPORT



Regional Council  
of Ostrobothnia



Interreg  
Botnia-Atlantica  
European Regional Development Fund



Region  
Västernorrland



UNIVERSITY OF JYVÄSKYLÄ  
KOKKOLA UNIVERSITY CONSORTIUM  
CIYDENUS

processum

Centria  
RESEARCH AND DEVELOPMENT

## **GREEN BIORAFF SOLUTIONS - GBS**

### **PROJECT OVERVIEW**

**TIME PERIOD: 2018-05-01 - 2021-04-31**

**TOTAL BUDGET: 1 606 000 EUR**

**PROJECT PARTNERS: Centria University of Applied Sciences, Kokkola University Consortium Chydenius, RISE Processum**

**FINANCIERS: Interreg Botnia-Atlantica, Region Västernorrland, Österbottens Förbund**

**COORDINATOR: Kokkola University Consortium Chydenius**

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## BACKGROUND

This project consortium has developed attractive biorefinery solutions for Sweden and Finland. The project has been active in finding and exploring products based on saw dust, bark and fiber sludge from the saw milling and pulp and paper industries. More specifically, we have produced the biobased plastic polylactic acid via lactic acid that is produced via microbial or chemical routes from fiber sludge and saw dust. Furthermore, we have refined hydrolysis lignin products for further production of e.g. activated carbon for which there is a large market in Sweden and Finland. Moreover, foams have been developed and produced from tannins, which are extracted from bark. Therefore, activities aiming at the production of products from saw dust, bark and fiber sludge has been conducted within this project (picture).



The persistent nature of fossil-derived plastics is a well-known environmental problem that could be tackled via the production of biodegradable plastics. If the biodegradable plastic is produced from a renewable source, such as forest biomass, then the carbon dioxide emissions would also be reduced. The same environmental benefits can be achieved by reducing the need of long-distance transportation of products, e.g. producing activated coal in Sweden and Finland using raw material from our forests instead of purchasing large quantities of activated coal from Sri Lanka. In this project, we want to produce the biodegradable and biobased plastic polylactic acid as well as activated carbon, from saw dust and fiber sludge which are byproducts from the saw milling and pulp and paper industries. Using bark, another by-product from those industries, we produced tannin-based foams, which are known for their high fire resistance. The target group consists of the raw material suppliers, the saw milling and pulp and paper industries and the end users, e.g. composite companies or construction companies.



Project kick-off 12 September 2018

# 1. WP1 Polylactic acid from forest-based biomass

## 1.1 INTRODUCTION

Biobased polymers or biopolymers are being used and produced at increasing volumes as there is an increased demand for more environmentally friendly and sustainable products. There are various types of biopolymers available at the market level today. One such biopolymer is polylactic acid (PLA) which is used in various plastic products. However, the current mode of PLA production involves raw materials such as corn, starch and sugar cane, all of which can be used as feed stocks rather than for the production of polymers.

The Swedish and Finnish forests provide a valuable resource as an alternative for the current production of biobased products such as PLA. By utilizing low value residual streams from the forest industry PLA can be produced in an even more environmentally sustainable matter as compared to the current use of corn and sugar cane as raw materials for PLA production. In the GBS project we have investigated the suitability and feasibility in using such forest industry residual streams in the production of lactic acid with further processing into PLA, see Figure 1.

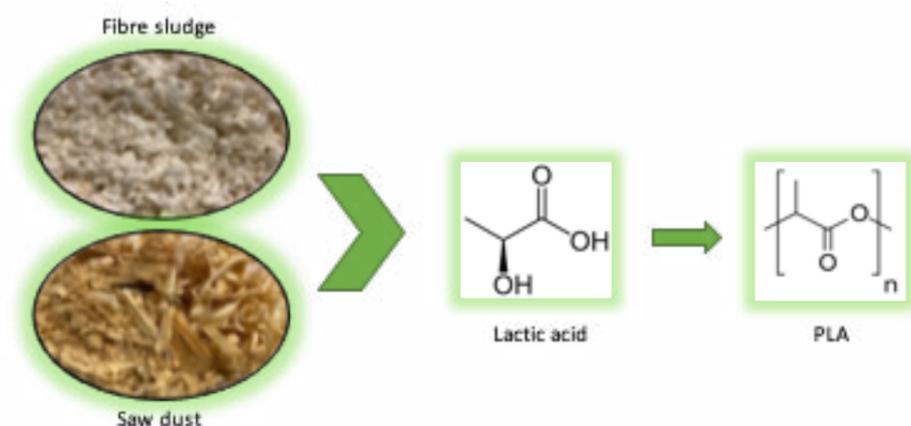


Figure 1. Fibre sludge and saw dust, two residual streams from the Swedish and Finnish forest industry, have been used for production of lactic acid with subsequent polymerisation to polylactic acid (PLA)

One of the investigated residual streams from the forest industry during the project is fibre sludge. Fibre sludge is a low value byproduct from pulp mills and is essentially cellulose fibers of varying purity dependent of the underlying process of the pulp mills. The volumes of fibre sludge produced are roughly 1000 tons/mill/year at current production rates. As the material contains high levels of pure cellulose there is no need for pretreatment of the material. Cellulose can be converted into single molecules of glucose by the action of specific enzymes. The glucose, and other sugars, can then be utilized by microorganisms that produce biobased compounds such as lactic acid through fermentation processes. The material can thus be converted into a high value product through enzymatic hydrolysis into sugar followed by fermentation to lactic acid and polymerization to PLA.

Another investigated residual stream from the forest industry is saw dust. Saw dust is generated at saw mills at large volumes and is mostly used for its energy value. Saw dust differs from fibre sludge in that some form of pretreatment is required prior to the conversion into fermentable sugars by enzymes. The pretreatment converts the wood fibers in the saw dust into more accessible forms in order for the enzymes to hydrolyse the cellulose, and hemicellulose, into various sugars. However, as the pretreatment of wood, depending on parameters such as temperature, catalyst and time, usually produces also various compounds that may be toxic for microorganisms, the resulting sugar-containing hydrolysate may need further processing in order to reach an efficient fermentation process.

The aim in WP1 has been to evaluate the residual streams from the forest industry in Sweden and Finland as possible raw materials for the production of lactic acid with subsequent processing into polylactic acid. The processes connected to lactic acid fermentation, chemocatalytic conversion into lactic acid and PLA polymerization have been extensively optimized during the project. As a result, both fibre sludge and saw dust provide suitable properties for lactic acid production. The lactic acid can be used for PLA production using synthesis parameters developed in the project. However, the polymerization process to high density PLA needs further investigation.

## 1.2 WP1.1 Enzymatic hydrolysis and bacterial fermentation for the production of lactic acid from forest based raw material

### 1.2.1 METHOD

#### Enzymatic hydrolysis of fibre sludge to generate hydrolysate for lactic acid fermentation

Fibre sludge has been provided by Domsjö Fabriker AB and Holmen AB (Iggesund). The fibre sludge has been used as raw material in an enzymatic hydrolyzation process using commercial enzymes. The hydrolysates have been produced in stirred bioreactors available at RISE Processum AB where the solid fibre sludge material has been converted to liquid hydrolysate containing sugars that are utilized by the lactic acid bacteria in the subsequent fermentation process (figure 2). The remaining solids have been separated after completion of the hydrolysis and the hydrolysates have been used in lactic acid fermentation trials. Various amounts of raw material and enzyme has been investigated and resulting amounts of sugars in the hydrolysates have been analyzed.



Figure 2. Fibre sludge (left) has been converted to hydrolysate (middle) through enzymatic hydrolysis. The hydrolysate has been used in lactic acid fermentations (right)

#### Lactic acid fermentation in fibre sludge hydrolysate

The resulting fibre sludge hydrolysates have been used in lactic acid fermentation trials in laboratory as well as pilot scale. Process parameters such as pH adjustment, nutrient supply and fermentation mode have been investigated and optimized continuously during the project in order to reach the most economical and highest yielding process. Successful lactic acid fermentations have been performed in 50L pilot scale and the produced lactic acid has been used in WP1.3 in polymerization experiments to produce PLA. The resulting amounts of lactic acid as well as sugars have been evaluated at RISE Processum and Centria.

## Lactic acid fermentation in spruce (saw dust) hydrolysate

Spruce (saw dust) hydrolysates have been provided by Sekab AB. For these hydrolysates, saw dust has been used in a process to generate hydrolysates containing sugars (figure 3). Various modes of fermentation and process parameters, including addition of detoxifying agents, have been investigated. The resulting yields of sugars and lactic acid have been analyzed by RISE Processum and Centria. Successful 50L pilot scale lactic acid fermentations have been performed using saw dust as raw material.



Figure 3. Saw dust (left) has been converted to hydrolysate (middle) through pretreatment and enzymatic hydrolysis and has subsequently been used to produce lactic acid (right)

## 1.2.2 RESULTS

### Enzymatic hydrolysis

Amounts of biomass and enzyme used in the hydrolysis reactions have been evaluated. The results indicate that the conversion of the cellulose present in the biomass to fermentable glucose is increasingly efficient with higher loading of both biomass and enzyme (figure 4). The process is most productive within the first 24 hours of the reaction.

### Lactic acid fermentations

The lactic acid fermentation experiments described here are outtakes of the most representative activities performed during the project. A full description of all experiments performed is beyond the scope of the report. The initial experiments were performed using a bacterial strain that produces a mixture of the two isoforms of lactic acid, D-lactic acid and L-lactic acid. Analyses of the PLA resulting from the fermentations revealed that it contained mesoform PLA as well as monomers of lactic acid. Since the properties of the resulting PLA from such a mixture is inferior to a more optically pure PLA, that is, containing either D- or L-lactic acid, we sought to isolate a bacterial strain that could produce either of the lactic acid isoforms. Isolation of several lactic acid producing strains was performed at the industrial site of RISE Processum AB and one of the strains, producing mostly L-lactic acid, were used in subsequent fermentation experiments. Lactic acid fermentations have been up-scaled from laboratory scale to 50L pilot scale (figure 5).

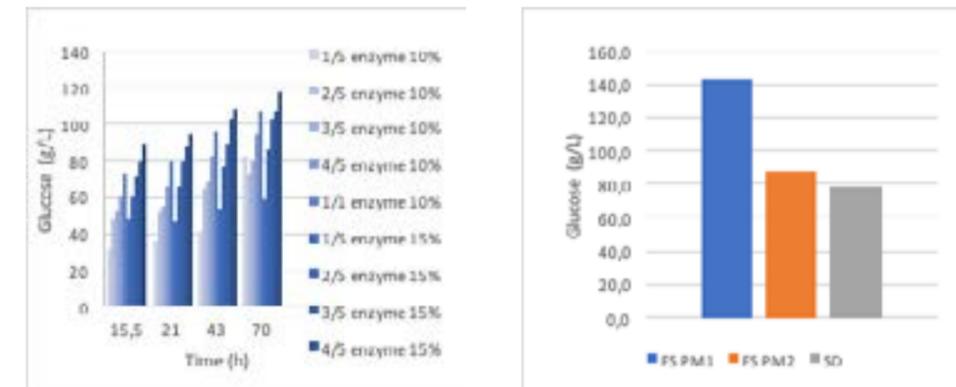


Figure 4. Effects of biomass and enzyme loading on hydrolysis of fibre sludge to fermentable sugar (left). Comparison of sugar amounts in different hydrolysates (right). PM = pulp mill, FS = fibre sludge, SD = saw dust.

The initial trials were performed with fibre sludge from pulp mills participating in the project. The resulting fibre sludge hydrolysates were used in lactic acid fermentation trials where the raw materials from the two pulp mills performed equally well (figure 4). However, fibre sludge from pulp mill 1 yielded more fermentable sugar and can thus be used for production of higher amounts of lactic acid. In comparison to fibre sludge hydrolysate, lactic acid production in saw dust hydrolysate is slower and requires detoxification for efficient fermentation due to the presence of inhibitors arising in the pretreatment of saw dust (figure 6).



Figure 5. Lactic acid fermentation has been performed in scales from shake flasks (left) to laboratory scale bioreactors (middle) and 50L pilot scale (right)

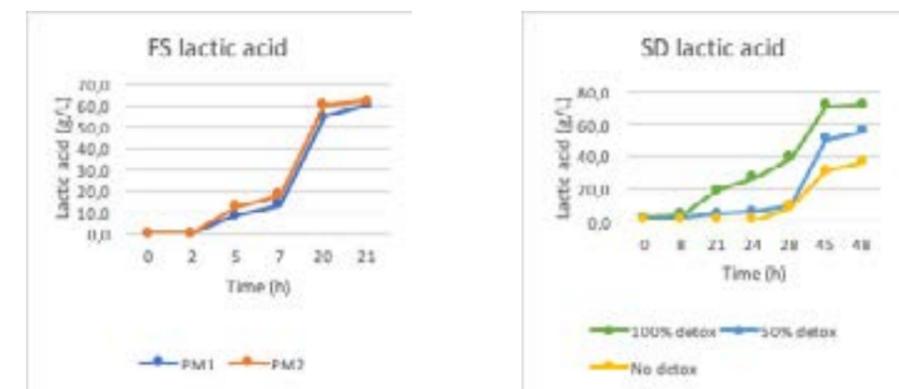


Figure 6. Lactic acid fermentation in fibre sludge (FS) hydrolysates and saw dust (SD) hydrolysates. PM = pulp mill

Since lactic acid bacteria need nutrients containing nitrogen, in addition to the sugar carbon source, for lactic acid production, extensive optimization of fermentation conditions has been performed resulting in a more economically relevant fermentation process due to a significant reduction of additives needed for efficient lactic acid production (figure 7). In addition, since large volumes of pH adjustment agents such as ammonium hydroxide are needed for an efficient fermentation, optimizations of required pH as well as pH adjusting agents have been performed continuously (figure 8, 10). As a result, the required pH level has been reduced, leading to a more economical process. Below are examples of optimization trials performed during the project.

