A sustainable process for production of green chemicals from softwood bark (PROBARK)

FINAL REPORT

Title of the research project	A sustainable process for production of green chemicals from softwood bark
Coordinator of the project	Tiina Nakari-Setälä

BASIC PROJECT DATA

Project period	1.1.2008-31.12.2010
Contact information of the coordinator (institute/unit, address, telephone, fax, e-mail)	VTT Tietotie 2 BOP 1000, FI-02044 VTT, Finland Tel. +358 20 722 5134 Fax. +358 20 722 7071 E-mail tiina.nakari-setala@vtt.fi
URL of the project	http://virtual.vtt.fi/virtual/probark/index.htm

FUNDING

Total budget in EUR	1 465 923 EUR
Public funding from WoodWisdom-Net Research Programme:	Total funding granted in EUR by source:
Finland Tekes - Finnish Funding Agency for Technology and Innovation	644 000 EUR
Germany Federal Ministry of Education and Research (BMBF)/ Project Management Agency Jülich (PtJ)	269 362 EUR
Sweden Swedish Governmental Agency for Innovation Systems (VINNOVA)	162 630 EUR

Other public funding:	0 EUR

Other funding:

VTT, Finland	82 974 EUR
Tecnaro, Germany	42 000 EUR
Companies, Finland	141 000 EUR
Companies, Sweden	123 957 EUR

PROJECT TEAM (main participants)

Katariina Nyman, MSc (Tech) Research Scientist	F	VTT	Tekes
Lotta Sorsamäki MSc (Tech) Research Scientis	F		
Jaana Uusitalo MSc (Tech) Research Scientis	F		
Sakari Kaijaluoto Dr Tech Senior Research Scientist	M		
Olli Aaltonen MSc (Tech) Senior Research Scientist	M		
Hannu Mikkonen Ph.Lic. Senior Research Scientist	M		
Monica Ek, Dr., Senior lecturer	F	KTH	Vinnova
Myriam Le Normand, M.Sc , PhD student	F	KTH	
Norbert Eisenreich	M	Fraunhofer ICT	BMBF
Emilia Inone-Kaufmann	F		

Detlef Schmiedl	M		
Wolfgang Becker	M		
Bjarne Holmbom Professor	M	Åbo Akademi	Tekes
Jarl Hemming	M		
Sina Rasela	F		
Lars Ziegler	M	Tecnaro GmbH	BMBF

DEGREES
Degrees earned or to be earned within this project.

2009	MSc	M	Jens Krogell	Åbo Akademi	Bjarne Holmbom, ÅA
2011	MSc	F	Sina Rasela		
2011	MSc (Tech)	F	Jenni Inkinen	Aalto University	Jaana Uusitalo, VTT
2013	PhD (Tech)	F	Katariina Nyman	Aalto University	Niklas von Weymarn, VTT
	PhD	F	Myriam Le Normand	KTH	Monica Ek, KTH

ABSTRACT

A summary of the project.

Bark forms an important part of trees, and is available in large amounts at paper mill sites but is currently mainly used as a fuel. The aim of the project was to develop an Integrated Bark Bio-refinery, in which softwood bark is efficiently used as a biomass feed stock for production of industrial and consumer products or suitable intermediates, and energy. A central part of the project was to develop and evaluate the Integrated Bark Bio-refinery as an economical and technological concept and to develop technology for production of chemicals, biomaterials and biofuels from softwood bark. During the project, a process concept was developed for bark with tannin and bioethanol as new products. Tannins were shown to be able to be used in replacement of phenols in biocomposites and adhesives. Spruce bark dichloromethane extract was shown to have insect anti-repellant properties. Hemicelluloses and pectins have also been extracted with hot water from both spruce and pine bark, and have furthermore been tested for certain bioactive properties.

1.1 Introduction

1.1.1 Background

Describe the background of the project and the basic problem that it sought to address.

