



Bioraff Botnia

Project Final Report

2018 04 30

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Background

The forest industry in Sweden and Finland is facing an increasingly tougher competition due to the decline of paper usage and the construction of modern pulp and paper mills in regions with fast-growing raw material. In order to tackle this problem, new industries and products are needed that can effectively utilize the raw material and accommodate the increasing amount of harvestable biomass, i.e. biorefineries. This project aims to nourish the emergence of new industries that produce products and materials from wood, as well as provide opportunities to strengthen businesses in an increasingly competitive market. This is done by making several and more profitable products with the same amount of wood that is used today. As a result, companies will increase their profit margins and contribute for a sustainable future. Overall, the project aims to develop biorefineries or biorefinery-related solutions for existing and new industries within the INTERREG area. These solutions also include re-launching of innovative companies within production, research and services.

Bioraff Botnia is a three-year project which aims to use the tree and preserve the forest resources in the best way possible in order to generate growth and sustainable business. By focusing on the development of completed basic research, the project selected the industry's most interesting areas of application to be able to achieve possible concrete results in terms of increased profitability and new products in such a short time.

The project will focus on applied and industry-relevant research and innovation projects (R & I projects). By applying biotechnology and chemistry know-how, the forest raw material, in the form of residues from forest industries, forestry and sawmill by-products, will be utilized for the development of new products, chemicals and materials. There will always be at least one company from Sweden and a company from Finland to participate in the R&I projects.

This is the first time that dedicated biorefinery partners from both Sweden and Finland implement a joint project, in which R&I research and knowledge will be made available to companies on both sides of the Gulf of Bothnia. Due to the limited cooperation between Sweden and Finland in this area, the implementation of this project will provide a strong signal towards a change. In general, the business structure in Finland is more directed towards the chemical industry, while in Sweden it's towards the pulp mill industry. As a consequence, this joint project will generate great opportunities to build competitive value chains and create new products and chemicals. And this is unique, i.e., that Finnish and Swedish companies are working together to develop new products with research institutions from both sides of the Gulf of Bothnia.

The project will focus on the following activities which are divided in five work packages (WP).

These are:

- Project and Process Management
- Furans
- Production of L-arginine from low-value fibre sludge
- Conversion of Lignin to Chemicals
- From Forest to Chemical Industry
- Cross-border exchange of information and market analysis

The project will not work with:

- The mills' main products
- Materials other than cellulose-based materials
- Stem wood or sawn timber from the forestry industry

The measurable goals of the project are to develop 5-10 new products or process prototypes during the duration of the project. This will be followed via personal contact with the participating companies under and at the completion of the project. We expect that three of the new products or process prototypes could be commercialized within a 5-year period. The long-term effects are that at least two of pulp and paper mills or chemical industry in the region will utilize more of the forest raw material and have at least two competitive products for sale in the market by 2020. Consequently, this will generate a significant contribution to the companies' respective owners in the form of value added.

Key words:

RISE Processum AB, Centria and University of Jyväskylä/Kokkola University Consortium Chydenius

Örnsköldsvik and Kokkola, 2018

1 WP 1: Furans

1.1 Introduction

Furans are a group of substances consisting of an aromatic 5-ring system containing an oxygen atom. Two interesting functionalized furans, furfural and hydroxymethylfurfural (HMF) can be prepared from sugar raw materials. These chemical structures can be seen in **Figure 1-1**.

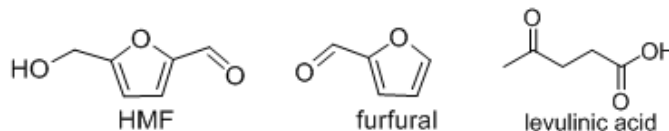


Figure 1-1: The chemical structure of HMF, furfural and levulinic acid.

Furfural and HMF compounds can serve as platform chemicals that can be chemically modified and used in many applications within the chemical industry to everyday products. Examples of products where derivatives from HMF and furfural are found are paints and varnishes, fuels, plastics and composites. Since the starting material is bio based, these products have great potential in becoming substitutes for these types of products that now are fossil based.

Levulinic acid (LA), seen in **Figure 1-1**, is another chemical that can be derived from sugars via HMF and furfural. LA is often formed as a degradation product in the same process as HMF or furfural and is more stable, so there can be a process advantage with aiming for LA instead. LA can also be used as a platform chemical for different chemical components.

A report on the production, applications and some techno economic evaluation of HMF, furfural and related chemicals has been done in the Bioraff Botnia project. The report is named "Furans from biomass - production, applications and techno economic potential".

1.2 Production of HMF from fructose and glucose

1.2.1 Background

HMF is formed in small amounts under relatively mild conditions, for example, you can always identify small amounts of HMF in honey. This process is accelerated by heat and in an acidic environment. However, it is a sensitive chemical that is also degraded under acidic conditions. In this work package, the selective process of converting sugar into HMF was investigated with the aim of obtaining as high yield as possible without further degradation. Normally, long reaction times for HMF to be formed are required, paradoxically, this also results in HMF being broken down to a greater extent. In order to get a good yield, it is therefore necessary to find a balance between the formation and the breakdown. One way other sensitive processes have proven to be successful is to heavily increase the temperature and lower the reaction time while eliminating the formation of the product to a minimum, thus protecting it from

degradation. This can be done by extracting the product into a solvent and thus avoiding the acidic conditions. Another effective approach is to run the process in a continuous flow, where the temperature can be rapidly increased and after the acid catalyzed reaction has taken place, rapidly lower the temperature. Ideally, you also want to remove the acid to further mitigate the conditions.

1.2.2 Method

Flow chemistry

The concept of "flow chemistry" defines a very general range of chemical processes that occur in a continuous flowing stream, conventionally taking place in a reactor zone. The application of flow chemistry relies on the concept of pumping reagents using many reactor types to perform specific reactions. The most common types of reactors are plug flow reactors and column reactors, whilst for specific chemistries more sophisticated reactor designs might be needed (e.g., photoreactors, electrochemical reactors, etc).

There are well-defined key advantages using flow technologies as compared to standard batch chemistry methods:

- Improved heat transfer
- Improved mass transfer/mixing
- Improved kinetics
- Heterogeneous reactions are easily managed
- Reproducibility
- Scale-up
- Extreme reaction conditions (high/low temperature, high pressure)
- Multistep (telescoping)
- In-line downstream processing
- Automation
- Improved Safety (managing hazardous reagents and intermediates)

In this work package, many of these advantages are being utilized, e.g. improved mass transfer, high temperature and pressure and benefits from increased catalyst loading in heterogeneous reactions. In addition to these and as mentioned before, the ability to transport the formed product away from the acidic environment aids in reducing degradation.

An apparatus specifically designed for flow chemistry was used in this WP [ref Uniqsys]. A modified column compartment allowed for higher temperatures (up to 200 °C) to be used. In addition, the heating module was modified to allow for even higher temperatures (up to 350 °C). Several catalysts and conditions were evaluated for the efficient production of HMF. Previous reports (Daorattanachai, et al 2012) have shown that a Calcium-Phosphate catalyst has produced interesting results in both rearranging glucose into fructose and to convert fructose into HMF.



Figure 1-2: *The microreactor-setup used for production of HMF*

For a reasonable productivity, 10% aqueous solutions of either fructose or glucose were prepared and subjected to the catalyst under heat. The output from the flow reactor was diluted for HPLC analysis and quantified using a calibration curve. This allows for a protocol for rapid testing different conditions such as temperature and retention time without too much sample preparation or long down-times for reloading catalyst etc. To isolate HMF, the aqueous solution can be extracted with a suitable solvent, eg. 2-methyl tetrahydrofuran or ethyl acetate.

1.2.3 Results

The calcium phosphate catalyst was also the catalyst that gave the most promising results in this project. In short, higher temperature yielded better conversions into HMF. Unfortunately, both the carbohydrate and the formed products can be degraded or polymerized thermally, thus competing with efficient production of HMF. At 220 °C the reactor could be operated only a short time before clogging forced stopping the process and cleaning the reactor. This gives us an efficient span of between 170 °C and 220 °C with yields between a few percent up to nearly 30%. The different tested temperatures and the corresponding yields can be seen in **Table 1-1**.

Catalyst loading, tested via varying the concentration of the carbohydrate solution, was of less consequence for the reaction. Yields were similar for a 10% solution as for a 5% solution. At higher concentrations, blockage of the reactor was more prevalent.

Table 1-1: Different treatment temperatures with corresponding yields.

