Project BioFoamBark – Executive summary on VTT results

Full title	Bark valorization into insulating foams and bioenergy
Call	Joint Call of WoodWisdom-Net and ERA-NET Bioenergy: "Sustainable forest management and optimised use of lignocellulosic resources" (2011)
Duration	1/2012-12/2014
International consortium	University of Freiburg (coordinator, Germany), University of Ljubljana (Slovenia), Université de Lorraine (France), University of Santiago de Compostela (Spain), Fraunhofer Institute of Solar Energy Systems ISE (Germany), Nova-Institut GmbH (Germany), Ledoga Srl (Italy)
Total budget	1 062 k€
VTT budget	240 k€
VTT funding	Tekes 60%, VTT 25%, Savanaho Oy 8%, Finnish Wood Research Oy 4%, Chemigate Oy 3%
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Background

Spruce bark is an abundant lignocellulosic feedstock available for biorefining in the Nordic countries. The use of Norway spruce, *Picea abies*, in forest industry operations produces 0.9-1.3 Mt (dry) bark in Finland making it a major sidestream for the Nordic forest industry. Spruce bark is available all year round in a convenient location suitable for integrated biorefinery operations, unlike many agricultural biomass residues. It is currently used for the production of renewable energy, but it could be refined into transport fuels and chemicals to improve the competitiveness of the forest industry. Spruce bark contains a high amount of hydrophilic extractives including condensed tannin, which is a market biochemical used for leather processing, clarification of beverages, animal nutrition and as an industrial dispersant or a coagulant. Tannins could potentially be used as a raw material for rigid foams and adhesives to replace fossil-based phenol, and to increase the fire resistance of construction materials.

VTT aims

- To develop and optimize hot water extraction of tannin from spruce bark.
- To develop an economic enzymatic purification method for hot water extracted tannin in laboratory and pilot scale.
- To produce crude and purified tannin in pilot scale and to supply it to project partners for application studies.

Results

Dry debarked spruce bark was obtained from Metsä Wood Lohja Kertopuu plant debarking unit and its composition was analysed in detail (Figure 1). Spruce bark was found to contain 11-12% tannin and 48-52% carbohydrates (mainly cellulose, non-cellulosic glucose and pectin), as well as lignin, ash, and lipophilic extractives. Glycome profiling of the bark carbohydrates was performed in co-operation with Complex Carbohydrate Research Centre (University of Georgia, USA) to identify the main hemicelluloses and pectic polysaccharides in bark[1].

The effect of temperature, solids loading and the use of extraction chemicals (sodium bisulphite and sodium carbonate) on the extraction yield and composition of the extract was studied in bench-scale extractions (8 L volume). Temperature had a positive effect on the extraction yield, which was 21% of bark dry matter at its highest at 5% solids loading and 90°C extraction temperature (Figure 2). Increase in solids loading reduced the

Collection time	2/2012	8/2012	6/2013
Carbohydrates	51.3	47.5	49.9
Acid insoluble lignin	31.1	33.5	30.7
Acid soluble lignin	2.7	3.3	2.3
Lipophilic extractives	2.9	2.4	2.6
Ash	3.1	3.1	3.3
Tannin	n.a.	10.7	11.7
SUM	91.1	100.6	100.6

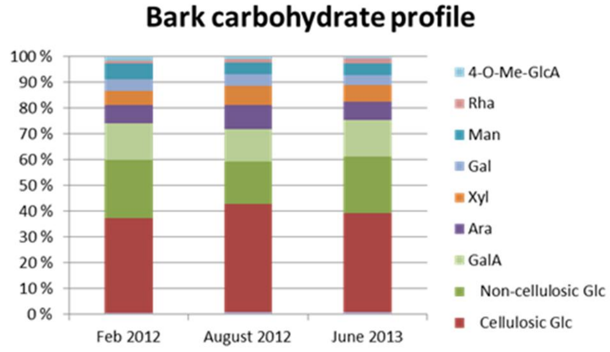

Figure 1. *Overall composition and carbohydrate profile of spruce bark samples studied in the project.*

yield of tannin more than the yield of carbohydrates. The use of extraction chemicals increased the extraction yield of tannin but not the total extraction yield. The solubilisation of carbohydrates as free monosaccharides during the extraction remained constant in different extraction conditions but appeared to vary between bark samples collected at different times of the year.