Bark is an important part of trees and amounts to around 10-20% of the tree depending on species and growing conditions. Bark is an existing industrial side stream. The Nordic pulp and paper mills and sawmills are large producers of bark yielding about 5 million tons of bark material per annum. In addition to debarking lines producing mixed bark varieties, also pure streams of e.g. spruce and birch bark are available. To date the major use of bark is as a fuel. The PROBARK project focuses on finding alternative uses for bark, especially softwood bark, as a source for bio-materials and value-added chemicals. PROBARK project continues research activities that were initiated in the Finnish-Swedish Wood Material Science project WoodBiocon but with further focused objectives, applications and raw materials.

1.1.2 Objectives

Describe the project objectives.

The aim of PROBARK is to develop an Integrated Bark Bio-refinery, in which softwood bark is efficiently used as a biomass feed stock for material and chemicals products or suitable intermediates, and energy. A central part of the project was to develop and evaluate the Integrated Bark Bio-refinery as an economical and technological concept and to develop a technology platform suited for production of chemicals, biomaterials and bioethanol from softwood bark components. In addition, the aim of the project was to evaluate possible business potential of the concept.

1.2 Results and discussion

Main achievements of the project, quality, innovativeness, industrial relevance and contribution to competitiveness, environmental and societal impact.

WP1. Fractionation and chemistry of softwood bark components

The aim of WP 1 was to provide chemically well-characterized softwood bark extracts and components for product development in WP2, WP3 and WP4. Separation processes have been developed mainly for bark tannins and for the sugar fraction. Stilbenes were found to be rather unstable and their concentration low in technical bark obtained from paper mill and therefore no further efforts were carried out to purify bark stilbenes. Pre-treatment methods were also evaluated for improved extraction and for optimal recovery of bark sugars.

Tannins were mainly extracted with hot water at 80°C or with Aquasolve at high temperature and pressure. Several kilograms of bark tannins from spruce and pine barks have been produced in the project. Some of the tannin fractions obtained contained also rather high amounts of hemicelluloses that co-extracted from bark material. Sugar analysis of these hemicelluloses indicate that they differ in chemical composition of other wood hemicelluloses, e.g. they contain rather high amounts of galacturonic acid. Since these polymeric sugars increase the viscosity of tannin preparates and affect adversely the gluing effect of tannins, attempts were made to reduce the sugar content of tannin preparates. Acetone extractraction and enzymatic treatment were both tested and found to reduce the sugar content.

Bark of both spruce and pine have been extracted with a multistep sequence of extractions, starting with hexane to extract lipophilic extractives, and ending with hot-water extraction at 160^{o}C recovering hemicelluloses and pectins. Detailed chemical analyses of the extract fractions, as well as the residue after all extractions, have provided a comprehensive picture of the composition of spruce and pine barks, separately for inner bark and outer bark. This work has also laid the base for setting up technical extraction and separation schemes for the barks.

Enzymatic hydrolysis of pre-treated bark to fermentable sugars was tested. Steam explosion and hot water extraction were tested as the pretreatment methods. Standard commercial cellulases were tested in hydrolysis. It was found out that hot water extracted bark polysaccharides were rather efficiently hydrolysed when also pectinases were used in the enzyme coctail. Thus steam explosion is not needed as a pretreatment method (reduced investments).

WP2. Biopolymer & composite products

The objective of the WP was to test the bark tannin and lignin components obtained from WP1 in various materials applications. Today lignin together with natural fibres and additives are already used in biocomposites and the aim was to obtain all main components for biocomposites from bark. Aquasolv extracted tannin/lignin preparates were used in biocomposites which were tested with respect to mechanical properties to evaluate their applicability compared to similar composites with lignin matrices.

The processing of these biocomposites started with a homogenous mixing of the components, natural fibers, lignin and functional additives including up to 15 % of tannin as a partial substitute of lignin. The mixed components were then processed to a granulate by a pelletizer, a granulate which is normally used for injection moulding. Injection moulding occurred under the same conditions as used for the standard biocomposites. It resulted in standardized material samples which are used for standard mechanical testing. The test included stress/stain curves, the strength, strain and the elongation at yield and break.