	Temp (°C)	Yield (%)
Glucose	170	2
	180	1
	190	2
	200	3
	210	4
	215	5
	220	6
	220*	12
Fructose	170	1
	180	2
	190	5
	200	9
	210	19
	215	27
	220	34
	200**	10

* Double retention time

** 5% solution

1.3 Production of furfural from fibre sludge

1.3.1 Background

This part of WP1 aims to convert secondary lignocellulosic raw materials from forest industry into furans, such as, levulinic acid and furfural. Sawdust (pine, spruce and birch) and fiber sludge were selected (**Figure 1-3**) as raw materials in WP1. Two types of fibre sludge (UPM Pietsaari and Domsjö Fabriker) were used in Finland. The first one was supplied by the local company UPM and the later type by Domsjö. It was delivered from Processum, Sweden to Centria and Chydenius, Finland. In this WP, a novel approach of mechano-catalytic pretreatment of biomass was applied (Schneider 2017; Schneider et al 2017; Lempiäinen et al 2018)

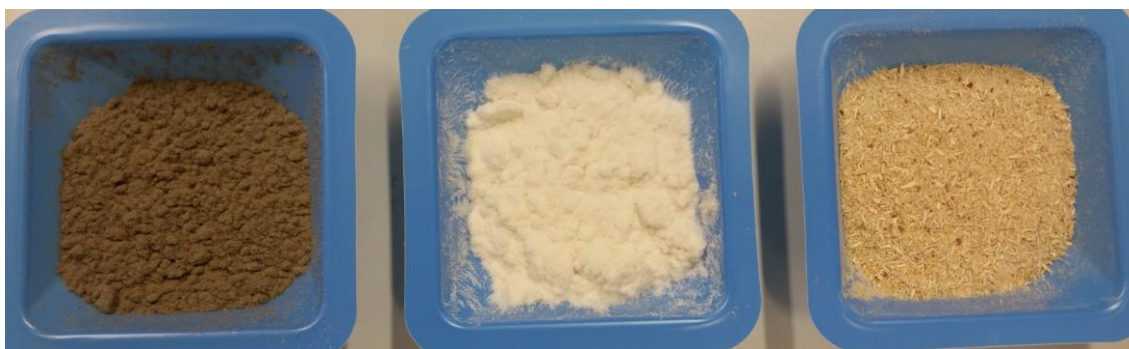


Figure 1-3: UPM fiber sludge (left), Domsjö fiber sludge (middle) and pine sawdust (right).

1.3.2 Method and results

Conversion of secondary raw material into levulinic acid and furfural was studied with a 1-step (hydrothermal) conversion and a 2-step conversion, containing a prior pre-treatment and hydrothermal conversion.

1.3.2.1 1-step conversion

1-step process (**Figure 1-4**) was tested mainly with fiber sludge and various sawdusts (pine, birch and spruce). Microwave irradiation was used as the heating method and reaction conditions (temperature, time and amount of catalysts) were studied extensively (Lappalainen et al. 2018). Best levulinic acid yield, 43%, was achieved with spruce sawdust. However, good yields were also gained with pine sawdust (33%) and fiber sludge (36%). Birch sawdust gave lowest levulinic acid yields (20%).

Since promising results were achieved with lignocellulosic biomass, the conversion method was tested with some other carbohydrate-based biomasses. Again good levulinic acid were achieved; for starch-based biomass 50% and for a chitin-based biomass 60%.



Figure 1-4: 1-step process conversion of sawdust and fiber sludge into levulinic acid.

1.3.2.2 2-step conversion

In 2-step process (**Figure 1-5**) biomass was first pre-treated with sulfuric acid-catalyzed mechanical depolymerization (Dong et al 2017). Various milling times, from 1 to 3 h, and sulfuric acid concentrations were tested. The pre-treatment method was studied with several raw materials (pine, birch and willow sawdust and fiber sludge). However, the further conversion reactions were studied only with pine sawdust. The milled pine sawdust sample was converted into levulinic acid and furfural in a biphasic (water:organic co-solvent, 1:4) system. Two heating methods were tested, oil bath heating and microwave irradiation.

Reaction conditions, such as temperature, time and the amount of additional acid catalyst were studied comprehensively. Also various co-solvents were tested for the biphasic system.

Similar levulinic acid and furfural yields (ca. 35% and 75%, respectively) were achieved with both studied heating methods, however with microwaves the reaction time was shorter, 20 min, while in oil bath longer time (3 h) was needed.

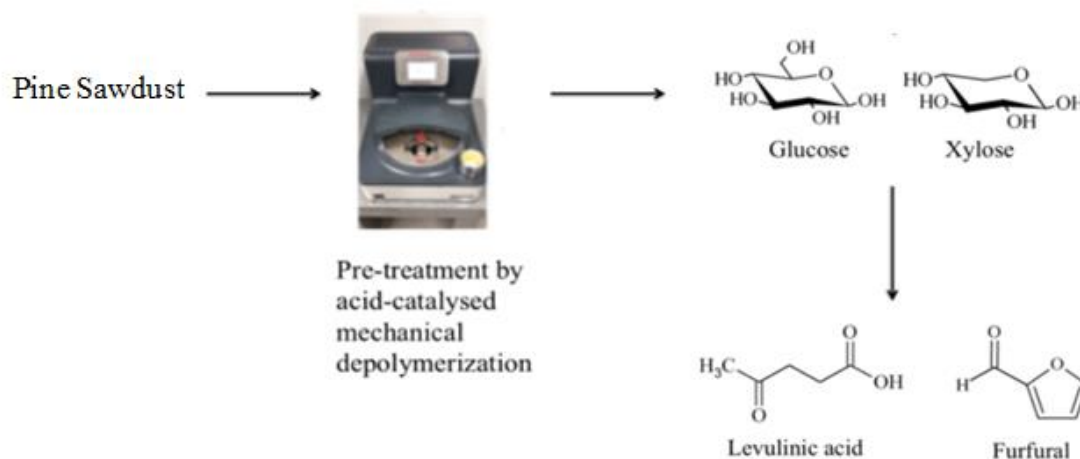


Figure 1-5: 2-step process conversion of pine sawdust into levulinic acid and furfural.

1.3.3 Analysis

Two analytical methods were developed during the project, GC-MS and HPLC-PDA. Methods were used to analyze levulinic acid, 5-HMF and furfural from the samples taken after the conversion reactions. HPLC was used mainly for aqueous samples and GC for samples prepared in organic solvents.

1.3.4 Conclusions

In this study various forest industry secondary raw materials were converted into levulinic acid and furfural. When 1-step process was used mainly levulinic acid was achieved. The best starting materials were softwood sawdust as well as fibre sludge (ca. 40% levulinic acid yield), whereas hardwood sawdust yielded only 20% levulinic acid. In 2-step process also furfural was obtained, since reactions were performed in biphasic system. Furfural yields were excellent, ca. 75%, while levulinic acid yields were similar as in 1-step process. The heating method didn't have much effect on the yield, however it had a great effect on the reaction time.

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2 WP 2: Production of L-arginine from low-value fibre sludge

In this WP we were interested in evaluating microorganisms that are able to utilize fibre sludge hydrolysates with high carbohydrate content as raw material for the production of the high value product L-arginine. This would be an economically and environmentally valuable alternative use of fibre sludge compared to burning, which is mostly used presently.

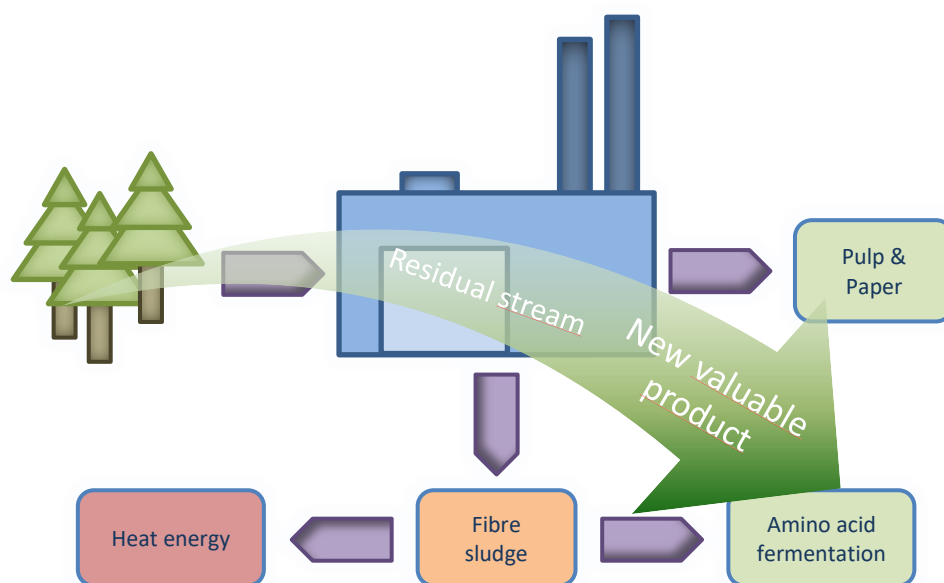


Figure 2-1. Illustration of the working theory in WP2. Pulp and paper is the primary product from wood based biorefineries. Fibre sludge, generated through residual streams in the process of the biorefinery, is mostly burned for heat energy purposes. However, it has potential as raw material in microbial fermentation of amino acids, a higher value product.

