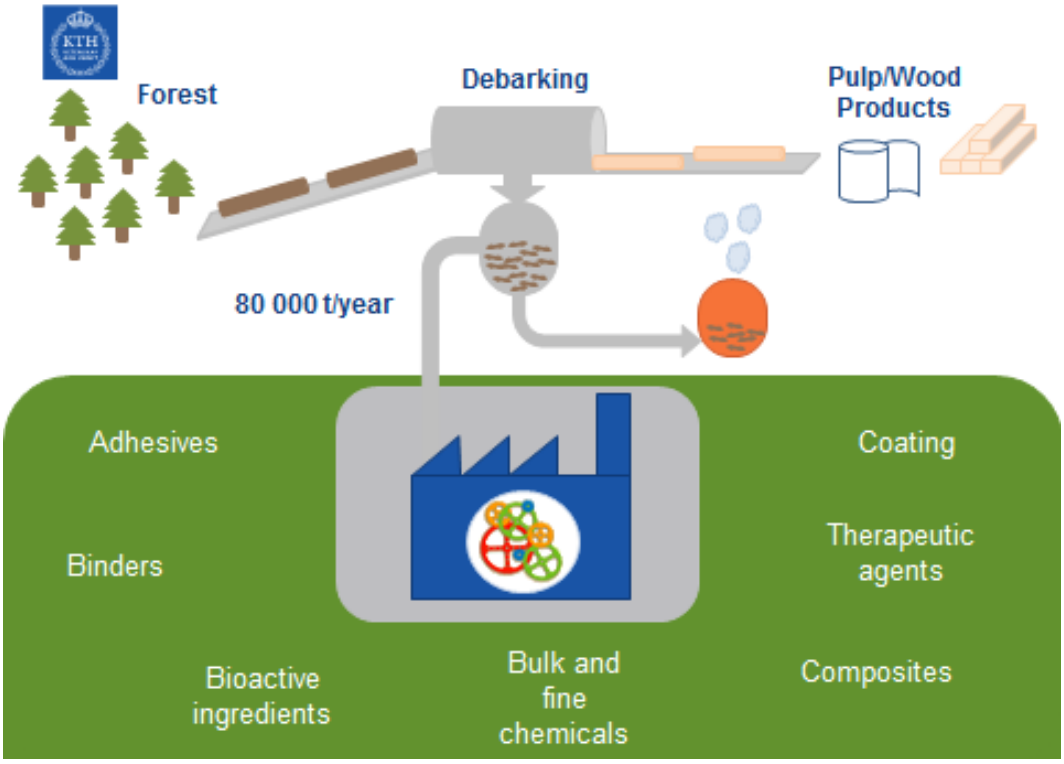
Bark Biorefinery 2013-2015
Final report



Vinnova Dnr: 2013-05107

Åforsk Dnr: 2013-448

Monica Ek (Project leader)

Myriam Le Normand

Dongfang Li

Åke Rasmusson

Summary

The present project has focused on getting a deeper fundamental knowledge of the bark biorefinery to create demonstrators and also possibilities to upscale the fractionation processes. Moreover, an important part has been the transfer of the obtained knowledge externally to the scientific community and the public.

The project has resulted in new methods for isolation and characterization of bark compounds such as polysaccharides, pectins, suberin and epoxy fatty acids as well as cellulose nanocrystals from bark. The bark compounds have successfully been used in material demonstrators such as barrier films with excellent results.

The promising results have lead to that the next step towards up-scaling has been taken for the isolation of suberin and epoxy fatty acids. Contacts have been established with the parallel Wood Wisdom project Wobama and Grease to obtain crude material to upgrade. New contacts with industrial partners considering upscaling of the bark biorefinery have also been established.