In summary, the tests showed that on increasing content of tannin:
- Young's modulus decreases
- Tensile strength increases
- Elongation increases.

This means the ductility of the material is increased on partial substitution of lignin by tannin. In addition, it seems that the Probark-tannin behaves even more effective as commercial available tannin, in comparison. However, this could not be proved with sufficient confidence.

Chemically characterized tannins (both crude and purified extracts) were also tested as adhesives in vaneer gluing. The results were rather promising showing that purified tannin preparates had good solubility, they were easy to spread and their gluing properties were reasonable. It was also shown that purified tannins performed better than crude tannins containing hemicelluloses.

WP3. Bioactive fine chemicals

The third workpackage focused on the potential bioactive properties of bark components. The main objectives of this workpackage were double: (1) to briefly test the repellent activity of the dichloromethane extract of spruce bark against pine weevils and ticks and (2) to extract, characterize and test the complement activity of hemicelluloses and pectins extracted from spruce inner bark.

The dichloromethane extract of spruce bark represents 5% of the bark. It mainly contains fatty acids, resin acids, sterols and terpenoids. Terpenoids are one of the largest groups of plant secondary compounds known to have insecticidal repellent properties. The dichloromethane extract was separated into petroleum ether soluble and insoluble fractions. The crude dichloromethane extract and the two fractions were presented to single pine weevils in two-choice laboratory tests using twigs of *P. sylvestris* with a test and a control area. The weevils were allowed to feed from the twigs during 24h and the eaten areas were thereafter measured and compared. We found that 1 g of the dichloromethane extract could repel 60 % of the pine weevils. The petroleum ether insoluble fraction showed even better antifeedant activity. Indeed, up to 75% of the pine weevils were repelled by 1g of this fraction. A repellence bioassay on ticks was also carried out using the crude dichloromethane extract as repellent agent. The tests showed promising repellent properties. 0.5 mg of this extract could repel up to 50% of the tested ticks. However, the results would need to be confirmed by performing hundreds of replicates for each test. Those tests were not carried out because of the lack of material and equipment. In addition, the composition of the dichloromethane extract of spruce bark appeared to be relatively similar to tall oil and would therefore have to compete with existing low-cost products. For these reasons, the risk of utilizing the dichloromethane extract of spruce bark as insecticide was considered to be too high.

Three hot water extracts (100°C, 140°C and 160°C) of spruce bark and preparates further purified by dialysis were used for bioactivity testing. A complement fixation test based on inhibition of haemolysis of antibody sensitised sheep red blood cells (SRBC) by the complement from human sera was carried out. All bark polysaccharide fractions showed significant complement-fixation activities. Moreover, we noticed two tendances: (1) The complement-fixation activity was high at low extraction temperature, (2) Dialysed extracts showed higher bioactivity than crude extracts.

WP4 Bioethanol production from carbohydrate-containing bark fractions
Bioethanol has been used as an example of a product that can be produced via sugar platform from carbohydrates of bark, and the ethanol case has been also the basis for evaluation of the technical and economical feasibility of softwood bark sugar platform. In this WP, a large effort has been done to understand the hydrolysability of bark polymeric sugars into monosaccharides and fermenting them to bioethanol using yeast. The enzymatic hydrolysis tests have been performed in a small laboratory scale using commercial enzymes (cellulases, β-glucosidase and pectinase). The interdependencies of enzyme dosage and composition for optimal hydrolysis were determined. It was shown that when small amounts of pectinases are added in the enzyme cocktail the amount of cellulases can be significantly reduced with a direct impact on enzyme cost in the process. Bioethanol is produced from pretreated and hydrolysed bark materials. The effect of dry matter content to ethanol production has been the main issue under investigation. Fermentation experiments are still on-going (Finnish part of PROBARK to end March 31, 2011)

WP5: Bark bio-refinery process concepts and techno-economical feasibility studies
The aim of the WP was to evaluate the technical and economic feasibility, as well as exploitation potential, of developed processes and products. The work has concentrated on developing the process concept for bark utilization, including the production of tannins (optionally also of stilbenes) and the fermentation product bioethanol. A large pilot-scale experiment was carried out for tannin extraction to obtain experimental input data and the results have been used to build a preliminary model of the biorefinery process. The model will be further refined when the bioethanol production data (hydrolysis and fermentation) will be available and can be used as input data for the model. Mass- and energy balance-simulations will be carried out to identify bottle necks and potentially favourable processing routes and products.