2.1 Introduction

2.1.1 Fibre sludge as raw material

Residual streams that contain organic material from the pulp and paper industries in Sweden and Finland are fibre sludge, chemical sludge and biological sludge from purification of waste water. Around 125 000 tons of fibre sludge was produced by Swedish pulp industries in 2010 whereas the amount of fibre sludge produced in Finland was about 314 000 tons (2012). Fibre sludge has high and pure cellulose content but the fibres are too small for paper production. In Sweden as well as Finland, the fibre sludge is mostly burned since landfill of organic waste has been prohibited. The economic value of fibre sludge could be increased if it could be utilised, for instance, as a carbon source for microbial fermentation (**Figure 2-1**). As such, this could potentially be of interest both for the amino acid and pulp and paper industries. The

production and market for amino acids has grown extensively during the past decades with market prices in the range of 7-40 SEK/kg depending on quality. Today, the main raw material for industrial amino acid fermentation is starches from tapioca and corn, but since these are also important as food it is of interest to look for other alternative feedstocks. One such feedstock is cellulose which is degraded to glucose when hydrolysed. Enzymatic hydrolysis has proven to give high sugar yields, but this requires the cellulase enzyme and method for biomass pre-treatment to be suitable for the microorganism in question. It is also important to consider the presence of hemicellulose and lignin in the feedstock as the presence of derivatives of lignin and hemicellulose in the solution might inhibit the activity of cellulases as well as microbes. Hence, since fibre sludge has a high and relatively pure cellulose content it might be a suitable feedstock for high value amino acid production. Our primary focus in this WP was to use available residual streams from biorefineries where we wanted to investigate if the project could result in a new higher value product for both the Swedish and Finnish forest industries by using fibre sludge hydrolysates as raw material for the production of L-arginine. To our knowledge, fibre sludge has so far not been tested as a feedstock for microbial fermentation of L-arginine.

2.1.2 L-arginine producing microorganisms

L-arginine is an economically important amino acid with applications within the food and pharmaceutical industries and as plant fertilizer (**Figure 2-2**). L-arginine can be produced industrially by chemical synthesis, a process which is however polluting, or by microbial fermentation.

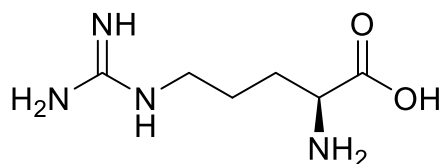


Figure 2-2. Structure of the amino acid L-arginine, a potential high value product for the biorefinery industry. L-arginine has applications in the food and pharmaceutical industries as well as additive in fertilizers.

The bacterial strains *Corynebacterium glutamicum* and *Bacillus subtilis* have been widely used as amino acid producers. *B. subtilis* is one of the most characterized bacteria and is a useful tool for industrial applications since it is metabolically diverse and can secrete high amounts of substances directly into the fermentation media. The strain is frequently used in biotechnological processes due to its appropriate fermentation properties, high yields and non-pathogenicity. *C. glutamicum* is a favourable species for arginine production due to its ability to utilize a wide range of substrates as carbon sources including carbohydrates and organic acids. *C. glutamicum* is used at industrial scale for amino acid production and can naturally utilize glucose but not the fraction of pentose sugars of hemicellulose. Hence, finding a cellulose-rich feedstock such as fibre sludge would be of importance.

2.2 Methods and results

2.2.1 Testing of fibre sludge from biorefineries

Fibre sludge from the industrial partners UPM Kymmene Pietarsaari, SCA Obbola, Metsä Board Husum and Domsjö Fabriker, including both sulphate and sulphite pulp mills, were initially tested for their suitability as sugar rich feedstocks. The fibre sludge was treated by ball milling, ionic liquid pretreatment or enzymatically hydrolysed by using different commercially available enzymes (**Figure 2-3**). As fibre sludge has high cellulose content, we reasoned that the enzymatic hydrolysis could yield hydrolysates rich in available sugars. However, the free sugar content in the hydrolysates differed quite significantly between the fibre sludges.



Figure 2-3. Left: picture of three of the four types of fibre sludge provided by the industrial partners UPM Kymmene Pietarsaari, SCA Obbola, Domsjö Fabriker and Metsä Board Husum. Right: Fibre sludge in dry solid form and hydrolysate after enzymatic hydrolysis.

As the sulphate and sulphite pulp milling use different chemical processes, we wanted to investigate whether different elements in the fibre sludges could have inhibitory effects on the enzyme mixtures used. Hence, the fibre sludges were further characterised with respect to components such as cellulose, hemicellulose, lignin, ash as well as basal elements. The analyses indicated differences that could be one reason for the observed differences in free sugar obtained in the enzymatic hydrolysis. As a result, from the initial four fibre sludges we were able to narrow it down to two fibre sludges that would be used in the subsequent experiments.

2.2.2 Culture and growth of microorganisms in fibre sludge hydrolysate; optimization of culture parameters

The two fibre sludges mentioned above were enzymatically hydrolysed using commercial enzymes and the amount of released sugars was measured in the filtered hydrolysates by a glucometer and by high pressure liquid chromatography (HPLC). Hydrolysate number 2 was, as it contained more free sugar, then used in laboratory scale experiments to evaluate bacterial growth. As a comparison, standard nutrient broth (NB) and secondary ethanol (EtOH) were used in these experiments.



Figure 2-4. To the left is a picture of *Corynebacterium glutamicum* and *Bacillus subtilis* strains streaked on agar plates. Right: the 1 litre multiple bioreactor system used in microorganism culture and fermentation trials at the facilities of RISE Processum AB in Örnsköldsvik.

Different bacterial strains of *Bacillus subtilis* and *Corynebacterium glutamicum* were used where the bacteria were grown in shake culture flasks. The growth was measured spectrophotometrically at OD600. In all cases, the bacteria grew better in fibre sludge hydrolysates compared to the NB and EtOH samples. This indicated that fibre sludge could be a good raw material for the growth of microorganisms. In the following experiment we repeated the procedure but at larger scale. Here we used 1 litre culture reactors where we had the ability to regulate parameters such as pH, temperature, oxygen content and stirring speed among others (**Figure 2-4**). Here we could also see that the bacteria grew better in fibre sludge hydrolysates compared to both NB and secondary EtOH, again indicating that fibre sludge is a valuable medium for bacterial growth (**Figure 2-5**). We were also able to select two bacterial strains that would be used in the L-arginine fermentation experiments.

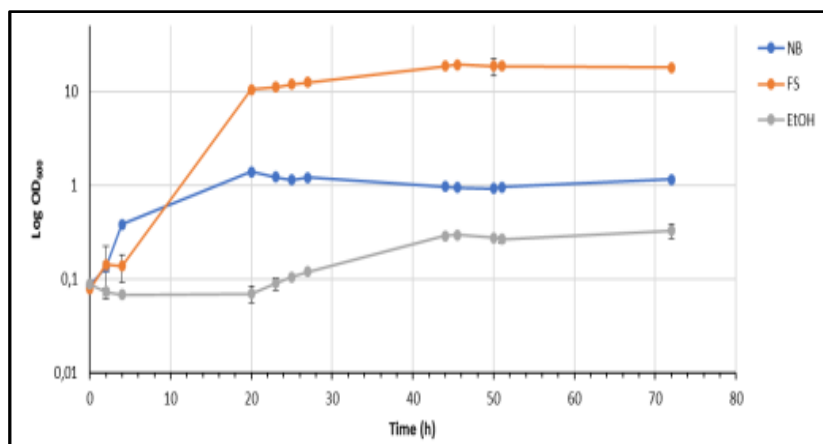


Figure 2-5. Growth curves of *Bacillus subtilis* used in growth optimization trials in the multireactor system with fibre sludge hydrolysates (FS) compared to nutrient broth (NB) and secondary ethanol (EtOH).

2.2.3 L-arginine fermentation in fibre sludge hydrolysate; optimization of microorganisms

After multiple rounds of optimization of culture parameters in the 1 litre bioreactors we investigated whether the two bacterial strains of *C. glutamicum* and *B. subtilis* were able to ferment the sugars in the fibre sludge hydrolysate into L-arginine. We observed the highest production, albeit still at insufficient levels, of L-arginine in fibre sludge hydrolysates compared to NB and secondary EtOH. Interestingly we observed a more pronounced production of L-alanine in the hydrolysates (**Figure 2-6**). After several unsuccessful attempts to adjust parameters for L-arginine fermentation we decided to attempt chemical engineering of the microorganism to enhance the L-arginine production. However, this proved to be both labour intensive and difficult with no improvement in L-arginine secreting mutants. As this method could potentially produce random mutations in the genome of the microorganism we decided for a more targeted engineering. By over expression of key genes involved in the L-arginine biosynthetic pathway we wanted to see how this affected the production of L-arginine. The over-expression mutants were used in fermentation trials and amino acids were analysed by HPLC. We were unsuccessful in achieving higher L-arginine production but we observed an increase in the amount of L-alanine produced.

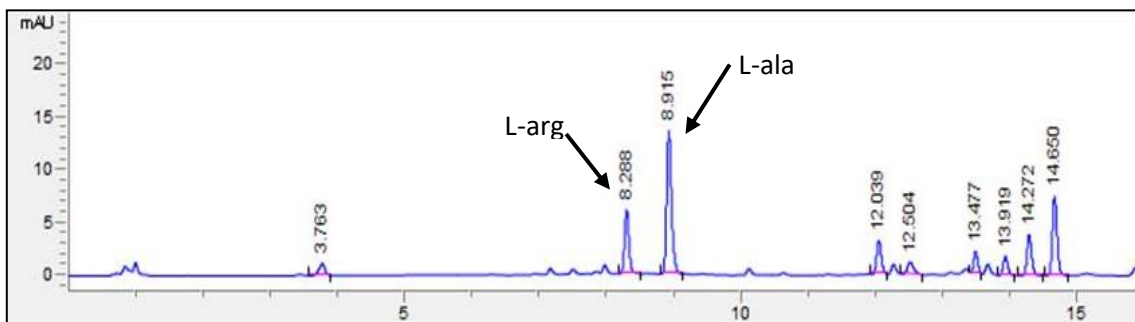


Figure 2-6. HPLC analysis of the amino acids L-arginine and L-alanine, measured from culture broth when *B. subtilis* was cultured in fibre sludge hydrolysate in the 1-litre bioreactor system.