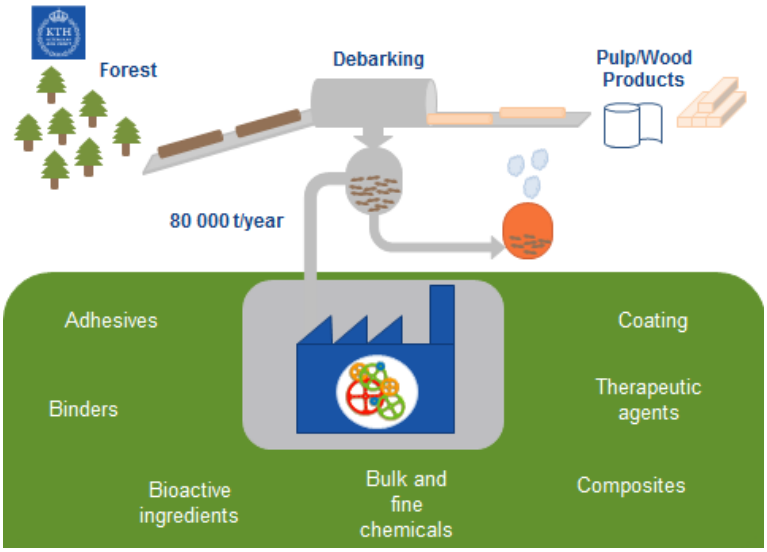
Within the project there has been one technical doctor exam. An additional thesis with results from the project is planned to be presented spring 2015. The scientific results have moreover been published in scientific journals and presented at international scientific conferences.

The Bark Biorefinery project

Bark is one of the largest byproducts of the Scandinavian forest industries. For example, the bark for the common Norway spruce (*Picea abies*) alone amounts to about 1.5 million tons/year in Sweden. This abundant biomass is commonly used as a fuel to produce heat and electrical energy in the mill, but in recent decades, there has been a growing interest in converting industrial bark into added value products in an approach called "the bark biorefinery".

The research project Bark Biorefinery has focused on a novel processes for fractionation of bark components. The target has primarily been to extract bark polysaccharides and extractives, such as suberin based epoxy fatty acids, and evaluate their properties in packaging applications.

There has also been focus on the knowledge-transfer, both to the parallel project Wood Wisdom ERANET project Wood Based Materials and Fuels (Wobama) and externally to society and stakeholders.



Figur 1. Illustration of the Bark Biorefinery concept for creating added-value products from bark

Project organization

The project has been conducted at KTH Wood Chemistry and Pulp Technology. The results have been reported and discussed with the parallel Wood Wisdom ERANET project Wobama, where the industrial partners Andritz, Akzo Nobel, Metso Fiber, OrganoClick, Processum and Stora Enso have constituted an advisory partner group.

The project has also established contacts with an additional parallel project, Grease, financed by the Wood Wisdom ERANET program. Their contribution has been to deliver crude samples based on birch bark extractions for further purifications.

Knowledge-transfer

An important part of the project at this stage has been to transfer the knowledge obtained, both between project partners and externally. Below is a short summary of the activities:

Academic theses and dissertation

PhD Myriam Le Normand defended her thesis titled *"The Bark biorefinery - extraction, characterization and valorization" (2014)* which is based on her work in the present projects and the previous Wood Wisdom project Probark.

MSc Dongfang Li will present his thesis 2015, with the tentative title "*Birch Suberin*"

Conference participation highlights

The project has been well represented at international scientific conferences, showing the high interest in the bark biorefinery. A complete list of the conference participation can be found in the section *Publications and conference participation* in this report.

Results achieved in the project

Spruce bark polysaccharides

Polysaccharides are one of the major constituents of the bark of Norway spruce. Altogether, hemicelluloses, pectins and cellulose constitute about 40 % of industrial bark collected at mill site. To be able to utilize the polysaccharides it is important to find an efficient and sustainable extraction process. In the Bark Biorefinery project, a process for the sequential extraction of noncellulosic polysaccharides (NCP) from industrial bark using an accelerated solvent extraction (ASE) with water was developed. Optimization of the process showed that the highest extraction yield of NCP was reached at 140 °C.