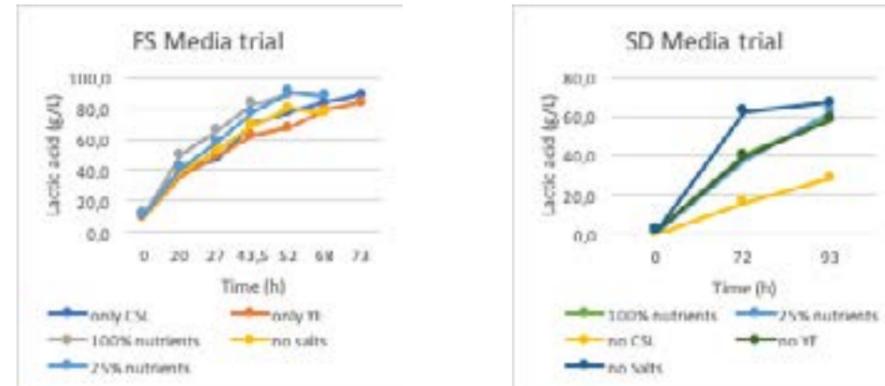


Figure 7. Effects of nutrient additives on lactic acid fermentation in fibre sludge (left) and saw dust (right) hydrolysate

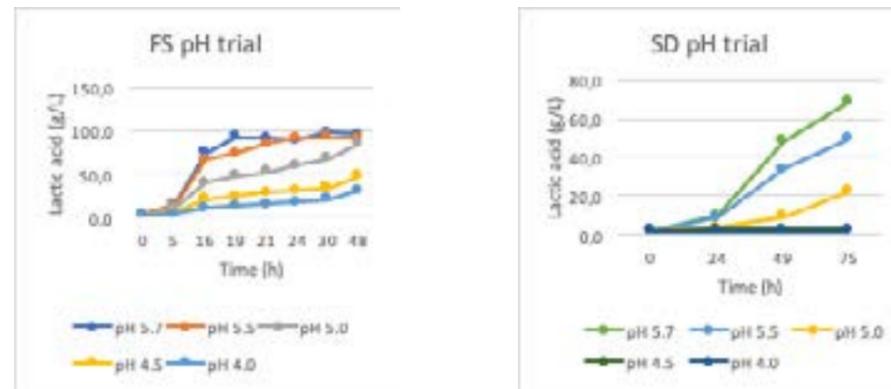


Figure 8. Lactic acid production at different pH in fibre sludge (left) and saw dust (right) hydrolysates

Different modes of fermentation have been evaluated within the project. The results indicate that fed-batch mode yields the most productive mode of lactic acid production in fibre sludge hydrolysate and even more so in saw dust hydrolysates where productivity in batch-mode is significantly lower (figure 9). Continuous fermentation mode has also been investigated and fed-batch mode was more productive than continuous mode as well.

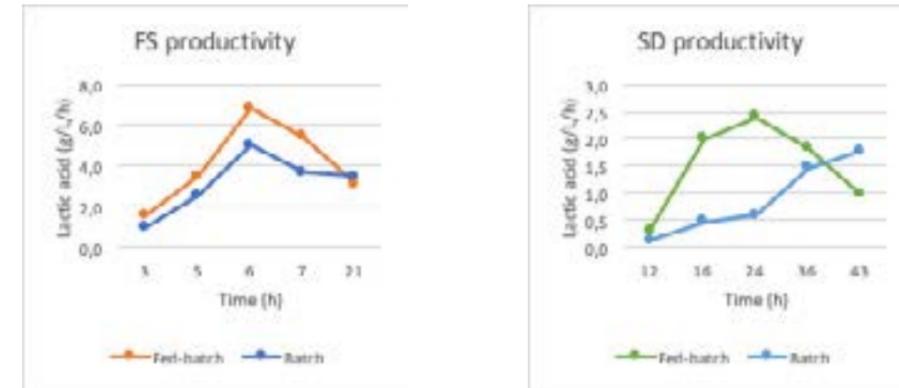


Figure 9. Fed-batch versus batch fermentation of lactic acid in fibre sludge (left) and saw dust (right) hydrolysates.

In the later stages of the project, a more pure and concentrated (with separated sugars and less inhibitors) saw dust hydrolysate from Sekab AB was used to investigate whether an improved lactic acid fermentation could be achieved using saw dust as raw material. Indeed, lactic acid was efficiently produced in this hydrolysate and no detoxifying agent was needed (figure 10).

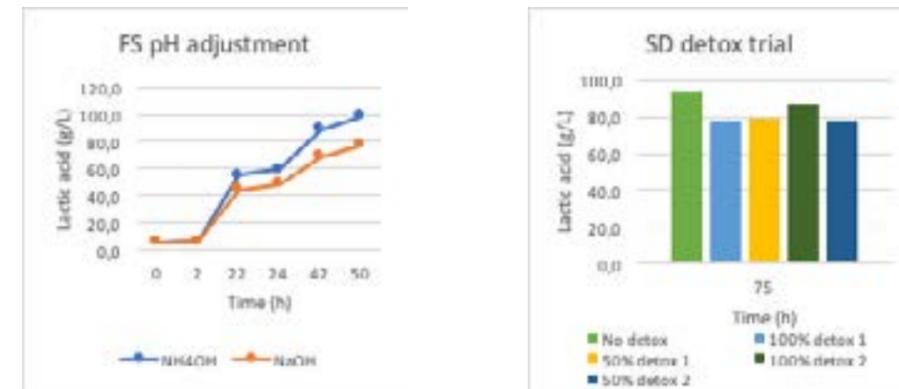


Figure 10. Effects of pH adjusting agents (left) in fibre sludge hydrolysate and detoxification (right) in pure saw dust hydrolysate

Successful 50L scale fermentations have been performed during the project to produce enough lactic acid for subsequent polymerization trials (figure 11). As an effect of the promising results using saw dust, an industrial scale lactic acid fermentation using saw dust as raw material is in the pipeline for the near future.

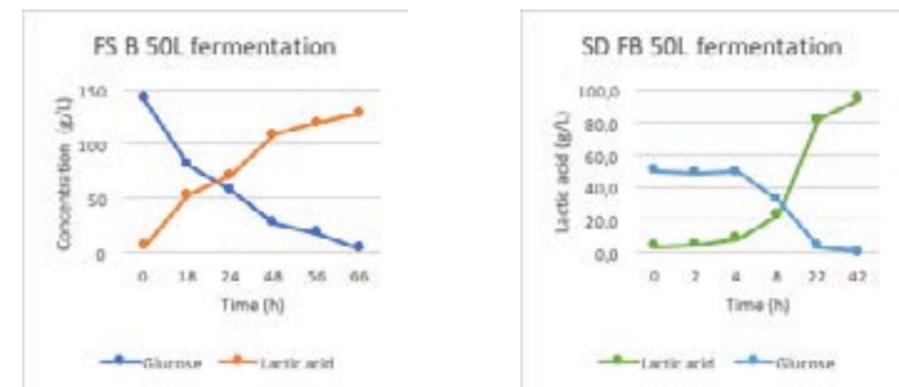


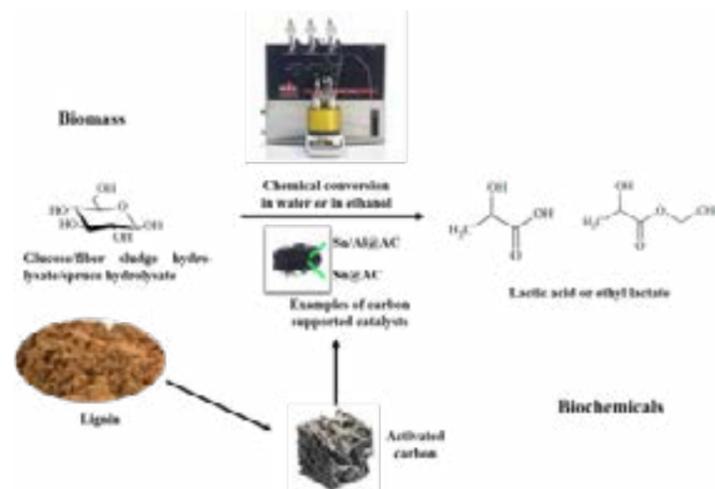
Figure 11. Lactic acid fermentation in 50 liter scale in fibre sludge hydrolysate (left, batch) and saw dust hydrolysate (right, fed-batch)

## 1.3 WP1.2 Chemocatalytic conversion of biomass-based sugars to lactic acid

### 1.3.1 METHOD

This part of the work package aimed for the chemically catalyzed conversion of biomass-based sugars to biochemicals, i.e. lactic acid or ethyl lactate. Selected raw materials were glucose, fiber sludge, fiber sludge hydrolysate and spruce hydrolysate. Fiber sludge was provided by Domsjö Fabriker AB, fiber sludge hydrolysate by RISE Processum AB and spruce hydrolysate by Sekab AB. The project was started with the development of an analytical method (HPLC-RI, Pirttimaa 2020) for the analysis of biochemicals as well as sugars. Also, the chemical composition of the fiber sludge was determined (Lappalainen et al., 2019).

Conversion of raw materials to biochemicals was studied with 1-step conversion reaction performed in a pressure reactor (HEL's DigiCAT, Figure 12) or in a microwave reactor (Biotage Initiator, Figure 13). Heterogeneous activated carbon-supported metal oxide catalysts or homogeneous metal chlorides or sulfuric acid were used to catalyze the reactions. Water or ethanol was used as the solvent for the conversion reactions. Reaction products were analyzed with HPLC-RI, HPLC-PDA or GC-MS. Schematic representations of the studied reactions are presented in Figures 12 and 13.



**Figure 12.** Chemical conversion of biomass to biochemicals in pressure reactor catalyzed by activated carbon supported catalysts. Water or ethanol was used as the solvent



**Figure 13.** Chemical conversion of biomass to biochemicals in microwave reactor catalyzed by Brønsted and Lewis acids. Water was used as the solvent

### 1.3.2 RESULTS

#### Biomass characterizations

The fiber sludge used in the studies consisted mainly of cellulose (98%, dry weight). In addition, it contained small amounts of hemicellulose (1%) and ash (1%). Fiber sludge and spruce hydrolysates were water solutions, which contained sugars (mainly glucose) 11.9% and 9.2%, respectively.

#### Glucose conversion to lactic acid with heterogeneous activated carbon-supported metal oxide catalysts

The catalysts (Figure 12) used to convert glucose to lactic acid were prepared from hydrolysis lignin in work package 2, where more information about catalyst preparation and characterization can be read. The glucose conversion reactions were performed in various conditions to find the best catalyst, and to optimize the reaction time, temperature, pressure, and catalyst amount. Selected results are given in Table 1. Based on the results the highest lactic acid yield achieved was 42%, which was produced with Sn/Al5/2.5@AC catalyst (prepared from steam activated and nitric acid modified activated carbon) at 180 °C in 20 min with the pressure of 5 bars. In order to study the recyclability of the used catalyst, it was recovered from the reaction solution, washed and used again four times. The yield of lactic acid varied from 15 to 20% during the recycling experiments. The decrease in the lactic acid yield indicated that the catalyst was not stable in the aqueous reaction solution, which was probably caused by the deposition of carbonaceous byproducts, such as humines, on the catalyst's active sites, as well as by the leaching of aluminum oxides as active metal. More detailed information about the glucose conversion to lactic acid can be read from the Kupila et al., 2021a.

Catalyst <sup>1</sup>	Catalyst support <sup>2</sup>	Reaction conditions	Lactic acid yield (%)
-	-	180 °C, 120 min, 30 bar	5
AC <sup>3</sup>	AC <sub>ZN</sub>	180 °C, 120 min, 30 bar, 0.1 g of catalyst	5
Sn <sub>10</sub> @AC	AC <sub>ZN</sub>	180 °C, 120 min, 30 bar, 0.1 g of catalyst	19
Sn/Al <sub>5/5</sub> @AC	AC <sub>ZN</sub>	180 °C, 120 min, 30 bar, 0.1 g of catalyst	27
Sn/Al <sub>5/2.5</sub> @AC	AC <sub>ZN</sub>	180 °C, 120 min, 30 bar, 0.1 g of catalyst	31
Sn/Al <sub>5/2.5</sub> @AC	AC <sub>S</sub>	180 °C, 120 min, 30 bar, 0.1 g of catalyst	24
	AC <sub>SN</sub>		34
	AC <sub>ZN</sub>		31
Sn/Al <sub>5/2.5</sub> @AC	AC <sub>SN</sub>	180 °C, 20 min, 5 bar, 0.2 g catalyst	42

**Table 1.** Glucose (0.1 g) conversion to lactic acid in water (20 ml) and N<sub>2</sub> atmosphere with various catalysts

<sup>1</sup> Sn<sub>10</sub>, Sn/Al<sub>5/5</sub> or Sn/Al<sub>5/2.5</sub> means that catalyst contains 10, 5 or 2.5 wt-% of the active metal(s)

<sup>2</sup> ZN means chemically activated, nitric acid modified AC, S steam activated AC, and SN steam activated, nitric acid modified AC

<sup>3</sup> AC means activated carbon

#### Glucose/hydrolysate conversion to ethyl lactate with heterogeneous activated carbon-supported metal oxide catalysts

Glucose, fiber sludge hydrolysate, and spruce hydrolysate were used as raw materials in ethyl lactate production (Figure 12). The catalysts used in the reactions were prepared from hydrolysis lignin in work package 2, where more information can again be read. The reactions were performed in various conditions to find the best catalyst, and to optimize the reaction conditions. With glucose as the feedstock the highest ethyl lactate yield was achieved with a zinc containing catalyst. The recycling experiments showed that the catalyst began to deactivate in use; however, reactivation of the catalyst increased the ethyl lactate yield to the same level as it was after the first cycle.

When fiber sludge and spruce hydrolysates were used as the raw materials the best ethyl lactate yields were achieved again with the zinc containing catalyst. The results from the reusability experiments were also quite promising, since the zinc catalyst seemed to preserve its activity even after multiple cycles i.e. there was no noticeable decrease in ethyl lactate yields. More detailed information about the glucose and hydrolysate conversion to ethyl lactate can be read from the Kupila et al., 2021b (manuscript to be sent for publication during spring 2021).

#### Glucose/fiber sludge conversion to biochemicals with homogeneous Brønsted and Lewis acids

Glucose and fiber sludge were used as raw materials in production of biochemicals with homogeneous acid catalysts (Figure 13). The studied catalysts were sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), which is a Brønsted acid, as well as SnCl<sub>2</sub>\*2H<sub>2</sub>O and AlCl<sub>3</sub>\*6H<sub>2</sub>O, which are Lewis acids (unpublished results). Selected results are given in Table 2. Based on the results, the homogeneous catalysts were not as efficient in lactic acid production than heterogenous carbon-supported metal oxide catalysts, even though there was the same active metal(s) present. The highest lactic acid yield, 30%, was achieved with glucose at 180 °C in 2 h with the pressure of 16 bars and with the mixture of SnCl<sub>2</sub>\*2H<sub>2</sub>O and AlCl<sub>3</sub>\*6H<sub>2</sub>O as the catalyst. When sulfuric acid was used as the catalyst, the reaction did not produce lactic acid as the product at all. Instead, levulinic acid was formed (Table 2). More detailed information about the fiber sludge conversion to levulinic acid can be read from the Lappalainen et al., 2019.