2.3 Conclusion

Although we were unsuccessful in achieving a sufficiently high production of L-arginine with the microorganisms used in this WP, we can still conclude that:

- Depending on the pulp manufacturing process, fibre sludge hydrolysate is a very promising feedstock for culturing of microorganisms since it has high sugar content and low amounts of inhibitory compounds.
- From the four initial fibre sludge samples from our forest-industry partners, we managed to narrow it down to two for sugar-platform-based trials.
- Pre-treatment to sugar-rich hydrolysate trials were done in both Centria (ball mill, ionic liquids and enzymatic hydrolysis) and RISE Processum AB (enzymatic hydrolysis).
- Fermentation trials: strain comparison and selection, growth trials (flask and bioreactor), random and targeted mutagenesis, glucose and arginine HPLC determination – RISE Processum AB with participation/visit from Centria.

- Low amount of L-arginine fermentation was achieved with the current bacterial strains. Acquisition of a high-producing strain, for instance through collaboration, is desirable.
- Final degree project student: completed her education in the Biotechnology program and is currently employed at RISE Processum AB.
- Research project student: final report concluded and delivered.
- Exchanged scientific and technological know-how between research organisations.
- Expanded industrial contacts with closer-to-market company (L-arginine fertilizer manufacturer).
- Publications: Dong Y *et al.* Biomass Bioenergy (2016); Doctoral Thesis Nov 2017.
- Another amino acid, L-alanine, was produced at higher amounts when fibre sludge hydrolysate was used: potential candidate as high value product?

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3 WP 3: Conversion of Lignin to Chemicals

3.1 Introduction

Lignin is one of the most abundant polymer found in nature and is a major residual in the pulping industry. Today it finds its most use as an energy carrier, being incinerated for energy, heat or steam. Lignin could however be imagined as a source for a variety of different products and chemicals. In this WP we have explored the liquefaction of lignin to a liquid product that can be regarded as a renewable version of crude oil and can for example be upgraded to chemicals or transportation fuels. This process is almost always accompanied by formation of solid products that in this WP has been activated into activated carbon.

3.2 Hydrothermal liquefaction

Hydrothermal liquefaction (HTL) is a process that has been known for almost a century and is frequently said to be the accelerated version of the process that is the source for the crude oil that is currently being pumped up from underground wells. HTL is one member in the direct liquefaction family, in which for example pyrolysis is also a member. One attractive feature of HTL is that this process doesn't require any drying of the biomass since water both acts as the solvent and as a catalyst for the conversion of biomass into liquid biocrude. By increasing the pressure and temperature to achieve supercritical or near-supercritical water the process is accelerated to the minute-range instead of the millions of years range. Thus it matches the requirements for renewable products that can be used in the same applications as products from fossil oil. A fuel derived from these biocrudes can allow us to continue to use combustion engines with a much-reduced environmental impact.

The interest in the HTL-process has over the years followed the world prices for crude oil; low oil prices equals low interest in alternatives and high prices generates more activities in finding viable alternatives. During the last decade an increased interest in different liquefactions routes has been observed, indicating a shift in regarding other values besides economical ones in deciding the road map ahead. From previous experience it is known that different catalysts and additives are beneficial for the HTL process. Among the catalyst simple alkali bases are common and an additive that has received some attention is glycerol. Glycerol is produced alongside biodiesel in trans-esterifying oils into eg FAME-fuels. Glycerol is still an expensive commodity but with a continued increase in biodiesel production, it is likely that glycerol will be widely available in the world market and prices can be expected to drop.

In this part of WP 3 we have investigated the use of glycerol and mixtures of mono-, di- and triglycerides that are isolated from trans-esterifying oils.

3.2.1 Method

Besides catalysts and additives there are other pertinent parameters that affect the outcome of the HTL-process. Such parameters are temperature, pressure, concentration and heating/cooling rates for the process. We have used equipment specifically designed to efficiently vary these parameters, pictured in **Figure 3-1**. The starting materials used were hydrolysis lignin from either softwood or from wheat straw. The starting materials were used as 10% aqueous slurries after milling them with a 0.5 mm sieve.



Figure 3-1: *Equipment used for the HTL process*

3.2.2 Results

It was observed that addition of either glycerol or the glyceride mixture has beneficial effects on the process, mainly on the yield of the oil fraction. Thus, it is possible to increase the productivity of the liquefaction and at the same time reduce issues that are associated with char formation. Glycerides were particularly effective, but unfortunately these are more expensive and less widely available compared to glycerol. The effect on the quality of the oils were less pronounced, leading to similar oxygen content and physical appearance.

Yields for the oils were typically around 40% with glycerol and as high as 80% with glycerides, albeit in the last case some of the added glycerides contributes directly to the yield.

The equipment used is simulating a continuous process with regards to the heating and cooling rates. Any equipment that requires very high pressure tends to carry large investment costs. A continuous process can mitigate this to a large extent, even though it usually is more technically challenging.

3.2.3 Conclusions

The use of hydrolysis lignin and glycerol or glycerides in the HTL-process can be an efficient combination, but the economic aspects of this needs a thorough analysis. The results

presented herein are preliminary and require further investigation, both in semi-batch and continuous mode.

3.3 Activation of biochar

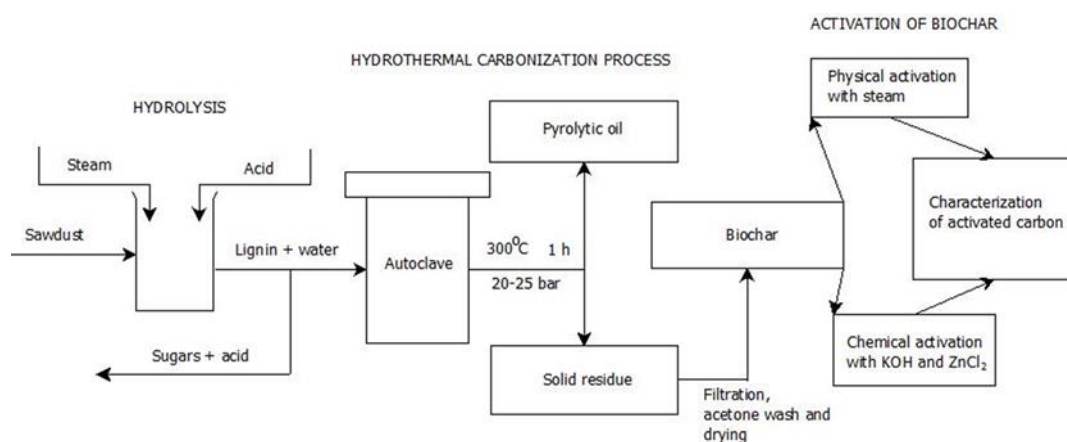
Over the last decades, the preparation of activated carbons (ACs) with proper chemical and physical properties has gained a lot of interest. [1] A highly porous structure and high specific surface area of activated carbons are features that are widely being used in many purification applications in industrial and municipal processes. Wastewater treatment, gas cleaning processes, metal removal from waste streams and usage as a catalyst are the main application for these activated carbons. [2]

Different biomasses, saw dust, lignin, peat, coconut shells etc., [3] can be converted into activated carbons in a two-step process including carbonization and physical or chemical activation. Physical activation includes high temperature activation, 750-900 °C, using steam or CO₂ as an activating agent. Chemical activation includes impregnation of the biomass with an activating agent (KOH, ZnCl₂, H₃PO₄), drying of the biomass and carbonization/activation in a one-step process.

In this part of the project the effects of different chemical and physical activation agent, on the specific surface areas, pore volumes, total carbon contents and yields of biochar, produced from lignin, were investigated.

3.3.1 Material and Methods

Biochar used in the activation was a side product from the production of pyrolytic oil. Lignin obtained by hydrolysis of softwood as 20 % aqueous slurry was rapidly heated to 300 °C in an autoclave and kept at this temperature for 1 h, then quickly cooled to room temperature. The resulting mixture was filtered and the solid residue was washed with acetone and dried to obtain biochar. Biochar production route can be seen in **Scheme 3-1**.



Scheme 3-1: Route for producing activated carbon from biochar

Chemical and physical activation were done using an apparatus shown in Figure 3-2.