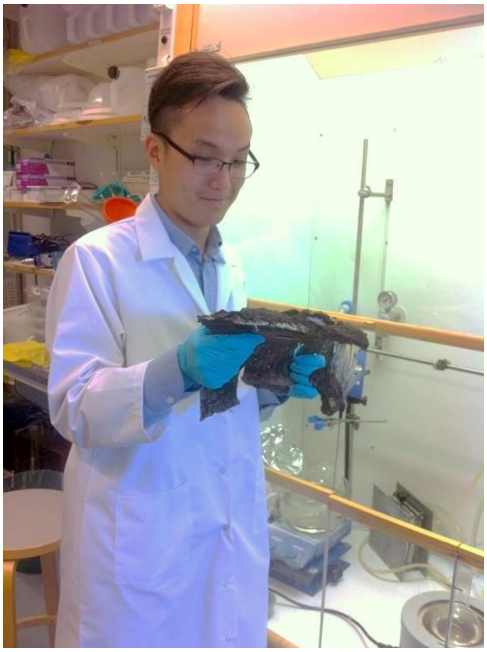
By performing structural analyses of the hot water extracts the presence of bark pectins was shown. The residue of the hot water extraction was further used to recover bark cellulose fibers and isolate cellulose nanocrystals (CNCs). Bark CNCs have a high aspect ratio, high crystallinity and good thermal stability, which mean that they have a great potential for use as reinforcement agents in the manufacture of nanocomposites at a reasonable low raw material cost.

A potential application for bark compounds is as raw materials in renewable nanocomposits. In the project NCP and CNC sequentially isolated from the inner bark was used to construct renewable nanocomposites with good mechanical and thermal properties, as well as a high oxygen barrier performance. The resulting all-bark nanocomposites showed properties similar to or even better than those of the conventional barrier materials used in packaging.

Materials based on a birch bark suberin monomer

In northern Europe, birch (*Betula verrucosa*) is the predominant hardwood species, which makes it an important resource for the local forest-related industries to produce pulp, paper, plywood, and furniture. The birch logs that are delivered to these industries usually contain around 11 wt% of bark that is normally burned as a low-value solid fuel for energy. However, based on the biorefinery concept, using biomass directly as solid fuels is a waste of valuable material. Instead, the natural and renewable resources should be used to prepare value-added products such as chemicals and materials.

About 45 wt% of the birch outer bark consists of suberin, which makes it the most abundant component in the bark. Suberin works as a water barrier as well as a shield against the external attacks from microorganisms. The complex structure of suberin is composed of phenolic compounds in the aromatic domain and hydroxyl-fatty acid esters in the aliphatic domain, in which *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid (hereafter denoted as epoxy acid) is the most abundant, amounting to around 10% of dry birch outer bark.



Figur 2. Dongfang Li working in the lab

In Dongfang Li's work, the epoxy acid was isolated from the birch outer bark with purity higher than 94%, and yield around 8%. Polyepoxy acid (PEA) was prepared by polymerizing the epoxy acid through lipase catalysis.

PEA could be used to impregnate paper. By curing the epoxy groups, the hydrophobicity, ultimate tensile strength, and ductility of the PEA treated paper were improved. On the other hand, the moisture sensitivity of the paper was lowered. This might be interesting for many applications that require moisture resistant, strong, and renewable materials.

PEA could also be used as a coating for nanocellulose based materials such as nanofibrillated cellulose films and NCP/CNC nanocomposites as mentioned in Myriam Le Normand's work. After the coating with PEA and subsequent curing of the epoxy groups, all of the nanocellulose based materials became hydrophobic, and showed good oxygen barrier properties at high relative humidity. In this way, the application area of nanocellulose based materials is widened.

Further, nanocomposites were developed by mixing PEA with nanofibrillated cellulose and subsequent curing of the epoxy groups. The tensile properties and thermal stabilities of the nanocomposites could be significantly improved with increasing the content of NFC. Moreover, all of the nanocomposites were hydrophobic and could hardly absorb any water. The performances of these materials were comparable to that of some commercial plastics.