Biomass	Catalyst <sup>1</sup>	Reaction conditions	Lactic acid yield (%)
Glucose	SnCl <sub>2</sub> *2H <sub>2</sub> O (32 mg)	180 °C, 2 h, 16 bar	15
Glucose	AlCl <sub>3</sub> *6H <sub>2</sub> O (16 mg)	180 °C, 4 h, 16 bar	14
Glucose	SnCl <sub>2</sub> *2H <sub>2</sub> O (8 mg) + AlCl <sub>3</sub> *6H <sub>2</sub> O (8 mg)	180 °C, 2 h, 16 bar	30
Fiber sludge	SnCl <sub>2</sub> *2H <sub>2</sub> O (32 mg)	180 °C, 4 h, 16 bar	14
Fiber sludge	AlCl <sub>3</sub> *6H <sub>2</sub> O (34 mg)	180 °C, 2 h, 16 bar	11
Fiber sludge	SnCl <sub>2</sub> *2H <sub>2</sub> O (8 mg) + AlCl <sub>3</sub> *6H <sub>2</sub> O (8 mg)	180 °C, 2 h, 16 bar	16
Fiber sludge	H <sub>2</sub> SO <sub>4</sub> (0.3 M)	180 °C, 1 h, 17 bar	49 <sup>1</sup>

Table 2. Biomass (55 mg) conversion to lactic acid in water (5 ml) with various homogenous catalysts

1 The formed biochemical was levulinic acid instead of lactic acid

### 1.4 WP1.3 Production of PLA from the obtained LA

#### 1.4.1 METHOD

The fermentation broths containing lactic acid that have been produced in WP1.1 have been used in polymerization trials with the aim to produce polylactic acid. For this purpose, different synthesis routes have been explored. The experiments have involved isolation of lactic acid from the fermentation broth through removal of water and unwanted salts followed by esterification and polymerization of pure lactic acid to PLA. There are various synthesis routes to produce PLA, among which are ring opening polymerization (ROP) of lactide and direct polycondensation. Both methods have been attempted during the project. However, although the ROP of lactide is commonly used in industrial production of PLA, we have not been able to produce larger quantities of PLA through this route. Instead, we have opted for polycondensation of lactic acid to PLA. This has involved purification of the crude lactic acid from the fermentation broth, esterification, oligomerization and finally polycondensation to produce polylactic acid.

#### 1.4.2 RESULTS

The fermentation broth containing lactic acid has been purified through a series of steps to yield a pure form of lactic acid. The lactic acid has thereafter been used in trials of ring-opening polymerization (ROP) to attempt to produce high-density PLA (HDLPLA). However, since the attempts to produce HDLPLA were unfruitful, and trials using various catalysts were unsuccessful, we opted to produce PLA of lower density (LDLPLA) through direct polycondensation of the produced lactic acid (figure 14-15) to gain PLA that could be used in application testing.

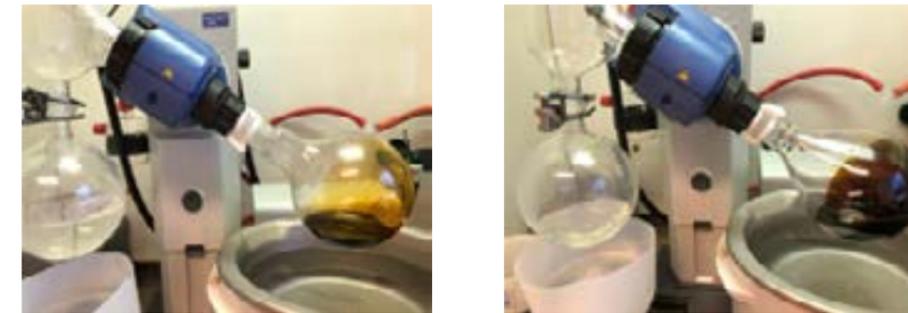


Figure 14. Water removal (left) and distillation of lactate ester (right) from fermentation broth (saw dust) containing lactic acid

The polymerization process has involved several reaction steps including removal of water and undesired salts, esterification of the crude lactic acid and direct polycondensation of purified lactic acid (figure 14). Reactions have been optimized regarding reaction times and temperature and attempts have been made to recycle reaction chemicals. For instance, ethanol that has been used during the process can be re-used after distillation and ammonium sulphate produced during neutralization can be filtered and re-used. We have been able to produce LDPLA using both fibre sludge and saw dust as raw materials and by polycondensation we have produced roughly 1 kg of L-LDPLA from lactic acid produced in fibre sludge hydrolysate (figure 15).



Figure 15. Roughly 50% pure lactic acid (left) produced from fermentation broth (fibre sludge). PLA (middle & right) produced from the pure lactic acid

## 1.5 WP1 CONCLUSIONS

- The two tested forest industry residual streams, fibre sludge and saw dust, are raw materials that are well suited for production of lactic acid through bacterial fermentation
- Fibre sludge can be used to generate a hydrolysate that has high sugar content, and since the raw material contains mostly pure cellulose no pretreatment is needed. Therefore, the process from starting material to lactic acid is less complex, and hence less expensive, compared to using saw dust as raw material
- Saw dust requires pretreatment that can, depending on process parameters, generate inhibitory agents that negatively affect an efficient fermentation process. The saw dust hydrolysate can, however, be separated into sugar streams of higher purity resulting in better suitability for lactic acid fermentation
- There is also a greater abundance of saw dust compared to fibre sludge which can be of importance for bulk scale production of lactic acid and subsequent PLA polymerization
- Both of the tested raw materials have been used in process optimization trials resulting in lactic acid fermentation that requires less additives, lower pH, no detoxification, higher yields and higher productivity
- The process has been upscaled from bench scale, through laboratory scale, into smaller pilot scale with an industrial scale fermentation trial scheduled for the near future as a result of the optimized process parameters
- Chemocatalytic production of lactic acid from biomass-based sugars is possible, especially with heterogeneous carbon-supported catalysts
- Higher yields are achieved in the chemocatalytic conversion reactions if ethyl lactate is produced instead of lactic acid
- Heterogeneous catalysts might deactivate when used in multiple reaction cycles. The active metal can also leach from the catalyst
- Less catalyst activation and metal leaching was observed when reaction solvent was changed from water to ethanol and also when the target product was changed from lactic acid to ethyl lactate
- Several scientific publications have resulted from the work in project
- Analysis methods for the evaluation of hydrolysates, organic acids and PLA have been developed and optimized
- The polymerization of lactic acid to PLA is a complex process that depends on factors such as lactic acid concentration in the fermentation broth, compounds present in the fermentation broth that interfere with upgrading process, temperature, time and catalysts for the various steps in the polymerization
- We have been able to produce PLA of lower density through direct polycondensation but more work is needed to achieve high density PLA synthesis
- PLA can be produced from low value residual streams from the forest industry such as fibre sludge and saw dust

Due to complications resulting from the Covid-19 situation there have been no trials performed using the produced PLA. There were interest and plans of using the PLA in compounder trials by project partners but these plans unfortunately had to be cancelled. However, the possibility of achieving an economically relevant production of PLA from forest industry raw materials has improved through the activities performed in GBS but further developments are needed to achieve production of high density L-PLA (HDL-PLA) from these raw materials.

## 2. WP2 Hydrolysis lignin upgrading

### 2.1 INTRODUCTION

Hydrolysis lignin is a residual stream from the biorefinery process. It is mainly burned for heat and electricity production in power plants. Valorization of lignin may improve the overall economics of biorefinery processes such as production of bioethanol. In this work package, the focus is on new applications for hydrolysis lignin. One possibility is utilization of hydrolysis lignin as a raw material for production of activated carbon, which might be utilized as a catalyst support material. Given the functionalities found in lignin, it may also be an interesting starting material for other applications such as fuels or chemicals. Much effort has been put in this line for Kraft lignin. However, hydrolysis lignin is not as well studied as Kraft lignin. Furthermore, hydrolysis lignin is believed to have fewer functionalities compared with Kraft lignin. This is linked to reactivity, which may be improved via functionalization, i.e. adding new chemically active sites via alkylation/de-alkylation, hydroxyalkylation, amination, and nitration. The molecular size is also important for some applications, therefore separation of different molecular size fractions or modification of molecular size via controlled polymerization or depolymerization is also of interest.

Activated carbons are known for their high surface areas and porous structures, which are capable of adsorbing i.e. holding large volumes of gaseous or liquid materials and chemicals. Activated carbon preparation is already a known and used process, with applications at the market. Applications considered are different technical carbons, especially activated carbon and structured carbons for catalyst support materials (Figure 16). In industrial processes, activated carbon is used for example in municipal water purification plants and water treatments processes as adsorbents to remove organic and inorganic material such as heavy metals. Other applications are for example the use in gas cleaning processes to remove volatile organic compounds, usage as pharmaceutical and cosmetic products or in battery technology as anodes. Activated carbon can be manufactured from a wide variety of raw materials. The most commonly used raw materials are coal (anthracite, bituminous, sub-bituminous and lignite), coconut shells, peat or wood (both soft and hard). The fundamental and industrial aspects of the production of various types of activated carbons from hydrolysis lignin are considered through the prism of future large-scale production of biofuels and platform chemicals from renewable lignocellulosic resources. Future biorefineries that are based on the sugar platform or direct conversion of cellulose/hemicellulose, and in both cases chemical upgrading to e.g. organic acids can be done in the presence of heterogeneous catalysts. These catalysts, in chemical production, can be based on the use of porous carbon supports.



Figure 16. Upgrading of the hydrolysis lignin to activated carbon and usage as catalyst support in the biochemical production (Kupila, 2021)

The work package is divided into two sections. In the first work package (WP 2.1) the focus is on the pre-treatment of the hydrolysis lignin and analysis of different lignin fractions. In the second work package (WP 2.2), the focus is on a carbonization and physical or chemical activation of hydrolysis lignin to obtain activated carbon. Hydrolysis lignin-based activated carbons and novel activated carbon catalysts are studied and developed.

## 2.2 WP2.1 Hydrolysis lignin raw materials

### 2.2.1 METHOD

SEKAB kindly provided hydrolysis lignin. The provided hydrolysis lignin contained quite high concentrations of sugars. Therefore, enzymatic hydrolysis was conducted in order to reduce the sugar content and increase the relative concentration of klason lignin. In brief, the hydrolysis lignin was hydrolysed using 0.1 g/g DM enzymes in a 50 L bio reactor. The reaction was performed at 50°C, pH: 4.9 – 5.2. The hydrolysis lignin was recovered by filtration via a filter press.

#### Washing of hydrolysis lignin

The hydrolysis lignin was washed with acids, bases as well as organic solvents under varying conditions, e.g. time, temperature and ratio between hydrolysis lignin and solvent aiming at obtaining a purer lignin. The effect of washing was evaluated by analysing the lignin fraction of the dried hydrolysis lignin after washing.

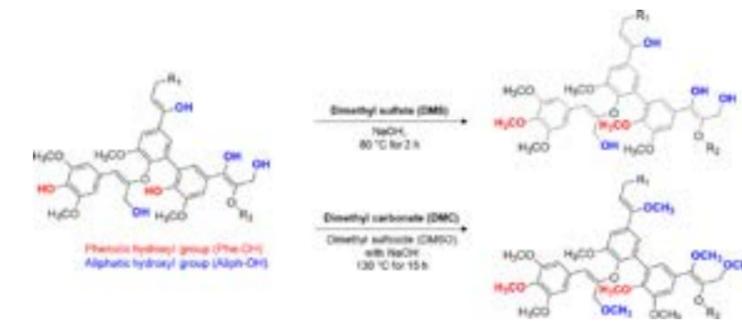
#### Oxidation of hydrolysis lignin

The hydrolysis lignin was also oxidized using two different methods, ozone and hydrogen peroxide. For oxidation by ozone, the hydrolysis lignin was first dissolved in a non-polar solvent which was mixed with water. The dissolved hydrolysis lignin was subsequently subject for oxidation. The reaction conditions were varied by controlling the flow rate of the ozone gas, where higher rates result in higher exposure of the oxidizing agent, and temperature, which has a positive influence on reaction speed. The dissolved hydrolysis lignin was later recovered by making the solution more concentrated and subsequently adding it drop-wise to acidified water where the hydrolysis lignin is no longer soluble and therefore precipitates as a solid. The solid was recovered via filtration and then dried.

For oxidation experiments using hydrogen peroxide, the hydrolysis lignin was added to a solution of formic acid and stirred at room temperature for 10 minutes. Hydrogen peroxide was then added and stirred for another 30 minutes. The solution was subsequently heated to 30-80°C for 1-5h. The progress of the oxidation reaction was followed via a special kit targeting peroxide and the oxidation was terminated via a combination of filtration, volume reduction and precipitation in acidic water. The solid precipitate was filtered and then washed with water before it was dried at room temperature. Milder oxidation conditions were also evaluated by conducting the experiment at a lower lignin and hydrogen peroxide concentration and reducing the temperature using an ice bath. Furthermore, instead of precipitating the lignin via dropwise addition of the lignin solution to acidified water, water was added to the lignin solution, which was subsequently filtered and washed with water until the washing solutions were pH neutral. The solid residue was dried at room temperature. The size of the hydrolysis lignin was evaluated using size exclusion chromatography, which is a separation technique that separates the lignin molecules based on their sizes and molecular weights.

#### Functionalization of hydrolysis lignin

Lignin reactivity may be modified via the introduction of new functional groups and new reactive sites. Alkylation is one of the most well-known chemical modification reactions attempted on lignin in which phenolic and aliphatic hydroxyl groups of lignin can be converted to less reactive phenyl methyl ether/aliphatic methyl ethers. It has been reported that DMS can selectively methylate all phenolic hydroxyl groups while DMC can methylate both phenolic and aliphatic hydroxyl groups (Scheme 1).