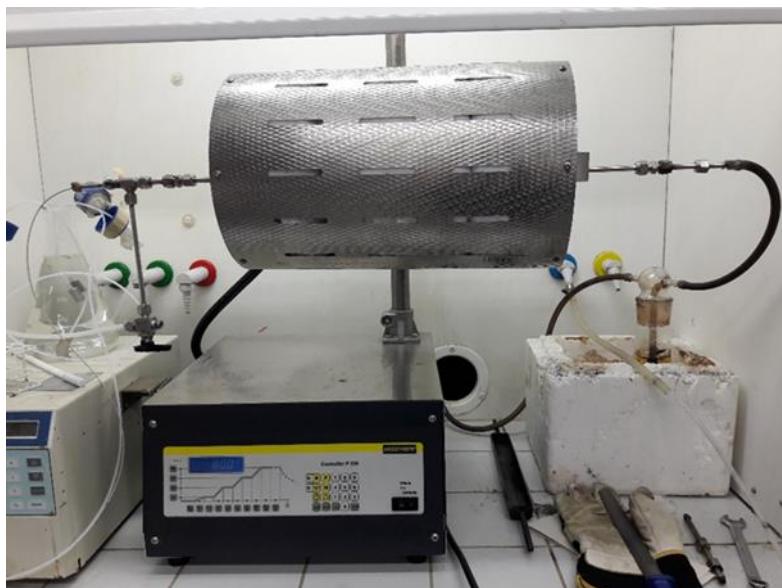


Figure 3-2. Carbonization and activation apparatus from Nabetherm.

3.3.1.1 Chemical activation

The char was impregnated with ZnCl_2 and KOH using 1:1 mass ratio. Mixtures were stirred for 3 h in 85 °C and dried in an oven at 105 °C for overnight. The impregnated char samples were activated in a stainless-steel fixed-bed reactor. The reactor was flushed with nitrogen in order to avoid oxidation. The oven temperature was increased from room level to 500 °C using a 5 °C/min heating ramp and a hold time of two hours at the target temperature. After carbonization the remaining chemical activating agent in the sample was removed by refluxing with 3 M HCl for 1 h. The carbons were filtered and washed with distilled water until a neutral filtrate was obtained. Activated carbon was finally dried in an oven overnight.

3.3.1.2 Physical activation

In this case, char was placed in the reactor without any pretreatments. Nitrogen flow was turned on and the carbonization temperature was increased from room temperature to 800 °C using a 5 °C/min heating ramp. As soon as the temperature reached the desired temperature the steam, activation agent, flow was turned on. Activation was continued for 2 h. Reactor was allowed to cool down to room temperature after activation.

3.3.1.3 Characterization

From all samples specific surface area, pore size distribution, total carbon content and yield were measured.

3.3.2 Results & discussion

Results from the experiments are listed in the **Table 3-1** below. According to the results, highest specific surface area, pore volume, total pore volume, total carbon content and yield was obtained by chemically activating biochar with ZnCl₂. On the other hand, pores created with ZnCl₂ were mostly in microporous region. Mesoporous structure can be obtained from biochar using KOH as an activation agent. Lowest yield was obtained during the physical activation of biochar with steam.

Table 3-1. Overall results from the biochar activation.

Sample	Specific surface area	Pore volume	Total pore volume	Micro (< 2 nm)	Meso (2-50 nm)	Macro (> 50 nm)	Yield	Total carbon content
	(m ² /g)	(cm ³ /g)	(cm ³ /g)	(%)	(%)	(%)	(%)	(%)
Biochar_800 °C_2 h steam activation	811	0,46	0,17	16,3	36,4	47,2	33,5	86,91
Biochar with ZnCl₂_500 °C_2 h activation AW	1660	0,78	1,19	75,6	21,0	3,4	48,2	87,81
Biochar with KOH_500 °C_2 h activation AW	489	0,31	0,17	17,6	70,6	11,8	41,8	75,45
Biochar blank	14	0,02	0,067	1	30	69	-	65,57

3.3.3 Conclusions

The results obtained [4] from the analyses showed that it is possible to:

- Obtain high specific surface area, yield and pore volume using ZnCl_2 as an activation agent.
- Modify the pore size distribution from microporous to mesoporous by changing the activation agent.
- Reach relatively high carbon contents regardless the activation procedure used
- Use low temperatures to produce highly porous activated carbon from biochar.

3.3.4 References

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4 WP 4: From Forest to Chemical Industry

4.1 Introduction

WP 4 consists of some smaller parts focusing on production of useful products from bio based by-products. These have been narrowed down to weed control foam, floating additives, bio composite materials, tannin extractions and a techno economic evaluation of extractives from the pulp and paper industry.

4.2 Tall oil to weed control foam

4.2.1 Background

Spuma is a foam extract used for thermal weed control. Spuma is mixed with hot water and sprayed over the weeds. The foam forms a protective film that allows the hot water to retain heat for a longer time and thus overheat the plant. Spuma is an alkyl-polyglycosides, a tenside with hydrophobic and hydrophilic ends and is today produced by using a polysaccharide and palm oil. In this project it is studied whether it is possible to replace palm oil with renewable tall oil, a by-product from the pulp and paper industry.

4.2.2 Method

Three possible compounds were investigated for characteristics close to those of Spuma. Common for all compounds were that the hydrofobic end could be derived from tall oil (C18). In the experiments tall oil fatty acid, tall oil acid chloride and 1-octadecanol (reduced tall oil) was used. These compounds were modified to produce surfactants. The mono-alcohols (hexanol and nonanol) theoretically derived from oxidized tall oil was also used as raw material for the possible SPUMA replacement product.

In parallel to this work, it was found that the solute of extracted bark was very prone to form stable foam at room temperature. The bark extract was therefore also investigated as a possible replacement of Spuma.

Evaluation of the compounds was done by a foam solidity test. One litre of water was used with a concentration of 0.2 wt % active substance. The solution was pre-stirred for one minute before each experiment. The foam depth was measured at certain times and the experiment was performed with water at 25 °C and 99 °C.



Figure 4-1: Foam solidity test. To the left: Bark extract. To the right: Spuma.

4.2.3 Results

The first compounds tested derived from tall oil fatty acid, tall oil acid chloride and 1-octadecanol did form foams but did not hold for as long as Spuma or at high temperatures. The bark extract tested did not withstand the foam tests either. The ones showing most promising results were the ones derived from hexanol and nonanol, however the products has to be refined to get a clearer result.

4.3 Modification of hydrolysis lignin as additive in concrete

4.3.1 Background

Hydrolysis lignin is a by-product obtained in the sugar platform that today is burned. In order to strengthen the competitiveness of the sugar platform, it is very important to find new products or applications for by-products to get as cost-effective as possible.

In the construction field concrete uses a lot of water to get the right consistency when moulded. The addition of some material with dispersive abilities can lower the water use and enhance the properties of the concrete. Today one commonly used product is lignosulfonate, a by-product from the pulping process.

4.3.2 Method

Hydrolysis lignin from SEKAB was washed with three different methods to get rid of the carbohydrates and obtain a pure lignin. The washed lignin was then oxidized and the liquid and solid fractions were tested separately as additive in concrete.

The consistency of the concrete was tested in a flow test. Inspired by EN 12350 standard, a flow test was conducted on a smaller scale. It was carried out by mixing 100 g of concrete with 12 ml of tap water (recipe on the concrete bag). Then the concrete was packed in a rubber

mantle standing on an aluminium tray. After about 30 seconds, the cuff was lifted and the tray lifted a few inches and released in the bench 15 times to get the concrete to flow out. The diameter of the concrete circle was measured. For each test, new concrete was mixed so that the resting period was the same. Any density reduction on the concrete mixture was noted by weighing the amount of concrete not held in the cuff.

The different fractions were analysed for its content, as lignin and carbohydrates, and for its molar mass distribution.

4.3.3 Results

The washing sequences of lignin behaved differently. Two of them were very time consuming due to clogging of the filtration equipment. Analysis of the product showed that every washing method increased the lignin content of the material but there were still some carbohydrates left in different amounts. The resulting look after washing and drying of the hydrolysis lignin can be seen in **Figure 2-2**.



Figure 2-2: Hydrolysis lignin after 3 different washing steps.

The floating tests were performed on the washed and oxidized hydrolysis lignin and compared to conventional floating additive lignosulfonate. In **Figure 4-3** the difference between concrete without additive and concrete with modified hydrolysis lignin added can be seen. The modified lignin showed the same floating ability as lignosulfonate.

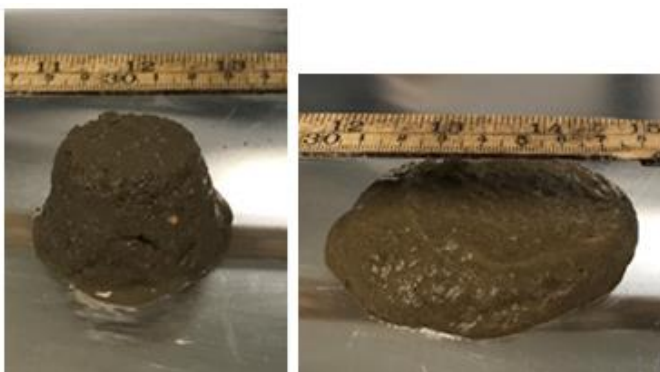


Figure 4-3: Flow test. To the left: Concrete without additive. To the right: Concrete with modified hydrolysis lignin added.

4.3.4 Conclusions

The modified hydrolysis lignin showed promising properties as a floating additive in concrete. The washing sequences and oxidation steps has to be optimized to get a viable production route. The addition of the modified hydrolysis lignin in concrete could also be optimized to get as good floating ability with as low addition as possible. This will all be investigated in the new Interreg project Green Bioraff Solutions.