1.3 Conclusions

The most important contributions to the state-of-the-art, derived from the results and discussion.

Most important contributions of PROBARK to the state-of-the-art include:

- Inner and outer barks of spruce and pine have been investigated using a multistep extraction scheme combined with chemical analyses of the obtained extract fractions, thus providing a comprehensive picture of softwood bark composition
- Both spruce and pine barks have been found to contain hemicelluloses that differ much from corresponding wood hemicelluloses
- Hot-water extracts of spruce bark rich in hemicelluloses and pectins have given promising immunological effects in a biotest.
- A novel process to extract, separate and purify tannin from spruce and pine bark has been developed
- Tannin extracts have been shown to be suitable to be used in biocomposites where they can substitute other phenolic components
- Tannins show good plywood gluing properties, structure-function relationship however not elucidated
- Hot water extraction combined with cellulase and pectinase treatment is a good method for efficient hydrolysis of bark polymeric sugars to fermentable monosaccharides
- Bark can be used as a 2^{nd} generation feed stock for the sugar platform
- A novel process concept developed for utilization of bark components in a Bark Biorefinery
- On-line measurement based on Near Infrared and Raman Spectroscopy seems to be a promising method to control Biorefinery processes

1.4a Capabilities generated by the project

Knowledge generated in the project / outcomes of the project, such as unpublished doctoral theses, patents and patent applications, computer programs, prototypes, new processes and practices; established new businesses; potential to create new business opportunities in the sector.

Outcome of the project includes:

- development of a strong knowledge base for processing and utilization of barks from softwoods, including extraction and separation technology, chemical analysis of bark components, bioactivity of bark components, enzymatic biomass hydrolysis and enzymology, fermentation and bioprocess technology, biomaterials and biocomposites, process concepts and modelling
- networking of excellent German, Swedish and Finnish scientists and research groups and networking of academic researchers with industry
- three MSc theses, two future PhD thesis will be co-funded by PROBARK
- several poster presentations and a few articles
- filing together with novel partners a proposal for WoodWisdom ERA-NET 3dr call autumn 2010 including further development of the tannin extraction process
- development of a process concept for a bark biorefinery and several unit operations that can be taken into practice by the industrial partners after further piloting

1.4b Utilisation of results

Give a brief description of how the results of the research and development have been used and/or what is the exploitation plan or plans for transferring the results into practice.

The industrial companies within PROBARK have actively participated project meetings and have also provided own work in the project. In particular, they have evaluated the possibility to utilize bark components as a raw material or in their own products, e.g. tannins in adhesives (UPM-Kymmene), tannins in cosmetics (Granula), tannins in biocomposites (Tecnaro) and softwood bark as a source of sulphur free terpenes and other starting materials (Arizona). Processum's interest has been to understand how bark biomass can be utilized for production of bioethanol. Södra has a general interested in biochemicals derived from bark components.

One central activity in the project has been to develop an extraction process for bark tannins. The extraction process has been scaled to 30-40 kg bark which sets good ground to upscale the process further to pilot and demo scale. Also the process concept developed in the project will provide valuable data on alternative extraction and pretreatment methods that can be applied for tannin extraction. The technical data and process options provided in the project will help the involved forest companies to take the lead in upscaling the tannin extraction process into industrial scale.

1.5 Publications and communication

a) Scientific publications

For publications indicate a complete literature reference with all authors and for articles a complete name. Indicate the current stage of the publishing process when mentioning texts accepted for publication or in print. Abstracts are not reported. Indicate the five most important publications with an asterisk.