Scheme 1. Representation of O-methylation with the alkylating agents dimethyl sulphate and dimethyl carbonate

Four different alkylating agents were used, of which three added a methyl group comprising one carbon and three hydrogens and one adding an ethyl group, comprising two carbons and five hydrogens, see Figure 17 below. In brief, the hydrolysis lignin was dissolved in a solvent together with the alkylating agent. For two of the alkylating agents, the solution was heated to increase the reaction speed. The reactions were terminated by lowering the pH which caused the hydrolysis lignin to precipitate. The lignin precipitate could then be filtered, washed with water until the washings had neutral pH and then left to dry in room temperature. The elemental composition of the samples was analysed via elemental analysis determining the concentration of C, N, H in the sample and calculating O concentration based on the other three elements.



Figure 17. Methyl group (left) and ethyl group (right)

## 2.2.2 RESULTS

The enzymatic hydrolysis lowered the sugar content in the hydrolysis lignin and thereby resulted in an increase in klason lignin.

#### Washing of hydrolysis lignin

All attempts to wash hydrolysis lignin with an organic solvent were unsuccessful. The hydrolysis lignin was either insoluble in the solvents or partly soluble resulting in fractionation of the hydrolysis lignin. In the latter case, one organic solvent soluble fraction and one organic solvent insoluble fraction was obtained. The hydrolysis lignin also turned darker after some washings, see Figure 18.



Figure 18. Hydrolysis lignin after washings with the moderately polar solvent tetrahydrofuran

The washings using acids or bases did not significantly improve the content of klason lignin in the samples, see Figure 19 below. The largest increase in klason content was observed in the experiment where the hydrolysis lignin was washed with 0.1 M NaOH at 90°C for 10 minutes. A small increase was also noticed for washing with acid. The low klason yields for the ethyl acetate washing may be caused by the insolubility and immiscibility of hydrolysis lignin in the organic solvent, i.e. as discussed above.

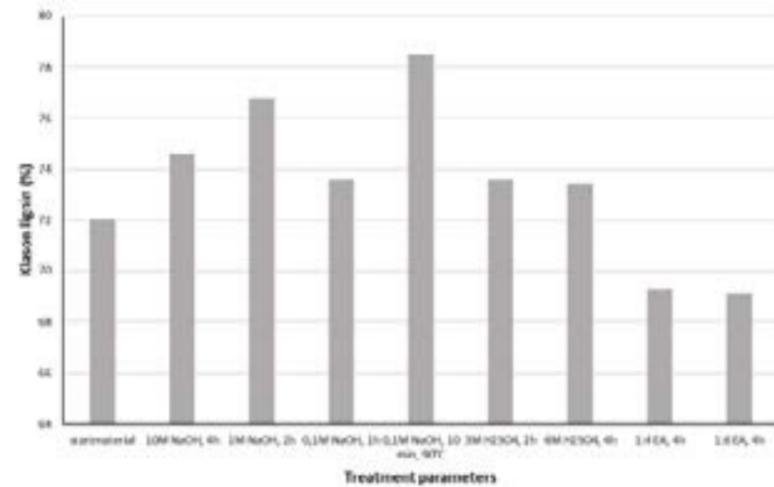


Figure 19. Klason content (%) after washing with acids (H<sub>2</sub>SO<sub>4</sub>), base (NaOH) and organic solvent (EA=ethyl acetate) at different reaction conditions

### Oxidation of hydrolysis lignin

The yield of oxidized hydrolysis lignin was positively correlated to reaction time and flow rate of the ozone, see Figure 20 below. Increasing the temperature from room temperature to 50°C for 30 minutes resulted in a 32% (w/w) increase in the yield. However, it was challenging to control the flow of ozone and furthermore, the required solvent is relatively expensive which could be limiting factor for scaling up.

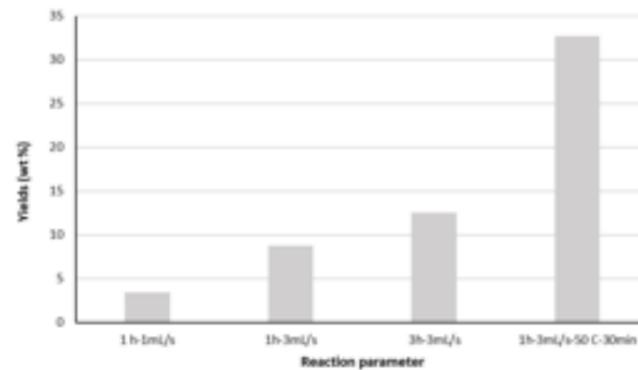


Figure 20. Wt % yields of ozone oxidized hydrolysis lignin at different reaction parameters as indicated by the labels in the figure

Analysis via size exclusion chromatography confirmed that the ozone oxidized hydrolysis lignin had been subject to depolymerisation or degradation during the oxidation reaction, i.e. the molecules were smaller than in the starting material, Figure 21. The smaller molecular size resulted in a longer retention time which is observed in the figure below.

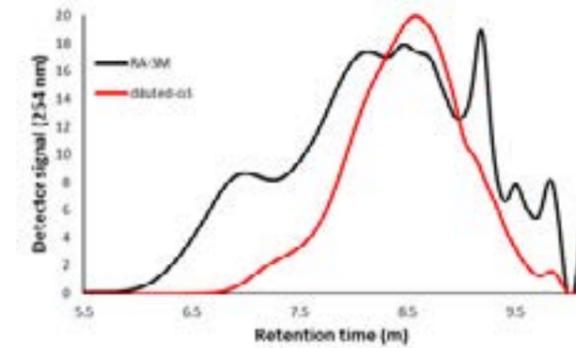


Figure 21. Size exclusion chromatogram of starting hydrolysis lignin (RA-SM) and oxidized hydrolysis lignin produced using an ozone flow of 3 mL/s for 1h and then heated at 50 °C for half an hour.

In contrast to the oxidation experiments with ozone, increasing reaction time and temperature for hydrogen peroxide mediated oxidation resulted in a decrease in oxidation yield, Figure 22 and Figure 23. This observation may be attributed to excessive oxidation and depolymerisation, i.e. degradation as was observed for the ozone oxidized hydrolysis lignin. Decreasing the hydrogen peroxide concentration, i.e. changing hydrogen peroxide to lignin ratio, resulted in a significant increase in yield, Figure 23 and Figure 24.

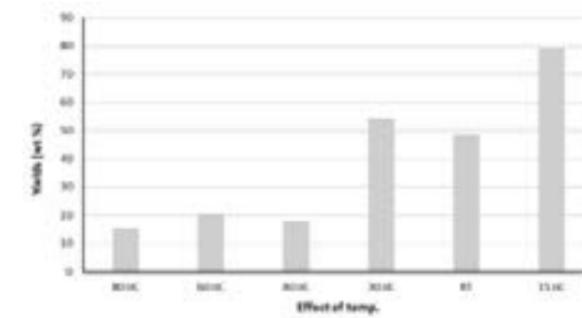


Figure 22. Oxidation yield of hydrolysis lignin as a function of reaction temperature under constant concentration of hydrogen peroxide as oxidizing agent

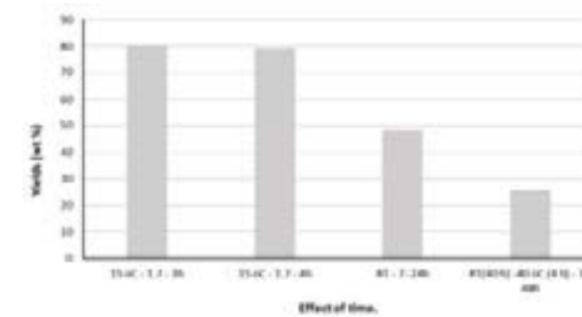


Figure 23. Oxidation yield of hydrolysis lignin as a function of reaction time and lignin to hydrogen peroxide ratio, i.e. hydrogen peroxide concentration at 15°C (left) and room temperature (right)

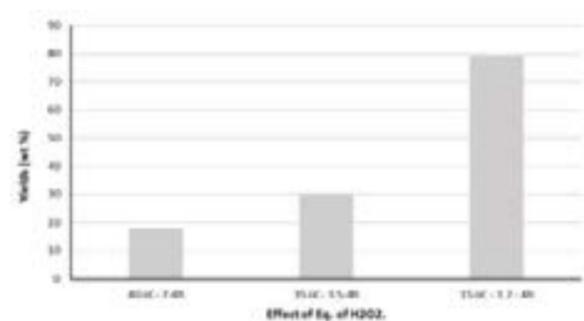


Figure 24. Yield of hydrogen peroxide oxidized hydrolysis lignin under varying temperature and lignin to hydrogen peroxide ratio, 7, 3.5 and 1.7, respectively

To summarize, milder reaction conditions are preferred to preserve the original structure of the hydrolysis lignin. However, one can tune the conditions to depolymerization/degradation. Furthermore, we propose the utilization of hydrogen peroxide as oxidizing agent instead of ozone. For comparison, native and oxidized hydrolysis lignin is shown in Figure 25 below.



Figure 25. Hydrolysis lignin before (left) and after oxidation (right)

### Functionalization of hydrolysis lignin

The yields of the alkylation experiments were in the range of 7,9-31,0% (w/w). Different reaction conditions, e.g. reaction temperature and alkylating agent make comparisons challenging. However, elemental analysis confirm that the reactions were successful, as indicated by an increase in carbon content and a decrease in oxygen content, Table 3.

Start		C	H	N	O
	HL	60.9	5.6	0.9	32.6
	MeI	65.9	6.2	0.8	27.0
	DMS	62.8	5.8	1.7	29.7
	DMC	63.3	6.1	1.1	29.6
	DEC	67.8	6.2	1.0	25.2

Increase                      Decrease

Table 3. Elemental composition (wt%) of hydrolysis lignin before and after alkylations

## 2.3 WP2.2. Thermochemical carbonization and activation of hydrolysis lignin

### 2.3.2 METHOD

This work package is based on the activated carbon preparation from hydrolysis lignin with a variation of preparation techniques. Prepared activated carbon are tested in various applications as catalyst support for valuable biochemical production.

The activated carbon is produced at a high temperature typically at around 600-1000 °C through slow carbonization of the raw material and activation by activating agent, which creates a high specific surface area and porosity to the material. The activated carbon preparation can be done by physical activation or by chemical activation. A schematic presentation of the activated carbon production process is presented in Figure 26. The surface areas of activated carbon can be approximately 500-2000 m<sup>2</sup>/g and porous structure build-up from channels. Depending on the diameter of the pores they can be classified as micropores (<2 nm), mesopores (2 to 50 nm) or macropores (>50 nm). The selection of the activator agent and the preparation temperature is a major step in controlling the physical and chemical structure and by these performances and applicability of activated carbon. In the physical activation process, the carbonization of the material is prepared typically at around 800 °C and by adding the steam or gas e.g. carbon dioxide to the process as an activating agent to create the porous structure. In chemical activation, the activating agent is a metal precursor such as ZnCl<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub> or KOH, which is impregnated to the raw material before the heat treatment process. In the chemical activation process, slightly lower temperatures can be applied than in the physical activation process. After the heat treatment i.e. carbonization and activation process, the activating agent is removed from the activated carbon by washing the material for example by acid wash. The specific surface areas and porosity of the prepared activated carbons can be determined by nitrogen physisorption analysis measurements.

In this project, both physical and chemical activation methods of the hydrolysis lignin are applied in the experiment of the activated carbon preparation processes and their effect on the prepared activated carbons are characterized with multiple analysis methods.



Figure 26. The preparation process of the activated carbon by physical or chemical activation (Kupila, 2021)

After the carbonization and activation process, the activated carbons are used in the variation of applications. Depending on the application, the activated carbon can be treated for example with different acid treatments to remove the remaining mineral content origin from the biomass of the preparation process, or to modify the surface to contain specific functional groups. In catalytic applications, the activated carbon is used as a support material for various metals or metal oxides. Activated carbon supports with high surface areas can generate large contact areas for metals when used in specific conversion reactions. Metal salts are usually added by impregnation method to the support and treated by heat-treatment to obtain corresponding metal or metal oxide on the support, see Figure 27. Depending on the catalytic application, catalysts are tested in the gas or liquid phase for the conversion reactions.

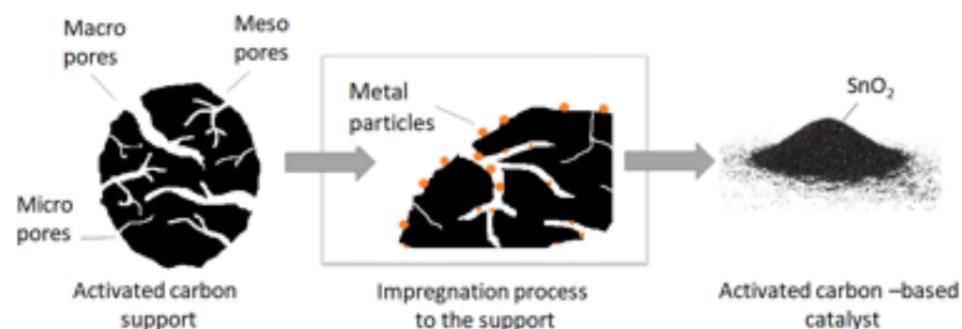


Figure 27. Preparation of activated carbon-supported metal catalysts (Kupila, 2021)

In the project, the activated carbons have been used as such in the catalytic conversion reaction or modified with acids and/or metals for the catalytic applications. Used metals for the catalytic experiments have been zinc, aluminum, tin and iron. The prepared activated carbons and supported metal catalysts have been characterized through multiple analysis methods and tested in the catalytic applications for the conversion of biomass-based molecules to valuable bio-based platform chemicals.

### 2.3.3 RESULTS

The obtained hydrolysis lignin from the biomass hydrolysis was used as such in the carbonization and activation process. Also chemically pretreated hydrolysis lignin to modify the lignin structure was tested. In the preparation process, physical activation (with steam) and chemical activation (with  $ZnCl_2$  and  $H_3PO_4$ ) were used. Depending on the activation process i.e. used activator agent, time and temperature, prepared activated carbons had varied qualities. Results are presented in Table 4. Steam activation of the hydrolysis lignin gave the surface area of about 400-850  $m^2/g$  with a mostly microporous structure. At lower temperatures (600-700 °C), lower surface areas were obtained with steam activation. It was noted that the pretreatment of the hydrolysis lignin with different chemicals (e.g. oxidation and methylation) didn't give a higher surface area compared to the untreated hydrolysis lignin. When the chemical activation was applied to the process, typically higher surface areas were obtained over 1500  $m^2/g$ . With  $ZnCl_2$  as activating agent reached 1500  $m^2/g$  surface area and micro-mesoporous structure were obtained. With  $H_3PO_4$  activation, the surface areas were even higher and approximately 1800  $m^2/g$  surface areas were obtained. Also, yields of the activated carbons obtained with chemical activation were higher than those obtained from physical activation with steam. The ash content of the lignin-based activated carbons was rather low and was less than 3 wt. %. It could be concluded that high quality activated carbons were able to prepare from hydrolysis lignin and depending on the preparation method, varied features (e.g. surface areas and porosity) were obtained for the carbons, which could be applied to specific applications.