4.4 New wood composites

4.4.1 Background

It is in many ways evident that fossil-based plastic materials needs to be replaced with materials made from renewable resources. This is a key step to shaping a sustainable future. Utilizing wood fibres from renewable forests to replace plastics presents both technological and economical challenges. At the same time the pulp and paper business faces a downward trend of newsprint. This means the industry faces a challenge to renew the utilisation of their current infrastructure. The startup company Biofiber Tech Sweden had an idea to develop new and cost-competitive technologies in collaboration with partners from both the forest industry and the plastic industry. Within the frames of this project the idea was verified.

4.4.2 Surface Modification

To investigate if it is possible to modify the surface of the fibres of mechanical pulp, a number of chemical reactions were performed. A range of conditions close to those within the refiner were investigated together with chemicals to graft the surface of the fibres. Small fibre sheets were dried and analysed by contact angle.

4.4.3 Results

Contact angle was the analytical method of choice. Below a selection of results are shown to describe the evaluation of the fibre modification. After chemical modification the fibres were filtered and washed thoroughly with water, acetone and finally with water again. After washing the samples they were pressed and dried in an oven over night. **Figure 4-4** shows the results of the modified samples as well as the results of two references, one where the sheets were washed with water only [Reference water] and one where the sheets were washed with water, acetone and finally water again [Reference acetone].

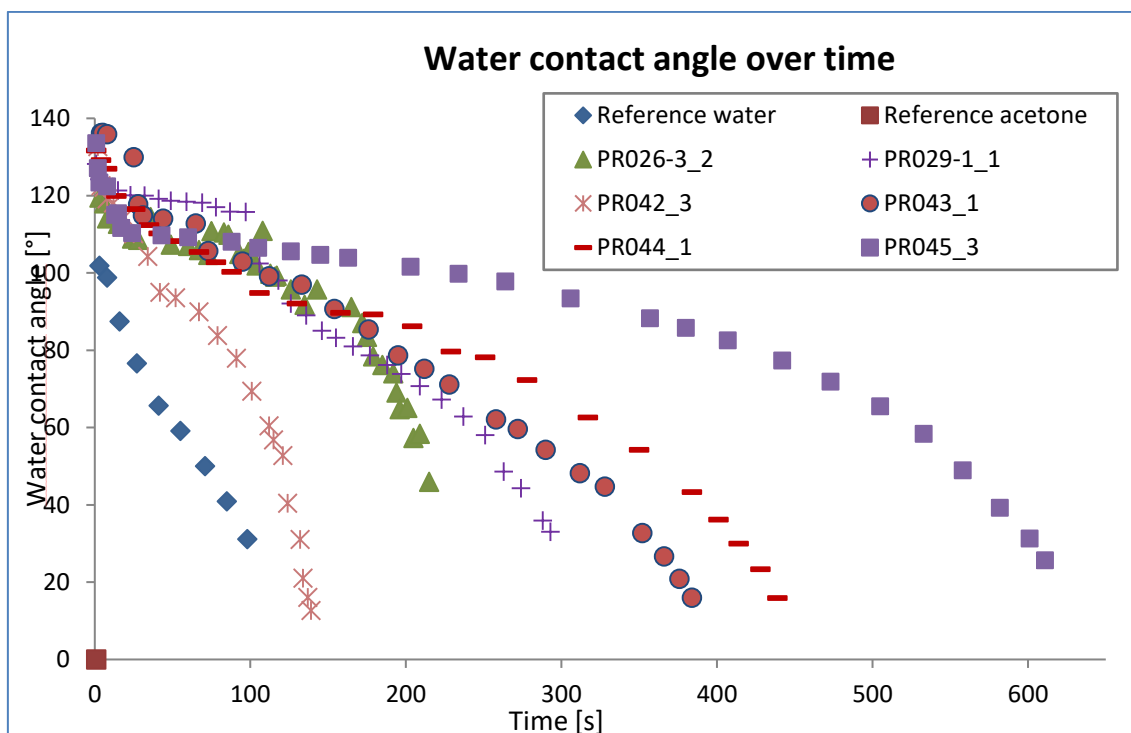


Figure 4-4: Water contact angle over time for the modified samples and two references.

In **Figure 4-4** a selection of water contact angle measurements of pulp modified with methyl methacrylate, tall oil or latex. A large range of experiments with two different oxidative systems with three different grafting additives at three different temperatures and three different reaction times were carried out. The results from this study where the modifications using latex and tall oil showed the most promising with a large increase in contact angle is the basis for the subsequent project.

Shortly after this a larger consortium was set up including Biofiber Tech Sweden AB and the institutes Swerea SICOMP and RISE Processum together with several well-known industrial partners such as Sveaskog, Holmen, Orthex, Inxide, PODCOMP, Plastkonsult i Ostvik and NEVS (National Electric Vehicle Sweden). The consortium was successful in a Vinnova application and is today running a project to develop a composite using current infrastructure and renewable materials.

4.5 Extractives from the pulp and paper industry

The forest industry is one of Sweden's and Finland's most important business sectors. Thanks to its biobased raw materials and products, the forest industry plays a key role in the development towards a sustainable, circular economy. To meet market needs, and to drive the growth of the circular economy, the forest industry is continually developing its processes and products. It is seeking to use its raw material, the forest, as efficiently as possible and is

constantly seeking to improve quality and incorporate new functions into materials and products.

The extractives from trees make up between 3 and 5 weight-% of the wood and consists of a wide range of compounds. The majority of those compounds are fatty acids such as oleic- and linoleic acid and rosin acids, such as abietic- and pimaric acid. The remaining compounds are commonly referred to as “neutrals” and are dominated by β -sitosterol. The extractives in Scots pine for example, consist of 70 % fatty acids, 20 % rosin acids and 5 % neutrals.

To meet market needs, and to drive the growth of the circular economy, extractives could potentially be used for the production of other products, either through new refinement routes or novel extraction and separation methods from the raw material. In order to identify opportunities for the production of other extractives-based products, the extractives value chain must be mapped. Second, refinement routes as well as extraction and separation methods suitable for isolation and processing of valuable compounds must be identified.

The objective of this work was to identify opportunities for the production of new products based on extractives as raw material. It resulted in the report “Extractives in the Scandinavian pulp and paper industry – current and possible future applications”.

4.6 Tannin extractions

4.6.1 Background

Wood bark is an abundant residue from the debarking processes in sawmills and pulp mills. The bark residues from the debarking process are generally burned to obtain energy, due to the relatively high heating value of the bark. The bark has typically low carbohydrate content and high lignin content. In addition, bark contains notable amount of different types of extractives. The inherent role of the extractives in bark is mainly to protect the wood.

Many of the wood extractives are insoluble in water. However, tannins are water-soluble polymeric compounds found extensively in bark. The use of tannins in leather production has been known for centuries. Other main uses include the wine production, and animal feed. Also, the proanthocyanidins (a type of tannin) are used as antioxidants in cosmetics and supplements. Recently, tannins have gained interest as a natural phenol source in the production of adhesives and insulation foams.

The aim of this WP was to find suitable extraction conditions to obtain value-added products from bark residues. Also, the aim was to develop methods to characterize the aqueous extracts to estimate the content of tannins and carbohydrates.

4.6.2 Method

Pine and spruce bark were used in the hot water extraction experiments. Pine bark samples were obtained from sawmills located in Utajärvi or in Kuhmo (Finland) and the spruce bark was obtained from UPM (Finland). The sample batches were obtained during different times of the year, they were from different sawmills and they were treated differently after obtaining them. Consequently, not all the results are comparable with each other.

4.6.2.1 Case 1

The effect of different pre-treatment conditions on the extractive yields from the pine bark samples were studied: drying temperature (air drying at 20 °C, oven drying at 70 °C, oven drying at 105 °C), particle size (non-refined, milled with cutting mill through 6 mm sieve, see **Figure 4-5**) and storage time (fresh sample from debarking process, old sample of bark).

In this case, the bark samples were extracted with distilled water only. The procedure for the extraction was as follows: 2 g of bark sample was weighed to a 100 ml round-bottomed flask and 40 ml of distilled water was added. The extraction temperature was set to 75 °C. The bark samples were extracted for 60 min. After the extraction, the samples were cooled in ice bath, and the mixture was filtrated and washed twice with distilled water. The filtrates were mixed, diluted with water and stored in freezer for further analysis.



Figure 4-5. Photograph of the original (left) and milled (right) pine bark sample, as well as extract sample from one experiment from case 1.

4.6.2.2 Case 2

The effect of different extraction conditions on the extractive yields from the fresh pine bark and fresh spruce bark samples were studied and compared: extraction time (60 min, 120 min), extraction temperature (60 °C, 100 °C), chemical additives (nothing, urea + Na₂SO₃, Na₂SO₃ + Na₂CO₃). In this case, the bark samples were freeze-dried and milled with Cutting Mill (Retsch SM100) through 1 mm sieve (at the Natural Resources Institute Finland (LUKE) in Kannus, Finland).

A different experimental set-up was used than in case 1: 2 g of sample was weighed to the 100 ml round-bottomed flask, and 20 ml of distilled water was added. In the case of chemical addition, either urea and sodium sulfate, or sodium sulfate and sodium carbonate were added to the flask. The extraction temperature was set to desired value. The bark samples were stirred with magnetic stirrer under reflux for desired time. After the extraction, the samples were cooled in an ice bath, and the mixture was transferred to a 100 ml centrifuge tube. The samples were centrifuged, and the supernatant was collected by filtration. Solid residue in the tube was washed with distilled water, and centrifugation was repeated, followed by collecting the supernatant. Finally, the residual solid was filtered and washed with distilled water. The

supernatants and filtrate were mixed, diluted with water, and stored in freezer for further analysis.