Last but not least, in the project we are ready to scale up the process and contacts have been taken and established with our parallel project Grease in the Wood Wisdom ERANET program. Samples of crude mix of suberin based fatty acids have been delivered and are ready for purification, i.e. evaluation of the crystallization technique.

Future biorefineries

The project focuses at processes and products that have the potential for use in a future bark biorefinery concept. Some of the challenges which have to be considered concern up-scaling, *i.e.* biomass stability, competition with energy and the quality performance of end products. The up-scaling often raises several issues, *e.g.* concerns about energy consumption and runnability problems. Therefore, in order to bring this work to the next level, there is a need to develop the overall concept feasibility with investigations into the up-scaling parameters for designing pilot plant devices.

The biomass stability is one of the main challenges when working with natural resources. Indeed, bark is a biomass that is sensitive to seasonal variations and storage conditions. Before implementing an actual bark biorefinery, it is important to consider that bark is already used in the mill to create energy by incineration. Therefore, the cost of using spruce bark in new applications should always be related to the loss of internal energy supply in the mill and the price of alternative fuels. In other words, techno-economic and environmental assessments based on material and energy flow balances should be performed. In order to limit the competition with other woody or agricultural biomasses, products based on bark should have special properties that are specific to the bark raw material.

Next step

During the last ~10-15 years a strong focus at Biorefinery concept has evolved. Many projects have been performed to create fundamental knowledge about fractionating techniques, characterization and modification of the various wood polymers and their products as well as new ideas for applications. This research has to a large extent been financed from Vinnova, Formas and Energy Agency within the Wood Wisdom ERANET program.

Today we have the basic knowledge and many ideas for new applications, due to the close cooperation within the WW programs with industrial partners from various parts in the value chain. There is also an increasing interest from industry to scale up and test the ideas in more close to market applications. There are more than one industrial requests based on the results from the present project and Wobama to continue the cooperation between industry and academy in new projects. Here we can see new possibilities within the new national program Bioinnovatio

Publications and conference participation

Scientific publications

Myriam Le Normand (2014) *Spruce Bark Polysaccharides : Extraction, Characterization and Valorization* PhD thesis. Thesis can be ordered from info-woodchempulptech@kth.se

Le Normand, Myriam, Moriana, Rosana and Ek, Monica (2014) *The bark biorefinery : a side-stream of the forest industry converted into nanocomposites with high oxygen-barrier properties* Cellulose, Vol. 21, no 6, 4583-4594

Le Normand, Myriam, Moriana, Rosana and Ek, Monica (2014) *Isolation and characterization of cellulose nanocrystals from spruce bark in a biorefinery perspective* Carbohydrate Polymers, ISSN 0144-8617, E-ISSN 1879-1344, Vol. 111, 979-987

Li, Dongfang., Iversen, T., and Ek, Monica (2015) *Hydrophobic Materials Based on Cotton Linter Cellulose and an Epoxy-Activated Polyester Derived from a Suberin Monomer* accepted for publication in Holzforschung

Related references from Wood Wisdom PROBARK project

Le Normand, Myriam, Mélida, Hugo, Holmbom, Bjarne., Michaelsen, Terje E and Monica Ek. (2014) *Hot-water extracts from the inner bark of Norway spruce with immunomodulating activities* Carbohydrate Polymers, ISSN 0144-8617, E-ISSN 1879-1344, Vol. 101, no 1, 699-704

Le Normand, Myriam, Edlund, Ulrica, Holmbom, Bjarne and Ek, Monica (2012) *Hot-water extraction and characterization of spruce bark non-cellulosic polysaccharides* Nordic Pulp & Paper Research Journal, ISSN 0283-2631, Vol. 27, no 1, 18-23

Conference participation

Myriam Le Normand

Le Normand, Myriam. *Nya material och kemikalier från bark*, Ekmandagarna, 2012, Stockholm/Sweden.

Le Normand, Myriam, Moriana, Rosana and Ek, Monica. *The bark biorefinery: creating value from polysaccharides of spruce bark*, Marcus Wallenberg Prize symposium, 2013, Stockholm/Sweden.