	Yield (%)	BET Surface area ( $m^2/g$ )	Pore volume ( $cm^3/g$ )	Pore size (nm)	Micro pores $d < 2nm$ (%)	Meso. pores $2 < d < 50 nm$ (%)	Macro pores $d > 50nm$ (%)
HL, raw		8	0.03	17.9			
Steam activated (1h carb. + 3h act.)							
HL 600 °C	37	260	0.14	1.8	88 %	12 %	0 %
HL oxidized 600 °C	38	220	0.12	2.0	80 %	8 %	2 %
HL methylated 600 °C	56	0	-	-	-	-	-
HL 800 °C	24	850	0.42	2.0	77 %	23 %	0 %
HL oxidized 800 °C	30	680	0.27	1.6	93 %	3 %	4 %
HL methylated 800 °C	32	710	0.33	1.8	84 %	16 %	0 %
Steam activated (2h carb. + 2h act.)							
HL 600 °C	38	440	0.19	1.8	94 %	6 %	0 %
HL 700 °C	35	480	0.20	1.7	95 %	4 %	0 %
HL 800 °C	29	640	0.32	2.0	78 %	22 %	0 %
HL 800 °C, 4h act.	9	815	0.61	3.0	43 %	57 %	0 %
Chemical activated (2h carb. + 2h act.)							
HL 600 °C, $ZnCl_2$	49	1500	0.94	2.5	47 %	52 %	1 %
HL 600 °C, $H_3PO_4$	47	1800	1.09	2.4	51 %	49 %	0 %

Table 4. Hydrolysis lignin (HL)-based activated carbon yields and physisorption analysis; surface area, total pore volume, average pore size and pore size distribution

Selected hydrolysis lignin-based activated carbons were tested as catalyst support for the specific catalytic application. Physically and chemically activated carbons were tested as such or with modification of acid and metal impregnation. The ash content of the activated carbon was already rather low and with acid treatment (nitric acid) the residual metals from the preparation process were completely removed from the surface. This is an important factor if the activated carbon is used as catalyst support since metals can affect the catalytic conversion reactions. After cleaning the support surface, the specific catalysts metal impregnation was done onto the surface. In experiments, approximately 2-10 wt.% of metal were added to the support. Used metal salt precursors were  $ZnCl_2$ ,  $Zn(NO_3)_2$ ,  $SnCl_2$ ,  $CrCl_3$ ,  $AlCl_3$ ,  $Fe(NO_3)_3$ , and  $FeCl_2$  and were used to obtain metal oxides on activated carbon support after heat treatment (around 400 °C). Hydrolysis lignin-based catalysts were tested at catalytic conversion reactions such as furfural production from xylose, lactic acid production from glucose and ethyl lactate production from biomass-based molecules. The catalysts used in the reactions; lactic acid and ethyl lactate production with chemocatalytic methods, were studied in work package 1, where more information can be read. The preparation methods of the activated carbon catalysts and used applications are presented in Table 5.

Catalyst	Support	Acid modification	Metal salt	Application
Fe@AC	HL-steam activated, HL- $ZnCl_2$ activated	Unmodified and modified with $HNO_3$	$FeCl_2$ , $Fe(NO_3)_3$	- Furfural production from xylose
Sn@AC	HL-steam activated, HL- $ZnCl_2$ activated	Modified with $HNO_3$	$SnCl_2$	- Lactic acid production from glucose - Ethyl lactate production from biomass-based molecules
Sn/Al@AC	HL-steam activated, HL- $ZnCl_2$ activated	Unmodified and modified with $HNO_3$	$SnCl_2$ , $AlCl_3$	- Lactic acid production from glucose
Sn/Cr@AC	HL- $ZnCl_2$ activated	Modified with $HNO_3$	$SnCl_2$ , $CrCl_3$	- Lactic acid production from glucose
Zn@AC	HL-steam activated	Modified with $HNO_3$	$Zn(NO_3)_2$	- Ethyl lactate production from biomass-based molecules

Table 5. Hydrolysis lignin-based activated carbon catalyst preparation methods and applications used (Kupila et al. 2021 a/b; Rusanen et al. 2020)

## 2.4 WP2 CONCLUSIONS

- Biological, physical, and chemical methods have been utilized to enhance hydrolysis lignin properties
- Carboxyl and alkyl functionalities have been successfully incorporated into the structure of hydrolysis lignin, aiming at increasing the reactivity of hydrolysis lignin
- Physical methods, i.e. washings, did not result in major increase of klason lignin
- Oxidation of hydrolysis lignin did not only result in incorporation of oxygen functionalities; polymerization and depolymerization of the material also occurred
  
- It was demonstrated that native hydrolysis lignin from the hydrolysis process was suitable for the activated carbon production without modification
- High quality activated carbons were able to prepare from hydrolysis lignin
- Modification of the hydrolysis lignin with oxidation and alkylation did not improve activated carbon quality
- Depending on the carbonization and activation preparation method, varied features (e.g. surface areas and porosity) were obtained for the carbons, which could be applied to specific applications
- Active carbon-based catalysts were prepared successfully from the hydrolysis lignin.

## 3. WP3. Tannins from bark and construction foams

### 3.1 INTRODUCTION

Tannins are naturally occurring high molecular weight substances that are present nearly everywhere in plant kingdom: in wood, bark, leaves, roots, berries, fruits, and seeds. Many people know tannins from the wine or tea, as they are present in skin and seeds of grapes or leaves of tea. Tannins are polyphenolic compounds, and their main function in plant is to protect the plant from pathogens, such as, fungi, bacteria and viruses. These kinds of compounds are called secondary metabolites, because they are not directly involved in the growth, development or reproduction of the organism. Some plants are richer in tannins, and are used most in industrial level as a raw material. The most utilized species globally are Chestnut wood, Quebracho, Tara, and Oak Galls. In Nordic countries major source of tannins is fresh bark obtained from pine and spruce, predominantly as a side product from the forest industries.

Forest industries, both in Finland and Sweden, use significant amounts of wood resources. In 2018, Sweden produced 75,1 million cubic meters of roundwood, whereas, in the Finland production was slightly less being 68,3 million cubic meters. (EUROSTATS 2020 p. 95-96) As the amount of bark is approximately 10 – 15 % of the round wood volume, pulp and paper industry and sawmills are producing large amounts of bark as a side product in their operations in Finland and Sweden. Typically, the bark is utilized in the production of energy in the wood processing plants. In Finland, the consumption of bark in energy production was 7.9 million cubic meters in 2019. (<https://stat.luke.fi/en/wood-energy-generation>) Similarly, in Sweden, approximately 8.7 TWh bark was sold from the forest industry to the cogeneration sector in 2019 (Skogsindustrierna, trädbränsleföreningen). That bark is part of the total volume of bark which is utilized for energy production at mills and at heating plants. According to statistics from 2014, that volume of bark was around 9.6Mm<sup>3</sup> (Staffas et al 2015). That volume is probably even higher today.

Both in Finland and Sweden the utilization of bark is limited to energy production, as well as, to a lesser extent in horticultural substrate or soil conditioner. However, there is a potential to increase the utilization of bark as a raw material for the production of renewable and sustainable chemicals and materials, and increase the added value for the side product. Bark contains large amounts of valuable organic compounds, and in particular, softwood bark is rich in phenolic compounds, being the second major source of phenolic compounds in nature after lignin. The content of bark differs from that of the round wood, which mainly consists of cellulose, hemicellulose, and lignin. The greatest difference between bark and round wood is the vast amount of extractives in bark. The content of extractives in bark is 2 – 6 times higher than in round wood. The total content of extractives can be as high as 20 – 40 % of the dry weight of bark.(Routa et al 2017).

The main source for tannins in Finland and Sweden, is bark from conifer trees, pine and spruce, which is obtained as a side product of the forest industries. The tannin content in spruce bark can be more than 10 percent of the dry weight (Kemppainen 2014). Thus, the separation of valuable compounds from undervalued bark before the energy production should be considered, in order to provide added value for the residual side product.

Usually, tannins are classified into two main groups with different chemical nature: hydrolysable tannins and condensed tannins. Figure 28 shows the difference between these types of tannins. Hydrolysable tannins consist of glucose at the center of the molecule, which is partially or totally esterified with phenolic groups, such as gallic acid (a) or ellagic acid (b). Thus, hydrolysable tannins are called either gallotannins or ellagitannins, depending on the phenolic groups attached to glucose. The production of hydrolysable tannins is less than 10 % of the commercial production of tannins. Gallotannins are mainly obtained from Tara, sumac and gallnuts. The ellagitannins can be found e.g. in oak and chestnut wood. The main use of hydrolysable tannins is in the tanning industry.

The second class on tannins, condensed tannins are polymers formed by the condensation flavonoid monomers. Each flavonoid has two phenolic rings A and B, see Figure 28, having different reactivities. Condensed tannins can be linear polymers, as in figure 28, or branched polymers, depending on how the monomers are attached to each other. More than 90 % of the worldwide production of commercial tannins are condensed tannins. (Arbenz and Avérous 2015) In addition, a third class of tannins, phlorotannins, have been found in marine species such as brown algae. In the bark of conifer trees tannins are mainly condensed tannins.

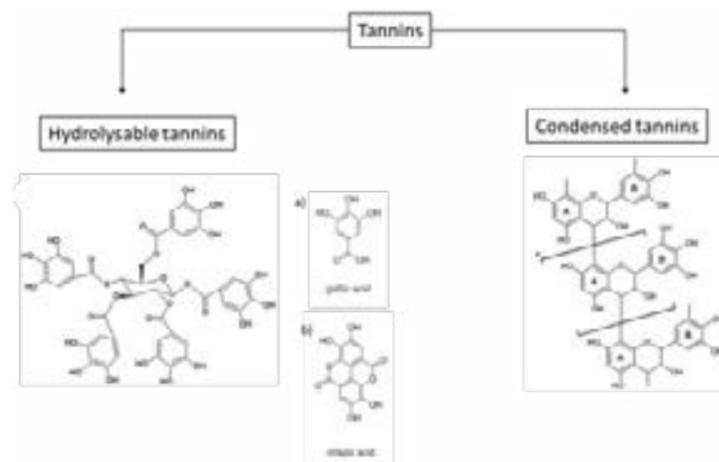


Figure 28. The structural difference between hydrolysable and condensed tannins (Modified from: Arbenz and Avérous 2015, and Hemmilä et al. 2017)

## Extraction of tannins

Tannins are separated from plants by a process called extraction. In an extraction process solid matter is introduced into solution, and soluble substances are then released into solvent. A simple example of extraction is an infusion of tea bag into hot water. Most tannins are water soluble, which makes the extraction of tannins natural and sustainable process. In a traditional tannin extraction process, hot water is utilized as a solvent. However, the phenolic materials differ from species to species, and some higher molecular weight tannins can be insoluble in water. Thus, also organic solvents, such as, acetone or methanol, or different chemical additives can be utilized to improve the solubility of certain polyphenols or extraction yield. Extraction yield of tannins are dependent on many variables, such as, extraction temperature, time, water to solid ratio, size of the bark particles and bark storage conditions. Typically, bark should be utilized soon after debarking, because the extractives tend to decrease rather fast during the storage. Extraction of tannins is non-selective process, which means that other substances, such as, smaller phenolic compounds, carbohydrates or inorganic are always found in extract. Thus, purification steps are necessary in order to obtain tannins with higher purity. Liquid tannin extract can be utilized as such, but storage, packaging and shipping requires often that tannin extract is converted into powder by spray drying. Schematic process for the production of tannins in powder form is shown in Figure 29. (Shirmohammadli et al. 2018, Bianchi et al. 2015)



Figure 29. Schematic extraction process to get tannin powder (Adapted from: Shirmohammadli et al. 2018)

Due to the phenolic structure and versatile properties of the tannins, they have found use in many different applications. Tannins have been utilized traditionally in the leather industry as tanning agent because of the characteristics of tannins to bind and precipitate proteins. Owing to their high antioxidant properties tannins are widely utilized in food and beverage industry, for example, in wine production. Due to the chemical reactivity of the phenolic structure, similar to synthetic phenols, condensed tannins have gained growing interest as a natural alternative in the production of wood adhesives. Other applications for tannins are, for example, animal nutrition, metal recovery, pharmaceuticals, cosmetics, in wood protection, and manufacturing of foams. (Shirmohammadli et al. 2018)

Globally, the estimated tannin market size in 2015 was more than 1 000 000 tonnes, and it is expected to continue to grow in the coming years. The leather manufacturing and winemaking industry are expected to be the key factors driving market growth. In 2015, the leather tanning represents 62 % of the total market revenue. Europe accounted for about 38 % of the total revenue in 2015, due to the need of tannin in wine industry. Also, demand for wood adhesives applications are increased due to growing manufacturing of wooden products (Grand View Research, 2017).

It is observed that the residual bark from forest industries can offer abundant and sustainable raw material for different applications. The following chapters take a closer look on the development of extraction processes and utilization of tannin extract. Optimization of tannin extractions and development of purification methods are focussed in the following section. Different extractions procedures are compared and purification test are performed. From the applications point of view, the utilization for tannin extracts are studied by producing tannin foams, and their properties are studied. Finally, literature research will focus on the possible applications for tannins.

## 3.2 WP3.1 Extraction/separation of tannins from fresh bark

### 3.2.1 METHOD

#### Small scale extraction of tannins from fresh bark

Extractions of condensed tannins from spruce bark at atmospheric pressure were done using following solvents: water, 2% Na<sub>2</sub>SO<sub>3</sub>(aq), 2% NaHSO<sub>4</sub> + 2% Na<sub>2</sub>CO<sub>3</sub> (aq) and 30, 50 and 70 % ethanol(aq) solutions. Each solvent was used in extractions in three different temperatures (60, 75 and 90 °C) with two different extraction times (60 and 120 min). 5 g of freeze-dried and grinded spruce bark was weighed

into a 100 ml round-bottom flask equipped with condenser. 50 ml of solvent was added to the flask (solid to liquid ratio 1:10). Magnetic stirrer was used for mixing. Round-bottom flask was heated using oil bath. Experimental set up is presented in Figure 30. After the heating period, mixture was let to cool to room temperature. The largest bark particles were filtrated from the cooled extract using sieve. Small bark particles were separated from the extract by using centrifuge (10 min, 4000 rpm). Total phenolic content (TPC) and condensed tannin (CT) content of the extracts were analyzed.