1. Articles in international scientific journals with peer review

2. Articles in international scientific compilation works and international scientific conference proceedings with peer review

LeNormand, M., Krogell, J., Willför, S., Holmbom, B. And Ek, M. 2010. Hot-water extraction and characterization of hemicelluloses and pectins from bark of Norway spruce (*Picea abies*). Proc. 11th European Workshop on Lignocellulosics and Pulp (EWLP 2010), vTI, Hamburg, Germany, 4 pp

3. Articles in national scientific journals with peer review

Unkelbach G., Pindel, E. and R. Schweppe. 2009. Lignin/tannin-Abtrennung aus Lignocellulosen. Lignin 81:1767-1771

4. Articles in national scientific compilation works and national scientific conference proceedings with peer review

5. Scientific monographs

Krogell, J. 2009. Chemical characterisation of spruce bark and extraction of hemicelluloses and pectins (in Swedish, with English abstract), MSc Thesis, Åbo Akademi, Department of Chemical Engineering, 46 pp.

6. Other scientific publications, such as articles in scientific non-refereed journals and publications in university and institute series

a) Other dissemination

Such as text books, manuals, user guidelines, newspaper articles, TV and radio programmes, meetings and contacts for users and results.
Dissemination of results to industrial partners and industrial partners dissemination within the company.

Holmbom, B. 2010. Exciting, health-promoting products from wood bark and knots. 15. Münchener Holzkolloquium, Technische Universität München, Munich, Germany, Invited oral presentation. [Text]

Holmbom, B. 2010. Lignans and other polyphenols in wood and bark of Nordic trees. Biorefinery 2010, Örnsköldsvik, Sweden, Invited oral presentation.

1.6 National and international cooperation

Give a brief description of the cooperation/ networking (partnership between the project participants and how this has developed; industrial involvement; synergies of industrial and research expertise; Has the project collaborated with similar projects in the WW-Net countries or other regions, or established new links with/ between local or international organisations involved in the respective research field? Describe how these partnerships have supported the project.
National vs. transnational aspects in the project; added value for the project and its impacts which result from transnational cooperation.

Collaboration has been active and includes:

- change of materials, information and ideas between research partners to aid achievement of common goals
- Industrial sponsors have provided raw materials for research
- change of materials, information and ideas between research partners and industrial sponsors that are (chemically) analysed and tested by the industrial partners to evaluate application/product possibilities
- short term researcher visits (in particular between KTH and ÅA)
- joined project meetings, topic-specific meetings and telemeetings with research partners and industrial sponsors (example on topic-specific meetings on fine chemicals, adhesives, tannin extraction, composites)
- researcher visit to Canada
- new project applications together with some of the partners
- joined publications to be expected

More specifically, Fraunhofer ICT and Tecnaro have been collaborating in the field of biomaterials Fraunhofer providing extracted tannin materials and Tecnaro testing it in its biocomposite materials. Also VTT has provided tannin materials to Fraunhofer for biocomposites. VTT has carried out an extensive experimental set-up to provide data for concept development. Analysis of the tests has been jointly carried out by VTT and ÅA. Tannin materials produced within the project by VTT and Fraunhofer have been delivered also to industrial partners UPM Kymmene, Granula and Arizona Chemical to analysis and testing. ÅA and KTH has cooperated within WP3 where ÅA has prepared and analysed water extracts of spruce bark rich in hemicelluloses and pectins for further studies at KTH. The extracts have been biotested in the laboratory of prof. Berit Smestad Paulsen at University of Oslo. Prof Paulsen visited ÅA in May 2010 for planning of this cooperation. More collaboration could have been envisaged between project partners but some partners had limited funding resources which set some limits.

Collaboration on exploitation of bark tannins has been started within the Finnish Forest Cluster Ltd FuBio programme. The collaboration partners are mainly Finnish universities, University of Joensuu, Åbo Akademi, University of Turku and University of Tampere and collaboration includes extraction, chemical analysis and bioactivity testing of tannins and their use as wood protection agents.