4.6.2.3 Pilot scale extractions

The pilot-scale extractions for pine bark were done in the ChemPlant pilot environment (Centria), with a 200 l reactor. After the first trials, a filter bag system was developed inside the reactor to simplify the separation stage of the process. Pine bark dried at 70 °C or 105 °C in oven and milled through 6 mm sieve was used in this case. Four filter bags with approximately 1.4 kg of pine bark were mixed with water (at 75 °C, 60 min, 230 rpm). The amount of bark used was doubled by changing the bark inside the filter bags for new batch after 60 min extraction and it was continued for another 60 minutes.

4.6.2.4 Analysis

The tannin content was evaluated from the extracts using the Folin-Ciocalteu method for the total phenolic content (TPC), and a butanol-HCl assay for condensed tannins (CT) (Mota et al. 2012). The butanol-HCl method used in these studies was slightly modified from the method given in the literature. The amount of carbohydrates in the extracts from case 2 was estimated by the analysis of total reducing sugars (TRS) using DNS method.

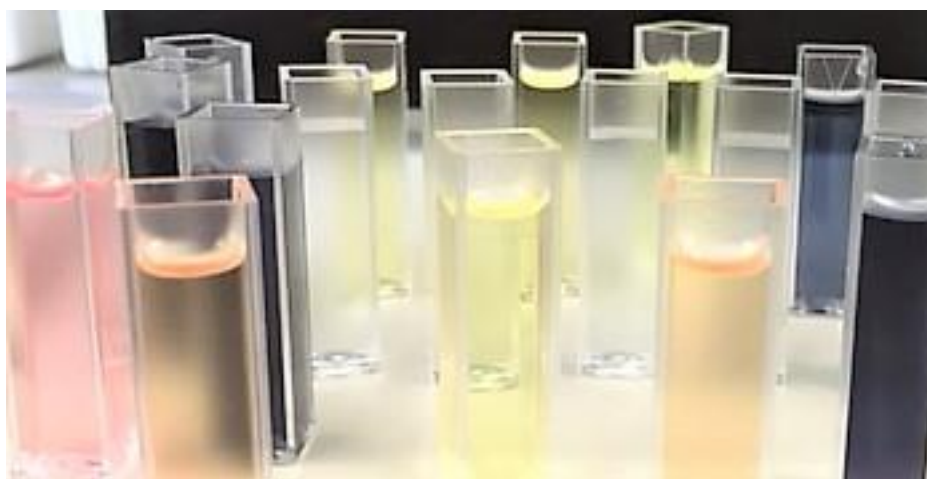


Figure 4-6. Sample cuvettes to be measured with the Shimadzu UV-1800 spectrophotometer to determine total phenolic content (TPC) and condensed tannins (CT) from the extracts.

4.6.3 Results

A summary of the effects of different pre-treatment parameters (case 1) and of the extractions parameters used (case 2) on the TPC, CT and TRS contents in the extracts are given in the **Tables 4-1 and 4-2**.

Table 4-1. Summary of the effects of the pre-treatment parameters on the tannin contents of the extracts studied in the case 1.

Pre-treatment parameter	TPC (mg GAE/g of dry bark)	CT (mg/g of dry bark)
longer storage time	decrease	decrease
higher drying temperature	slight decrease	slight decrease
smaller particle size	increase	increase

Table 4-2. Summary of the effects of the extraction parameters on the tannin and carbohydrate contents of the pine bark extracts studied in the case 2.

Extraction parameter	TPC (mg GAE/g of dry bark)	CT (mg/g of dry bark)	TRS (mg/g of dry bark)
longer extraction time	slight increase	slight increase	no effect
higher extraction temperature	increase	increase	slight increase
addition of urea + Na ₂ SO ₃	increase	increase	increase
addition of Na ₂ SO ₃ + Na ₂ CO ₃	increase	increase	no effect / increase

Some parameters seemed to have combined effects on the tannin and carbohydrate yields, no analysis of variance was performed in this study.

In addition to pine bark, spruce bark was also extracted with hot water and the results were compared with the results obtained with pine bark (case 2). The effect of the extraction conditions was quite similar for the yields in the spruce extractions as in the case of pine bark. In the case of spruce, the extraction temperature played a minor role and the extraction time a major role, being opposite to pine extractions. However, the amount of all measured values (TPC, CT, TRS) was much higher in the case of spruce than pine. In the case of pine bark, the extract with highest amount of extractives had total phenolic content of 51 mg GAE/g (dry

bark), included 59 mg /g (dry bark) condensed tannins and the amount of total reducing sugars was 40 mg/g (dry bark). The same results for the extract with highest tannin contents in the case of spruce bark were TPC of 101 mg GAE/g (dry bark), CT 87 mg /g (dry bark), and TRS 67 mg /g (dry bark). In addition to the sugar content, the effect of chemical additives on the properties of the obtained extract, on the purification of it and its possible applications should be considered.

In addition to the laboratory scale extractions, also pilot-scale extractions were performed. The results for tannin contents (TPC, CT) obtained in the pilot-scale were very comparable to the results obtained in the laboratory scale, even though the solids content in the pilot scale was remarkably lower than in the laboratory scale experiments.

4.6.4 Conclusions

The effects of different raw materials and extraction related parameters on the tannin content of the hot water extract were studied. Folin Ciocalteu method and modified HCl-butanol assay were used to evaluate the tannin content and DNS method to evaluate the carbohydrate content of the extract. In addition to laboratory scale, also pilot scale extractions were performed. The knowledge of the raw material and extraction parameters, know-how of the analytical methods and the modified ChemPlant reactor will be utilized in the new Interreg-project Green Bioraff Solutions.

5 WP 5: Market analysis

5.1 Introduction

There are several inherent difficulties in assessing markets for new products. The precise properties of the product may not be known, and therefore its area of use is not well defined. In some cases, the new product is a direct replacement for an existing, conventional product and its potential market can be estimated using information about the existing product. Also in this latter case, the new product would be likely to enter into a smaller part of the market, a niche, where it has some unique advantages.

The development stages of several of the products which have been studied in this project are not at a development stage where their market potential can easily be estimated. The market analysis has also been limited by time and data constraints, and has therefore been limited to two groups of products: lignin products as dispersants and biochars for various applications.

The market analysis has been performed through compilation and analysis of inhouse information and review of public literature.

5.2 Lignin dispersants

The project has found that modified hydrolysis lignin could be used as a dispersion agent in concrete for construction. Addition of a material with dispersive abilities can lower the water use and enhance the properties of the concrete. Today one commonly used product is

lignosulfonate. Most lignosulphonates are separated from the spent liquor of sulphite pulping operations. However, a small share (1% of total) is produced by post-sulphonation of lignins from kraft process. This might increase if the supply of spent sulphite liquor is restricted in the future.

The current market volume for lignosulphonates is estimated at 1.3 Mt. Dispersant applications command slightly above 60 % of the total market volume. The largest end-use in this segment, and largest overall, is additives for concrete and cement. Within this end-use, more than 90 % of lignosulphonates are used in concrete mixtures, where lignosulphonates function as a plasticizer. The prices of different LS grades vary between depending on the grade. Currently the average prices of standard grade powder delivered are around 400-600 EUR/t

The market for lignin dispersants is expected to grow only very moderately (1-2 %/a). No major changes in the markets by application are anticipated in the coming years.

The dispersant segment for lignins consists of one high-volume end-use, concrete, and a number of high-value uses. The key drivers are GDP, construction activity and competing products.

Table 5-1. Market drivers for Dispersant Applications

Application area	Description	Key Drivers	CAGR 2017-2030
Concrete & cement additives	<ul style="list-style-type: none"> + Plasticity and flowability improving additive for concrete. The largest end-use. + Lignosulphonates are used in smaller extent also as additives to increase solids content of raw slurries in cement manufacturing. Declining market in areas where wet-process plants are replaced by dry process. 	<ul style="list-style-type: none"> + Construction activity in emerging markets + Demand for higher strength materials - Slow construction activity in the west. - Decreasing activity in China and other emerging markets - Replacement of lignin dispersants by other concrete additives, particularly polycarboxylates 	0 - 1 %
Oil well drilling muds	<ul style="list-style-type: none"> • Mud thinner, clay conditioner, dispersant, viscosity controlling and fluid loss additive 	<ul style="list-style-type: none"> - Low oil prices result in decreasing oil drilling activity - Competition particularly from oil-based drilling muds 	0 - 1 %
Agrochemicals	<ul style="list-style-type: none"> • Dispersant for e.g. herbicides • Granulation aid for e.g. fertilizers 	<ul style="list-style-type: none"> + Agrochemicals are a growing market - More efficient pesticides require less dispersants - Competition from synthetic surfactants 	1 - 5 %
Dyes, pigments and inks and leather Tanning	<ul style="list-style-type: none"> • Dispersant, diluent and grinding aids in dyes • Reduce the formation 	<ul style="list-style-type: none"> + Growing textile industry in Asia has driven growth - Market in western 	0 – 1 %

	of agglomerates during leather tanning	-	countries is small and slowly declining Lignosulphonates and sulphonated kraft lignin have traditionally commanded a considerable market share of the disperse dye market which limits growth opportunities.	
Other Dispersants	<ul style="list-style-type: none"> Used e.g. water treatment, lead batteries, paper and board and gypsum wallboards 		Depending on the application, but expected to increase due to product development and new emerging applications	1.5 – 2.5 %

The global Lignosulphonate capacity's utilization rate was estimated to be around 80% during 2016. In the future the utilization rate is estimated to climb to 85-90% even with the planned capacity expansions (Borregaard and Rayonier). If the price of lignin dispersants rises significantly, some of the lignosulphonates currently burned for energy could be utilized in other applications.