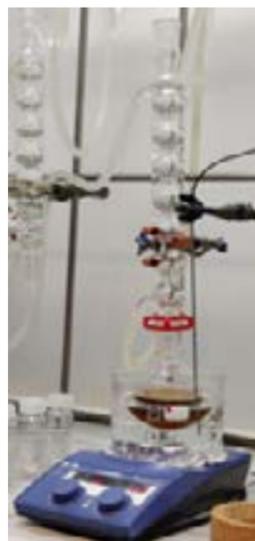


Figure 30. Experimental set up in extractions done in atmospheric pressure

Extractions of condensed tannins from spruce bark at elevated pressure ( $\approx 100$  bar) were done using accelerated solvent extractor (ASE). Method used in the extractions: 5 min heating, 10 min extraction, flushing 50 % and purge 100 s. Following solvents were used in extractions: water, 30 and 70 % acetone(aq), 30 and 70 % ethanol(aq), 2 %  $\text{Na}_2\text{CO}_3$ (aq), 2 %  $\text{NaHSO}_3 + 2$  %  $\text{Na}_2\text{CO}_3$ (aq), 2 % urea(aq) and 2 % urea + 2 %  $\text{NaHSO}_3$ (aq). 5 g of freeze-dried (in salt solutions 2.5 g of bark and 2.5 g of diatomaceous earth) and ground bark (particle size 1 mm or 0.5 mm) were weighed and transferred into the 34 ml sample cell. Each sample was extracted consecutively four times in different temperatures: room temperature, 40 °C, 60 °C and 80 °C. If precipitation formed in extract after cooling, extract was filtrated before TPC and CT content were analyzed.

### Hot water soxhlet extraction of tannins from fresh bark

Industrial bark comprising outer bark, inner bark and some pieces of wood were used as starting material for the hot water extractions of tannins. In some experiments, a mixture of spruce and pine bark, kindly provided by Domsjö Fabriker was used, and in some experiments only spruce bark was utilized. The bark was not pre-treated or sorted for any extractions. The bark was added to a 100  $\mu\text{m}$  filter bag and put in the Soxhlet extractor.

The reactor was heated by a mantle with circulating oil. The oil was set to keep a temperature of 135°C. The method varied slightly between experiments. In Figure 31 the setup of the Soxhlet is illustrated. For the first couple of runs the emptying was done with a siphon but later the emptying was done via pneumatic valve activated by a level sensor when the reactor was full.

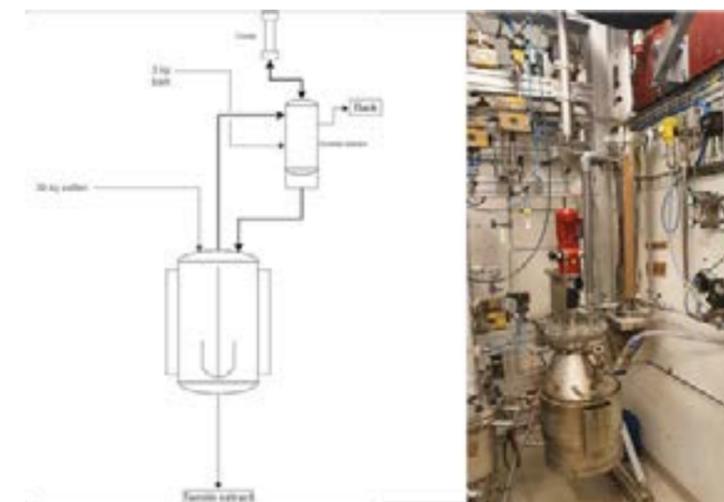


Figure 31. Soxhlet setup

Extraction conditions were varied. A typical extraction comprised  $\sim 5$  cycles over the course of 24h. After extraction, the volume of the extract was reduced in a rotary evaporator, Figure 32. Several classical hot water extractions without addition of chemicals or solvents were conducted. The effect of an initial cold-water extraction prior hot water extraction was evaluated in one experiment. In other experiments, we investigated the effect of ethanol washing aiming at reducing the concentration of carbohydrate extracted together with the tannins and thereby obtaining a purer tannin extract. In one experiment we utilized a 50/50 water/ethanol mixture also aiming at obtaining a purer tannin extract. The stability of the extracted tannins was evaluated in an extended reflux boiling experiment. Freeze drying was also evaluated as this method improves handling as well as storage stability of the tannins.



Figure 32. Tannin extract in rotary evaporator

Tannins were analyzed via the Folin-Ciocalteu method, a spectroscopic method based on the formation of colored complexes. It measures phenols, but other reducing substances also contribute to the measured value via formation of colored complexes. We also employed a gravimetric method based on a special reagent, Divergan®. The carbohydrate analysis was done with HPLC and the sugar standard comprised arabinose, galactose, xylose, mannose and glucose.

### 3.2.2 RESULTS

#### Small scale extraction of tannins from fresh bark

In Figure 33 are presented the best result based on the highest extraction yield of condensed tannins for each solvent system. Results presented in this figure are from extractions done in atmospheric pressure. Figure clearly shows that the yields of condensed tannins in all extractions was quite low. The highest yields of condensed tannins were ca. 3.4 % in three extracts: 30 and 70 % ethanol(aq) and 2 % NaHSO<sub>4</sub> + 2 % Na<sub>2</sub>CO<sub>3</sub>(aq). In addition to condensed tannins, other phenolic components also dissolved. Total phenolic content (includes also condensed tannins) in the extracts varied more than the condensed tannin content. In 2 % Na<sub>2</sub>SO<sub>3</sub>(aq) and in 2 % NaHSO<sub>4</sub> + 2 % Na<sub>2</sub>CO<sub>3</sub>(aq) extracts phenolics content was significantly higher than in other extracts. It seems that in alkaline conditions more phenolic components dissolve from the bark.

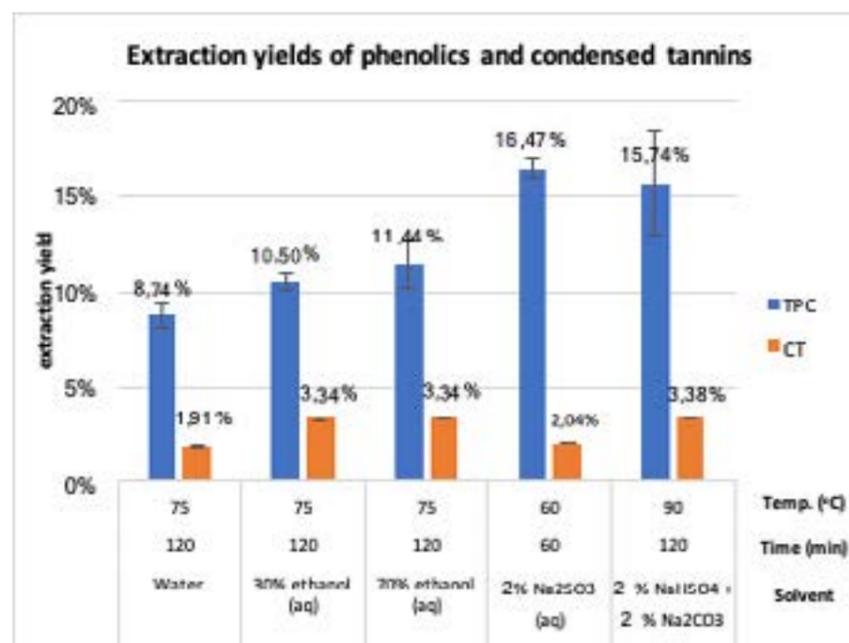


Figure 33. Extraction yields of phenolics and condensed tannins in extractions done in atmospheric pressure

Bench scale extractions of spruce bark were also done in order to provide one of the project partners with condensed tannin extract. In Figure 34 is presented experimental set up that was used in bench scale extractions. Similar procedure was used in bench scale extractions as in small scale extractions except for mixing mechanical stirrer was used and heating was done without oil bath. 200 g of bark was used in bench scale experiments. S:L ratio was 10. Water was the extraction solvent in these experiments. Project partner was provided with four extracts. In two of the extracts, ethanol was added after separating the bark from the extract to precipitate hemicellulose. When ethanol:water -ratio was 7:3 hemicellulose precipitated, after which it was filtrated off. Two of the extracts were dried using rotary evaporator. Project partner was provided with two dried and two undried extracts.



Figure 34. Experimental set up in bench scale extractions

Series of extractions were done at elevated pressure in four different temperature using accelerated solvent extractor. In Figure 35 is a picture of four consecutive 30 % ethanol extracts. Yields of condensed tannins in extracts are presented in Figure 36. Combined extraction yield from four consecutive extractions in all used solvent was as high or significantly higher in ASE-extractions than they were in extractions done in atmospheric pressure. In some cases, extraction yields even in extractions done in room temperature were higher in ASE-extractions than extractions done in atmospheric pressure. In addition to lower temperature, extraction times in ASE-extractions were significantly shorter, 10 minutes. 2 % NaHSO<sub>3</sub> + 2 % Na<sub>2</sub>CO<sub>3</sub>(aq) as extraction solvent afforded the highest extraction yield in condensed tannins, almost 7 %. Extraction yields in aqueous acetone and 2 % Na<sub>2</sub>CO<sub>3</sub>(aq) solutions were ca. 5 %. Water would be in large part ideal solution for extractions. Unfortunately, extraction yield in water extractions in this study was not nearly as good as in other solvents. Extraction yield of four water extracts combined was lower than the extraction yields only in room temperature extract in solvents such as 30 % ethanol(aq), aqueous acetone, 2 % Na<sub>2</sub>CO<sub>3</sub>(aq) and 2 % NaHSO<sub>3</sub> + 2 % Na<sub>2</sub>CO<sub>3</sub>(aq). Noteworthy is also the fact that several of the used solvents dissolved more than 90 % of all the dissolved condensed tannins in 40 °C or below.



Figure 35. Four consecutive 30 % ethanol(aq) ASE-extracts of spruce bark. Extraction temperature from right to left: RT, 40 °C, 60 °C and 80 °C. Amount of condensed tannins in extracts from left to right: 1.99, 2.74, 5.65 and 34.13 mg/g of dry bark

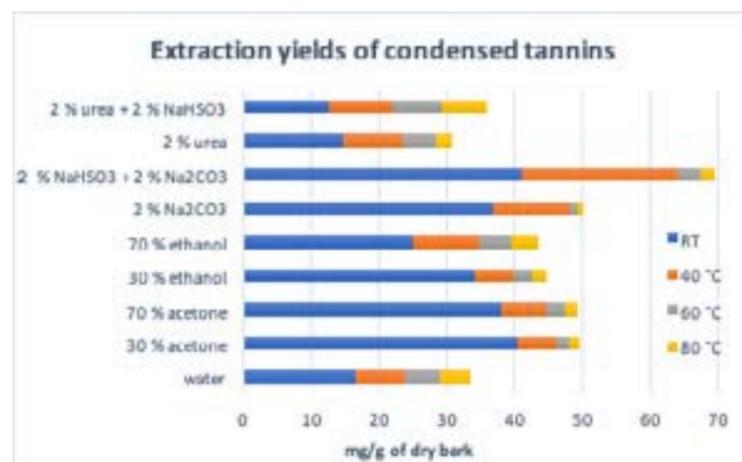


Figure 36. Extraction yields of condensed tannins in ASE-extractions (particle size of bark 1 mm)

Selective extraction of condensed tannins from spruce bark did not occur in extraction experiments. Extracts were always mixture of different components from the bark. Column purification of condensed tannins was tried to develop (Figure 37). Column was packed with AMPERLITE® XAD-7HP resin. Packed column was first loaded with the extract (organic solvents were first evaporated if used in extraction, alkaline extracts were neutralized), washed with water and then condensed tannins were removed from the column using aqueous acetone solution. Condensed tannins turned the white resin to light brown and when washed from the column solution containing tannins was dark brown. Analysis revealed that after the purification step the extract still had impurities. Sugar components that dissolved during extraction were removed but extract contained still at least phenolic impurities. Amount of condensed tannins in the dried extract was less than 30 %.



Figure 37. Purification of spruce bark extracts

Divergan RS® is a material that is used for instance to remove tannins from beer in order to prevent hazing of the beer. Condensed tannins adsorb strongly on to the Divergan RS®. In Figure 38 is presented two spruce bark ASE-extracts adsorbed on to the Divergan RS®. Divergan RS® was mixed with the extract, filtrated, washed with copious amount of water and dried. Clearly depending on the extraction solvent, the color of the adsorbed tannin varies. In Figure 38 on the left light brown color comes from the 2 % NaHSO<sub>3</sub> + 2 % Na<sub>2</sub>CO<sub>3</sub>(aq) extracted tannins, and on the right dark brown color comes from the 30 % ethanol(aq) extracted tannins. Most likely a chemical reaction happened during 2 % NaHSO<sub>3</sub> + 2 % Na<sub>2</sub>CO<sub>3</sub>(aq) extraction and chemical structure of the tannin changed and thus it's color also (Arbenz & Avérous 2005, 2633).



Figure 38. Condensed tannins adsorbed on to Divergan RS®. On the left 2 % NaHSO<sub>3</sub> + 2 % Na<sub>2</sub>CO<sub>3</sub>(aq) extract and on the right 30 % ethanol(aq) extract from ASE-extractions

Effect of the particle size of the spruce bark on extraction yields of condensed tannins in ASE-extractions was also studied. In Figure 39 is compared results from the extractions where the particle size of the bark was 1 mm and 0.5 mm. Particle size had the most significant effect on the extraction yield when 30 % acetone(aq) was used as solvent. Combined extraction yield from four extracts almost doubled to 9 % when smaller particle size bark was used. Extraction yields in room temperature 30 % acetone(aq) extractions more than doubled from 4 to over 8 %. More than 97 % of all the condensed tannin that dissolved in 30 % acetone(aq), dissolved in 40 °C or below. In all other solvents except 2 % Na<sub>2</sub>CO<sub>3</sub>(aq), there was also increase in extraction yields of condensed tannins when smaller particle size bark was used. Increase was not though as significant as it was in 30 % acetone(aq).