Le Normand, Myriam, Moriana, Rosana and Ek, Monica. *The bark biorefinery: creating value from polysaccharides of Norway spruce bark*, 3rd Avancell conference, 2013, Göteborg/Sweden.

Le Normand, Myriam. *Creating value from the bark of Norway spruce*, Svenska Pappers- och Cellulosaingengörsföreningen (SPCI) convention, 2013, Stockholm/Sweden.

Le Normand, Myriam, Mélida, Hugo, Holmbom, Bjarne., Michaelsen, Terje E, Inngjerdingen, Marit, Bulone, Vincent, Paulsen, Berit Smestad, and Ek, Monica. *Characterization of polysaccharides from the bark of Norway spruce and their immunomodulating properties*, 3rd European Polysaccharide Network of Excellence (EPNOE) conference, 2013, Nice/France.

Le Normand, Myriam, Moriana, Rosana and Ek, Monica. poster at 5th Nordic Wood Biorefinery Conference (NWBC) 2014, Stockholm Sweden

Dongfang Li

The 243rd ACS National Meeting & Exposition, 25-19 March, 2012, San Diego, California, the US. The results regarding "Biocomposites based on birch suberin" were presented.

The 2nd Avancell Conference, Chalmers University of Technology, 2-3 October, 2012, Gothenburg, Sweden. The posters "Polyesters and biocomposites based on birch suberin" and "Wobama" were presented.

The 4th Nordic Wood Biorefinery Conference (NWBC 2012), 23-25 October, 2012, Helsinki, Finland. The poster "Polyesters and biocomposites based on birch suberin" was presented. The corresponding summary was published on the conference proceedings.

The 5th Workshop on Cellulose, Regenerated Cellulose and Cellulose Derivatives, 13-14 November, 2012, Örnsköldsvik, Sweden. The posters "Polyesters and biocomposites based on birch suberin" and "Wobama" were presented.

Ekmandagarna 22-23 January, 2013, Stockholm, Sweden. An oral presentation (so-called "elevator pitch") about WOBAMA and more specifically, Dongfang Li's project was given.

The 17th International Symposium on Wood, Fibre and Pulping Chemistry (ISWFPC 2013). 12-14 June, 2013, Vancouver, Canada. An oral presentation about "Polyesters and composites based on birch suberin" was given. A poster about WOBAMA was shown.

Marcus Wallenberg Prize Event Special Sessions for Younger Researchers and Scientists, 23-24 September, 2013, Stockholm, Sweden. A poster about "Polyesters and composites based on birch suberin" was shown.

SPCI Convention 2013, 25-26 September, 2013, Stockholm, Sweden. An oral presentation (so-called "elevator pitch") about WOBAMA and more specifically, Dongfang Li's project was given.

International Polysaccharide Conference (EPNOE 2013), 21-24 October, 2013, Nice, France. A poster about "*Polyesters and composites based on birch suberin*" was shown.

The 5th Nordic Wood Biorefinery Conference (NWBC2014), 25-27 March, 2014, Stockholm, Sweden. The poster "*Polyesters and composites based on birch suberin*" was presented. The corresponding summary was published on the conference proceedings.

The 13th European Workshop on Lignocellulosics and Pulp (EWLP2014), 24-27 June, 2014, Seville, Spain. An oral presentation "*Polyesters and composites based on birch suberin*" was given. The corresponding summary was on the conference proceedings.

The 4th Avancell Conference, Chalmers University of Technology, 7-8 October, 2014, Gothenburg, Sweden. A poster "*Hydrophobic materials based on cellulose and a suberin monomer*" was presented.

The 6th Workshop on Cellulose, Regenerated Cellulose and Cellulose Derivatives, 11-12 November, 2014, Karlstad, Sweden. An oral presentation about WOBAMA was given.

External media:

ÅF Green Advisor report 2014

MSc Dongfang Li, presenting at European Workshop on Lignocellulosics and Pulp, 2014