It is likely that some of the older sulphite mills will be closing down in the coming years as majority of the mills are rather old. This will have some effect on the availability of lignin dispersants in the longer term making investments in new production more attractive.

The most significant competing products in the concrete admixtures are polycarboxylates which are currently sold at 1000-7000 EUR/t. In oil drilling muds polyacrylates compete with lignosulphonates. Their prices are currently around 1000-2600 EUR/t.

5.2.1 Summary

- Lignin dispersants are dominated by lignosulphonates separated for sulfite pulping processes.
- The market is slowly growing and fragmented
 - Lignosulphonates have varied end uses making the market rather fragmented. The market demands a capable sales organization and efficiency for small sales batches.
 - With the slow world economy, only very moderate market growth (1.3 %/a) is expected. No major changes in the markets by application are anticipated in the coming years.
 - Most of the markets are expected to grow slowly with the exception of Latin America and Middle East, which are expected to have somewhat faster growth in the near future
- For lignosulphonates, utilization rates have gone up lately, but new capacity could still face challenges

- Borregaard dominates the markets especially in the higher value added application areas. They have technical knowhow and capacity to purify and modify lignosulphonates to enable better performance and thus better price.
- Global production of sulphite pulp will continue to decline in the long term due to likely shut-downs of existing old capacity. This will also eventually result in a decline in lignosulphonate production. This development is also reflected in the global capacity utilization rate, which was estimated to be around 80% in 2016, up from previous years. However, as lignosulphonates are still burned, new capacity could face challenges in the slowly growing market

5.3 Biochar

There is a wide range of carbon based products on the global market that are currently being produced from fossil raw materials. Examples of carbon based products are coal used for heat and power production, carbon black used in catalyst supports in fuel cells, and graphite used as anode materials in Li ion batteries. Replacing these with products made from renewable alternatives, would aid in the transition towards a circular economy. There are many carbon containing low value renewable waste streams available. Conversion of these into high value carbon based products will require technological development and innovation.

One way of increasing the value of renewable waste streams is to carbonize them through heat treatment to produce char. This is already carried out today using pyrolysis and the resulting product is called biochar. However, pyrolysis is only suitable for dry, bulk solid materials and hydrothermal methods, such as hydrothermal carbonization (HTC) and hydrothermal liquefaction (HTL) are methods which have been suggested for large scale treatment of liquid or high moisture solid materials into a mixture of gaseous, liquid and solid products. The solid is sometimes called hydrochar. Today, the biochar being produced has only found limited applications. However, both hydrochar and biochar could be processed further to renewable carbon based products that can replace those made from fossil raw materials.

The production of biochar through pyrolysis is a mature technology, and biochar is traded on a global market.

90 % of biochar production was used for soil treatment while 10% was used as a filter media/ adsorbent etc. The heat/power production application of biochar is not the focus of biochar producers. Other current applications include compost additives and carrier for fertilizers, manure treatment and litter (bedding) materials to silage additives, feed-additives, and medical applications. Biochar has successfully been used to increase plant growth by adding it to soil. Biochar has also successfully been used to remove organic contaminants such as polyaromatic hydrocarbons (PAHs) from soil. Lately, biochar has been used as a cattle feedstock supplement and there are indications that this could improve animal health, increase weight, and reduce methane production. However, this has not been conclusively demonstrated. The number of registered biochar producers has increased. More seasoned producers focus on one or two applications while the more recently started biochar companies focus on multiple value streams. Most of the biochar being sold worldwide is sold by a small number of companies in Asia. Woody biomass is the most common raw material. The mean

cost of biochar was 0.56-4.2 USD kg⁻¹ in 2013 [1]. As of 2014, the biochar industry has yet to make a substantial entry into large-scale agricultural operations. Currently, the major obstacle is the lack of standardization which is needed if any commodity is to be traded internationally. Some standardization has evolved, for example, biochar is sold in a variety of particle sizes, chip (3-6 mm), medium (0.7-3 mm), small (0.3-0.7 mm), and powder (<0.3 mm). Efforts to further standardize biochar products with regards to composition, quality etc. have been made. The European biochar Foundation has published guidelines which are voluntary for producers of biochar. It is worth noting that biochar is defined by this guideline as a product which does not release CO₂ [2]. This partly explains why the heat/power production application of biochar is not the focus of biochar producers.

5.3.1 Carbon based products

The different carbon based products all contain carbon, but in different forms. They can differ chemically, e.g. in different allotropes or with different composition, ranging from pure elemental carbon down to ≈70 % carbon, or physically, e.g. display different pore size distributions. Processing of carbon containing raw material into carbon based products often involve heat treatment. This can be used to remove water from the raw material, to open up pores in the material or to rearrange the chemical structure. Other processing steps could be chemical treatments such as dispersion in alkaline solutions or physical processes such as pelletization, or milling.

Elemental carbon can exist in several different allotropes, e.g. graphite, diamond, fullerene, lonsdaleite etc. The least complicated carbon based products, such as pellets or activated carbon, are heterogeneous and contain a large variety of carbon allotropes as well as carbon containing organic compounds such as alkenes, alcohols, carboxyl acids etc. The most advanced carbon based products such as graphene, or carbon nanotubes contain only one allotrope. The elemental carbon allotropes are more chemically and thermally stable than the carbon containing organic compounds. They also have more well defined properties.

Below, the most relevant carbon based products with regards to hydrochar as a raw material are listed and reviewed. They represent the products that can be produced through chemical and/or physical processing of hydrochar.

5.3.1.1 Pellets

The hydrochar produced in the HTC process is in the form of a powder and powders are challenging to transport and store. Therefore, if the hydrochar is to be used directly without further chemical upgrading, it is suitable to convert the powder into pellets. This is carried out through compression. The pellets are then ready to be packed, shipped, and used for heat and power production through combustion or for soil remediation.

5.3.1.2 Activated carbon

Activated carbon is conventionally produced from coconut shells or similar carbon containing material. The activation process refers to the formation of pores in the carbon containing material which increases the surface area. Physical activation means heating in inert

atmosphere at 400-900 °C to remove volatiles, following by heating to 350-1000 °C in the presence of an oxidizing agent (CO₂, air, or steam) to produce pores in the raw material. The suggested mechanism is that tars are burned off by the oxidizing agent, thus opening up pores. The oxidizing agent then continues to open up pores by burning of more of the carbon matrix inside the material. Chemical activation involves mixing the raw material with an activation solution and heating the resulting mixture to 450-900 °C. There is a wide range of activating agents but ZnCl₂, H₃PO₄ and KOH are the most common. Recent developments have made it possible to fine tune the pore size distribution which in turn has widened the applications for activated carbons towards more demanding applications [3]. Examples include catalysis/electrocatalysis, energy storage (anode material) in supercapacitors and Li ion batteries, CO₂ capture and H₂ storage. Commercially available activated carbon is available either as pellets or as powders, and is referred to either as granular or powdered activated carbon. Common applications involve separation processes, either in gaseous or liquid streams. The activated carbon adsorbs nonpolar compounds, thereby separating them from the gaseous or liquid streams.

5.3.1.3 Graphite

Graphite is one of the allotropes of carbon and pure graphite can be shaped into cylinders, sheets, etc depending on the application. Applications include anode material for Li and Na ion batteries. While Li ion batteries are currently on the market, Na ion batteries are still under development. Other forms of carbon can also be used as anode material.

5.3.1.4 Carbon black

Carbon black is conventionally produced from anthracene oil and is an industrial bulk chemical product (C.A.S. NO. 1333-86-4) which essentially consists of elemental carbon in the form of near spherical particles of colloidal size (15-300 nm), coalesced into particle aggregates (85-500 nm) and agglomerates (1-100 μm). Carbon black consists of amorphous carbon which is distinguished from graphite by the crystalline structure and the hybridization of the carbon atoms within the structure [4]. In contrast to graphite, amorphous carbon does not have a long-ranged crystalline ordered structure, although locally, the carbon atoms can be bound together, forming graphite-like nanoclusters. The anthracene oil raw material is heat treated in a furnace at very high temperatures with a very short residence time. This causes the formation of amorphous carbon fines. There are several grades of carbon black and these are produced under different temperatures and residence times. The higher grades are produced at the highest temperatures and the shortest residence times. Carbon black is used in the production of tires, where it is mixed with rubber. It is also used in toners for printers. Carbon black is also a raw material for the production of catalysts used in proton exchange membrane fuel cells. It is mixed with Pt and functions as a support upon which Pt particles are dispersed across the finished catalyst.

5.4 References

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