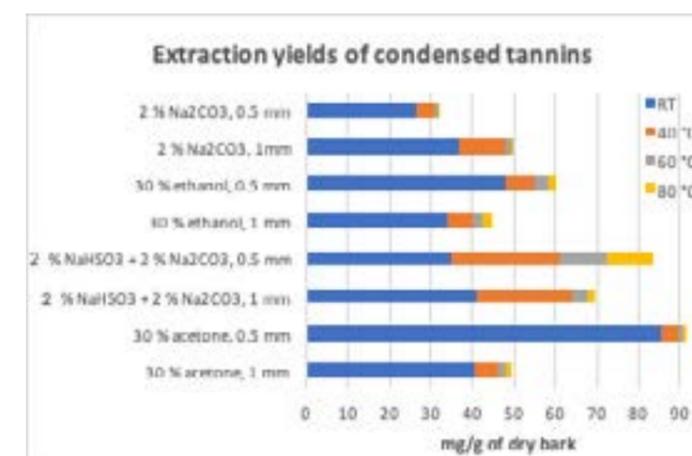


Figure 39. Effect of particle size (1 mm vs. 0.5 mm) of spruce bark on extraction yields of condensed tannins in ASE-extractions

We are first to report efficient extraction of condensed tannins from spruce bark at low temperatures in short period of time. It has significant implications when considering commercial large-scale extractions. For instance, commercial scale extraction of tannins from quebracho wood is done in 130 °C (Kemppainen, 2014). Due to low tannin content, energy costs from heating to high temperatures can make large scale extractions of tannins from spruce bark too expensive to compete with currently commercially available tannins. As our results show, extensive heating in extractions of tannins can be avoided. Low temperature and short extraction times also reduces potential degradation of tannins. An efficient extraction in low temperatures though requires high pressure, small particle size bark and use of chemicals such as acetone, ethanol, Na<sub>2</sub>CO<sub>3</sub> or NaHSO<sub>3</sub>. Only water is used in extraction of tannins in atmospheric pressure from quebracho wood (Kemppainen, 2014). A major drawback of using water as extraction solvent for extracting tannins from wood is long extraction time, which can range from several hours to even several days (de Hoyos-Martinez et al., 2019).

Selective extraction of condensed tannins did not occur in low temperature extractions. Extracts were always mixture of different components from the bark. We were able to remove some of the impurities by using AMBERLITE® XAD-7HP resin. Tannin content in the dry extract after purification was 25–30 %. Spruce bark contains in addition to condensed tannins other phenolic components. Separation of small phenolic components from large phenolic tannins needs to be developed if more tannin rich extract is required. Ultrafiltration could be an option. Evgen (2018) has reported separation of small phenolic stilbene glucosides from condensed tannins by using ultrafiltration to industrial debarking waters of spruce.

### Hot water soxhlet extraction of tannins from fresh bark

In total, more than 10kg of dry bark was extracted in a total of 10 extractions. Extraction yields varied between experiments but were in the range of a few percent which is in line with the expected yields for hot water extraction. Based on the gravimetric method employed on the last extract, the tannin yield was 6% based on the dry bark. Given that the purity of the extract is around 40%, this corresponds to an extract yield of ca: 15%. The carbohydrate analysis of two of the dried extract is shown in Table 6 below. In brief, glucose and arabinos are the dominating carbohydrates which are co-extracted with the tannins in the hot water extraction.

	g/kg TS	g/kg TS
Arabinose	70	63.2
Galactose	34	31.6
Glucose	170	169
Xylose	3.5	3
Mannose	12.2	10.9

Table 6. Carbohydrate concentrations in two of the tannin extracts

Cold water extraction of the bark prior to the hot water extraction resulted in a significant decrease of carbohydrates in the hot water extract. Almost all glucose and galactose were recovered in the cold-water extract. So was about half of the tannin extract. It was possible to remove some carbohydrates via ethanol washing resulting in precipitation of carbohydrates which could be removed via filtration, see Table 7. The combined removal of carbohydrates comprised 16%. Extraction with a 50/50 water/ethanol solution in the Soxhlet resulted in similar tannin yield as when pure hot water was utilized.

	Before [g]	After [g]	Removed [%]
Arabinose	2.873	1.468	48.92%
Galactose	2.466	1.844	25.25%
Glucose	23.986	21.595	9.97%
Mannose	0.443	0.260	41.38%
Xylose	0.458	0.140	69.46%
Sum	30.226	25.306	16.28%

Table 7. Carbohydrate removal by EtOH addition and filtration

No degradation was observed in the 24h reflux boiling experiment, see Figure 40.

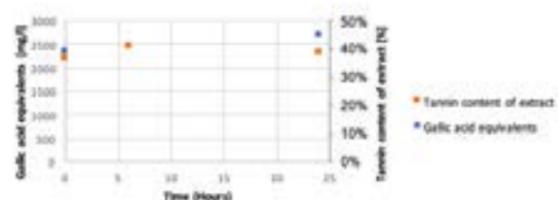


Figure 40. Gallic acid equivalents and tannin content as a function of time during the reflux boiling experiment

Freeze-drying did not result in any changes in the tannins which could be detected via the analysis employed in this project, Folin-Ciocalteu and the gravimetric method based on Divergan®. Therefore, freeze-drying is recommended for ease of handling as well as stability. An example of a freeze-dried sample is shown in Figure 41.



Figure 41. Freeze-dried tannins

### 3.3 WP3.2 Tannins upgrading by foaming

Finland produces around 80 million cubic meters of forest industry products annually and, as a by-product, 7.7 million tons of bark. In addition to the use of bark and sawdust as an energy resource in Finland, these materials can be further processed at bio-refineries to produce value-added chemicals and end products, as Figure 42 shows. In particular, tannin foams derived from biomass have gained significant interest among scientists.

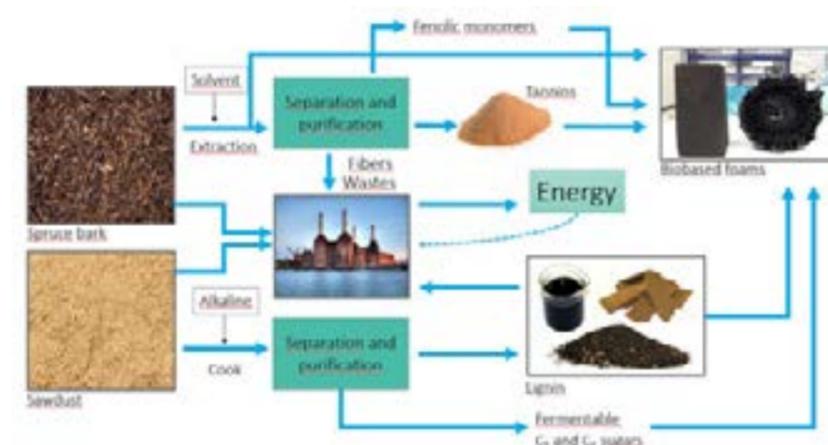


Figure 42. Tannin foam production using spruce saw dust and bark as starting material (Varila 2020)

Tannin-based foams are considered environmentally friendly, renewable materials and their use reduces the need of plastic, toxic foams, and chemicals derived directly from fossil fuels. The main goal in this work packet was to develop a route for making tannin-based foams from bark extracts and utilize the properties of them. According to literature, the most promising applications for tannin foams is thermal insulation alternatives for building purposes. Another quite interesting development route for tannin foams has been their thermal upgrading at high temperatures to produce tannin-based carbon foams. These carbon foams have a unique structure and properties that benefit their use in applications such as energy storage, electrode material, and adsorbents.

#### 3.3.1 METHOD

In the synthesis of tannin-based foams, the key ingredients are cross-linking agents, which can be for example aldehydes or alcohols such as formaldehyde or furfuryl alcohol. These agents are responsible

for the porous like structure, which is forming during the polymerization reaction between the individual condensed or hydrolysable tannin molecules. Furfural alcohol is preferred in the polymerization reaction more than formaldehyde due to the toxicity of and environmental impact of it. Practically the bio-based foams were prepared as can be seen in Figure 43.



Figure 43. Preparation of the skeletal backbone for carbon-foam support materials using either tannic acid or pine bark extracts. (Varila, T; Mäkelä, E. et al, 2020) Reprinted with permission from Elsevier

After the curing of the foams, some characteristics of the foams, such as density, foam rise and mechanical strength were measured. The hardened foams were upgraded to activated carbon foams via chemical or physical activation routes as shown in Figure 44. Later on, the specific surface area, pore volumes and pore size distributions of the foams were analyzed using the nitrogen adsorption technique.

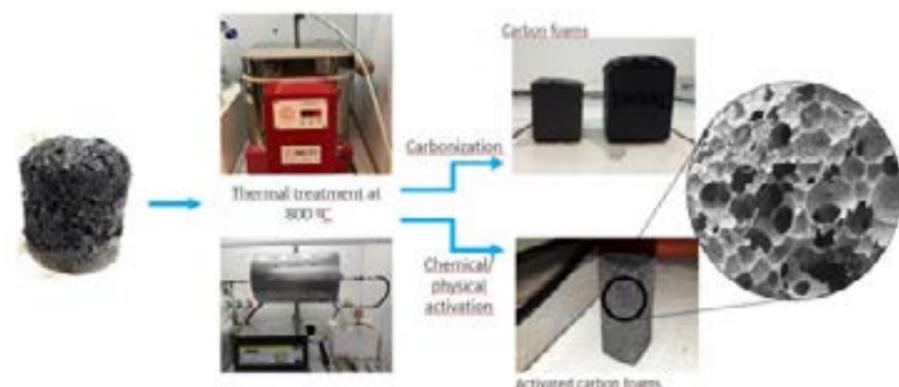


Figure 44. Tannin foam upgrading to carbon foams and activated carbon foams with carbonization or physical/chemical activation method (Varila 2020)

### 3.3.2 RESULTS

Foam synthesis done within this project were conducted using extracts from a mixture of pine and spruce bark or extracts from pine or spruce bark. Extracts were separated from biomass using different solvents followed by, in some cases, purification with ethanol or water. Physical properties such as foam rise and density were calculated from each foam after the foam maturation. The pine or spruce extraction were done in lab scale. According to results, the foam rise and density of the foams were highly dependent on each other as can be seen from Figures 45, 46 and 47.

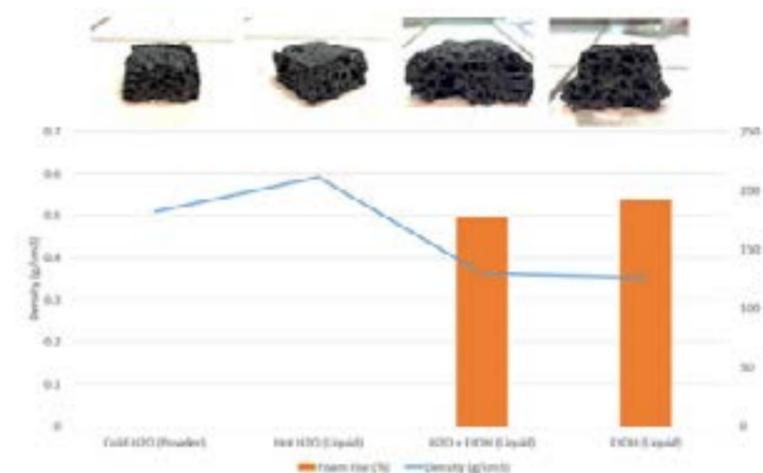


Figure 45. Relationship between the foam rise and density of the foams made with pine bark extracts. Powder or liquid represents the state of the extracts how they were used in the foaming synthesis

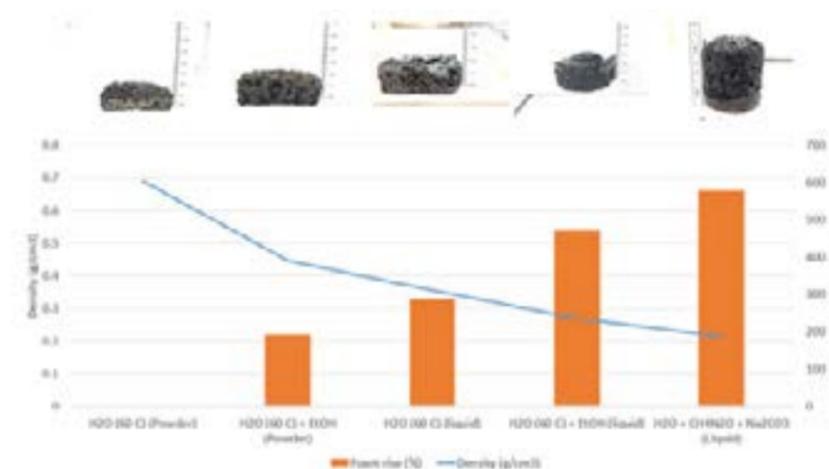


Figure 46. Relationship between the foam rise and density of the foams made with spruce bark extracts. Powder or liquid represents the state of the extracts how they were used in the foaming synthesis

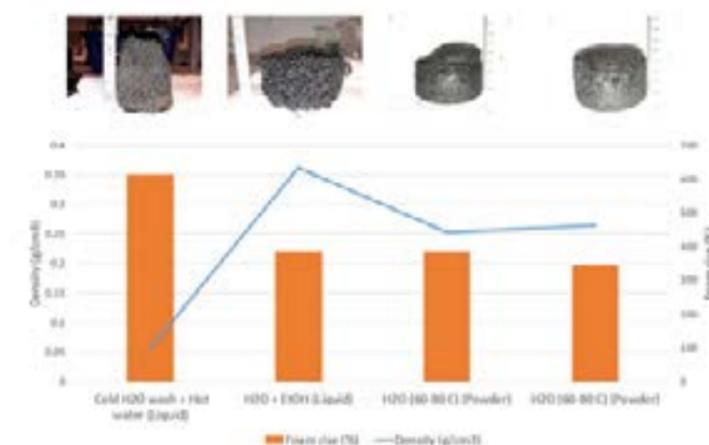


Figure 47. Relationship between the foam rise and density of the foams made with 50/50 spruce and pine bark extracts. Powder or liquid represents the state of the extracts how they were used in the foaming synthesis

In other words, solvent selection plays a major role when extractions of bark are carried out. In case of pine bark, Figure 45, extraction done with ethanol created the best performing foam while the extract extracted with cold or hot water did not give any rise to the foams. Reason for this might be, that with cold water it is not possible to extract enough tannins in order to foam to work properly. On the other hand, hot water extraction will most likely evaporate some of the light-weight polyphenols and dissolve more carbohydrates from the bark.

Spruce bark extracts, Figure 46, worked much better than pine bark extracts in foaming due to the higher tannin content in spruce. Extracts extracted with solvent combination of urea, water and sodium carbonate, yielded the highest foam rise and lowest density for the spruce bark extract based foam. Combination of 60 degree water extraction followed by ethanol washing yielded good foam properties as well.

Extracts extracted from 50/50 mixture of pine and spruce bark where also tested in foam synthesis. In this case the extractions were conducted in pilot scale. From the results presented in Figure 47 it can be stated that with cold water washing followed by hot water extraction lowest density and highest foam rise were obtained. The foam itself was very brittle but compared to pine or spruce bark extracted with water completely different kind of foams were obtained. The other foams prepared from extracts extracted with water + ethanol or just with water at 60 to 80 degree were much harder and durable then the foam prepared from extracts extracted with cold water washing followed by hot water extraction. Reason for this might be that, during hot water extraction some of the volatile materials inside the bark structure are evaporating away and there for the extracts don't have tannins to sustain the overall foam structure.

#### Activated carbon foams

Some of the produced foams were further upgraded to activated carbon foams with physical or chemical activation methods as shown in Figure 44. According to the results, presented in Table 8, with steam activation it is possible to achieve specific surface areas around 500- 700 m<sup>2</sup>/g and with ZnCl<sub>2</sub> activation over 1100 m<sup>2</sup>/g. Also the pore sizes distributions of the foam varied greatly depending on which activation method was used. With steam activation method very microporous carbons are produced and with chemical activation with ZnCl<sub>2</sub> mainly mesoporous carbon is formed.

Foam type	Extraction solvent	Activation agent	BET (m <sup>2</sup> /g)	PV (µm <sup>2</sup> /g)	TPV (µm <sup>2</sup> /g)	2 nm (%)	2-50 nm (%)	50 nm (%)
Pine extracts	Cold water	Steam	499	0.229	0.175	92	7	1
Pine extracts	Hot water	Steam	573	0.277	0.212	81	5	14
Pine extracts	H <sub>2</sub> O + EtOH	Steam	703	0.32	0.242	83	6	0
Pine extracts	EtOH	Steam	548	0.224	0.209	92	7	0
Pine + Spruce extract	Cold water wash + Hot water	Steam	403	0.254	0.193	63	37	1
Pine + Spruce extract	H <sub>2</sub> O + EtOH	Steam	481	0.212	0.167	93	7	0
Pine + Spruce extract	H <sub>2</sub> O + EtOH	ZnCl <sub>2</sub>	1136	0.724	0.608	48	52	0

Table 8. Surface analyses of foams activated with steam and ZnCl<sub>2</sub>

### 3.4 WP3.3 Tannin derivatives as construction materials

#### 3.4.2 METHOD

The focus of the work was on literature survey. The literature survey on tannin materials was partly done as a bachelor thesis. The results from the literature survey on the tannin derivatives were published in the thesis work:

Nhan Phan: Tannin Derivatives as Potential Materials: Review (Thesis, Centria, University of Applied Sciences, Environmental Chemistry and Technology, December 2020).

#### 3.4.3 RESULTS

##### Tannin derivatives as adhesives in glued wood products

Various synthetic materials have been used as components in wood resin adhesives. Wood resin adhesives are often accompanied with carcinogenic formaldehyde used as a hardener. As such, wood resin adhesives pose considerable threat to the environment generally and human health specifically. In order to tackle the problem caused by formaldehyde and to replace synthetic materials with nature-based materials, alternative adhesive materials have been under research. Tannin-based materials together with lignin stand as suitable candidates to be utilized in wood resin adhesives.

Tannin-based adhesives have better hardness ability compared to synthetic components used in adhesives due to greater number of linkages with aldehydes or with different non-aldehyde hardeners, and with the glued wood material. Condensed tannins, particularly mimosa and quebracho-based tannins, have been shown to have great influence in reducing formaldehyde emissions. In addition, mimosa tannin has been considered the most successful material due to its ability to deal with different resin synthesis reactions and also due to its hyperactivity (= fast curing) in wood resin adhesives (Singh & Kumar 2019, 8.). Condensed tannins in spruce bark have similar chemical structure to condensed tannins in mimosa. Therefore, one could expect that spruce bark tannins have similar properties in wood resin adhesives as mimosa tannins have been shown to have.

Thermoset tannin resin adhesives are used in preparation of wood products such as plywood, particleboard, wood-impregnated paper which is used for production of laminated wooden floor and panel furniture overlays. Fibre veneer composites, medium density fiberboard, oriented strand boards, wafer boards, container boards, and other furniture panels could also be prepared with thermoset tannin resin adhesives. Resin adhesives with high tannin contents can be cured at room temperature (coldset). They exhibit good performance, and can be used to produce veneer and finger joint lumbers and glulam. (Zhou and Du, 2019).

##### Tannin derivatives in wood protection

Wood preservation is vital for protecting wooden products. Traditional approaches for wood preservation include the treatment of wood with various chemical agents to prevent attack by different organic microorganisms and insects. Although traditional wood preservatives confer good effects and strong durability, they inevitably introduce various other problems, such as environmental pollution and carcinogenic effects. Tannin is a natural fungicide and good preservative that can be used to prevent fungal and bacterial damage (Zucker WV. 1983).

Most plant pathogens secrete enzymes that degrade cellulose and lignin. Tannin can effectively inhibit the activity of these enzymes and prevent the proliferation of pathogens by complexing with protein (Laks et al, 1988). Pizzi and Conradie (1986) confirmed that the antifungal activity of wood treated with flavonoid tannin resins is twice as intense as that of neat wood. Additionally, veneer treated with tannin resin modified with a small amount of boric acid avoided the fungal attack and exhibited high durability, mechanical strength, and fire resistance because tannin and boric acid can simultaneously inhibit bacterial and fungal growth. Meanwhile, the fixation of boric acid in wood with tannin resin and hexamine prevented loss and exerted a good preservative effect that met the requirements of the European standard EN 113 (Thevenon et al., 2009).

### Tannin foams – fireproof and insulation

Chemically self-expanding rigid foam formulations based on tannin extracts have been developed since 1994. These foams, composed of 95% natural materials, have mechanical and physical properties comparable to synthetic phenol-formaldehyde foams. Originally, the fluid phase before foaming is composed of a tannin, with formaldehyde as a hardener, both mixed with furfuryl alcohol used as an exothermic reaction agent by its self-polymerization reaction and its reaction with the tannin under acid conditions. Expansion to a foam of the fluid phase is caused by a low-boiling physical blowing agent, while simultaneous cross-linking of the resinous mixture provides dimensional stabilization at the desired low density. These foams have been tested and are totally fire resistant, this being their major interest. (Pizzi, 2019)

Research on tannin foams during the last ten years has aimed to eliminate the use of formaldehyde, aldehydes, organic solvent and furfuryl alcohol in tannin foam production, and at the same time improve the properties of tannin foams. New modified tannin foams have been designed to meet practical applications such as acoustic absorbing panels for soundproofing, floral foams used in the gardens and foam sandwich panels for construction. (Phan, 2020)

### Cement Superplasticizers

Common plasticizers have retardation effect while fluidifying cement. Superplasticizers have been developed to eliminate this retardation effect. By eliminating retardation effect superplasticizers improve the facility of working cement, they also reduce the amount of water needed, and also improve cements final strength. Cement pastes are turned into flowing fluids by these materials. (Pizzi, 2019)

Commercial superplasticizers are synthetic resins such as sulfonated melamine-formaldehyde or naphthalene sulfonate-formaldehyde. Their mechanism is based on their adsorption on the cement grain surface while maintaining the water orientation of their sulphonyl groups. The water monolayer that is formed around the grain causes a dispersion of the grains contributing to the fluidification of the cement/concrete paste. Moreover, the surface tension of water is not much reduced and there is no significant retardation of cement setting or hardening. (Pizzi, 2019)

Characteristics of polyflavonoid tannins make them attractive superplasticizers for cement. Several tannins, especially sulphited, have performed well as cement superplasticizers. Extracts of sulphited mimosa, quebracho, and pine tannin all behave very well as cement superplasticizers, with mimosa and pine being those with slightly better behavior. A dosage of 0.25 to 0.5% by weight on the cement has a significant effect of fluidification. Modified condensed tannin extracts behave as superplasticizers. Cement and concrete flow better and the onset of hardening is not retarded. (Pizzi, 2019)

### Corrosion inhibitors

Corrosion and corrosion-induced safety problems are among the main issues in the water industry and because of a global scarcity of water, it is often necessary to recycle process water as much as possible. This, in turn increases the number of cycles in steam boilers, thereby increasing the concentration of corrosive salts inducing higher corrosion rates and other process problems. To minimize corrosion and corrosion-induced risks and maximize equipment life expectancy, it is crucial to understand the nature and mechanisms by which corrosion occurs and then inhibit it as much as possible. (Dargahi et al, 2015)

One of the most common techniques to minimize corrosion in the water industry is the application of corrosion inhibitors, which form a protective (blocking) layer on the metal surface and minimize the access of corrosive electrolytes to the surface. An anticorrosive primer added before the main paint will markedly improve the protection of the substrate imparted by the paint finish. Unfortunately, conventional corrosion inhibitors (e.g., phosphates and sulfites) are neither renewable nor have a reliable performance in highly conductive environments. Therefore, developing new, highly protective, and environmentally friendly corrosion inhibitors for steam boilers, hot-water closed-loop systems, pipelines, and tanks is critical. (Dargahi et al, 2015)

Tannin-based corrosion inhibitors are becoming popular in the water industry because of their renewable/green nature and their ability to perform under much higher conductive/corrosive environments (8,000  $\mu\text{S}/\text{cm}$  to 10,000  $\mu\text{S}/\text{cm}$ ) than the ASME guidelines (< 3,000  $\mu\text{S}/\text{cm}$ ) (Dargahi et al, 2015). Unitán has commercialized quebracho tannins for anti-corrosion treatments (Unitán, 2021).

## 3.5 WP3 CONCLUSIONS

- Accelerated solvent extractor (ASE) can be used efficiently to extract condensed tannins from spruce bark
- Extraction yields of condensed tannins in ASE-extractions (high pressure) are significantly higher than extraction yields in extractions done in atmospheric pressure
- Extraction yields of condensed tannins in ASE extractions depends on the particle size of the bark and the used solvent. Aqueous acetone and alkaline sulphite -solutions are the most efficient solvents
- Extraction yields of condensed tannins in ASE-extractions are high even in extractions done in room temperature
- Isolation of condensed tannins from the spruce bark extracts needs further research

In this work package, tannins separated from pine, spruce and 50/50 mixture of them were used in foaming synthesis. Based on the results we can say that it is possible to utilize the extract in foaming application with good success. In addition, it is possible to produce carbon -and activated carbon foams from tannin-based foams with thermal treatments.

Additional work done within the project, which includes tannins, lignin and sugar based-foams, was also carried out during the project. In total, seven research publications and one doctoral thesis was achieved from tannin upgrading by foaming subject.

## 4. SUMMARY AND CONTINUATION

### WP1

Fibre sludge and saw dust, both residual streams from the forest industry, are raw materials that are well suited for production of lactic acid through bacterial fermentation. The lactic acid produced from these raw materials can be polymerized to produce PLA. Both raw materials have been used in process optimization trials resulting in lactic acid fermentation that requires less additives, lower pH, no detoxification and producing higher yields and higher productivity of lactic acid. The process has been upscaled from bench scale to pilot scale with an industrial scale fermentation trial scheduled for the near future as a result of the optimized process parameters. Chemocatalytic production of lactic acid from biomass-based sugars is also possible, especially with heterogeneous carbon-supported catalysts and when lactate is produced instead of lactic acid. Greater efficiency is also reached when ethanol is used in the reactions compared to water. Analysis methods for the evaluation of hydrolysates, organic acids and PLA have been developed and optimized. The polymerization of lactic acid to PLA is a complex process that depends on factors such as lactic acid concentration in the fermentation broth, compounds present in the fermentation broth that interfere with upgrading process, temperature, time and catalysts for the various steps in the polymerization. We have been able to produce PLA of lower density through direct polycondensation. The possibility of achieving an economically relevant production of PLA from forest industry raw materials has improved through the activities performed in GBS but further developments are needed to achieve production of high density L-PLA (HDLPLA) from these raw materials.

### WP2

Hydrolysis lignin was successfully modified via oxidation and alkylation. More specifically, oxygen functionalities as well as methyl and ethyl groups were incorporated into the hydrolysis lignin structure. Elemental analysis, FTIR, SEC and 31P-NMR were utilized to evaluate the results of the modification efforts. Activated carbon was successfully produced from the hydrolysis lignin. Furthermore, it was found that the native hydrolysis lignin resulted in higher quality activated carbon compared with the modified hydrolysis lignin. Hence, other routes should be explored for the modified hydrolysis lignin. In addition, prepared hydrolysis lignin-based activated carbons were used as a support material in catalytic applications successfully as a part of the biomass valorization to high value products and chemicals.

### WP3

An alternative end use for residual bark was successfully developed within this work packet. In small scale extractions accelerated solvent extraction (ASE) was found to be superior in extraction of condensed tannins from spruce bark compared to extractions done under atmospheric pressure. Under high pressure, condensed tannins can be efficiently extracted from spruce bark even in room temperature in short period of time. Isolation of condensed tannins from the extract needs to be developed if pure tannin extracts are required. Separation of small phenolic components from large phenolic condensed tannins proved to be difficult. Tannin yield, from softwood bark, in larger scale extractions are in the range of a few percent which is in line with literature values. Coextraction of carbohydrate in hot water extraction of tannins may be problematic for some applications. Ethanol washing followed by filtration removes some carbohydrates. Extracts from pine and spruce bark and mixture of these two were used as a feedstock for foaming experiments. Depending on the extraction method, different compounds can be separated from the bark structure, which plays a key role in foaming synthesis and therefore the physical properties of the foams are affected. The foams produced with different extracts had a unique structures and properties depending on the composition of the extracts. Some of the foams were upgraded to activated carbon foams with chemical and physical activation methods. Their quality was similar to granulated commercial activated carbons. From an application point of view, these activated carbon foams can potentially be utilized in many industrial or household applications.

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