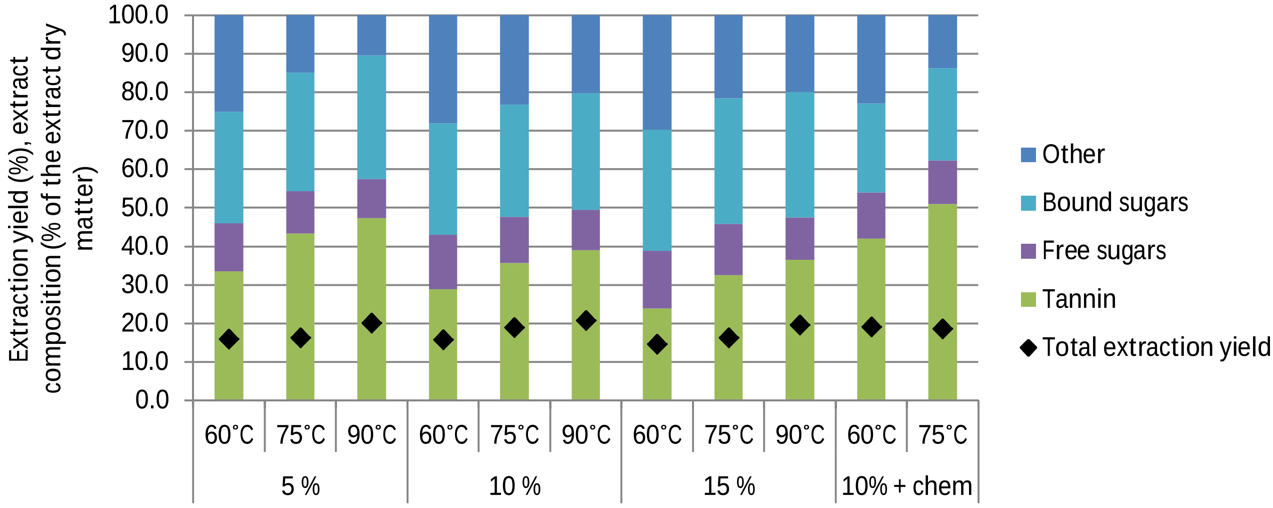

Figure 2. *Total extraction yield and composition of the extract dry matter in hot water extraction of spruce bark. Sodium bisulphite (2% of bark dry matter) and sodium carbonate (0.5%) were used in the two last extractions.*

Two pilot-scale extraction trials were carried out at VTT Rajamäki pilot facility to produce material for project partners for application studies (Table 1). Extraction conditions differed to some extent in terms of the particle size and the amount of residual wood in bark raw material, the use of extraction chemicals, extraction temperature and solids content. Extraction yields reflected these changes to some extent. Material losses occurred during the concentration and drying of the product. It can be concluded that 12-16% extraction yields could be obtained in industrial equipment designed for the purpose.

Crude pilot-scale tannin extracts contained 22-30% carbohydrates and a purification method was developed to remove this fraction from the product. The idea was to enzymatically hydrolyse bound carbohydrates to monosaccharides and remove them from the product by ultrafiltration, where smaller monosaccharides permeate the membrane and larger tannin molecules are retained. The effect of over 20 enzyme products was evaluated and an optimized mixture was found to be able to fully hydrolyse bound carbohydrates in an extract produced from bark collected in the winter but reach only 60-70% hydrolysis yields in an extract produced from bark collected in the summer (Figure 3). Especially the hydrolysis yield of glucose remained lower in the second extract and it was speculated that this finding could be related to the seasonal variation in the form of glucose in the bark.

Enzymatically treated bark extracts were ultrafiltrated in laboratory-, bench- and pilot-scale to produce purified tannin samples for project partners (Table 2). Over half of the carbohydrates in the extract could be removed but at a loss of some tannin through the membrane. Difficulties were experienced especially in pilot-scale where the breaking of the membrane lead to early finish of the filtration and a low degree of sugar removal. Industrial partner Ledoga, a tannin company with production in Europe and South America, was able to increase the tannin content of the crude pilot-scale extract to 80% by using their proprietary solvent-based purification procedure.

Table 1. Extraction parameters and extract composition in pilot-scale extraction of spruce bark.

	Extraction parameters	
Collection and extraction time of the bark	8/2012	6/2013
Amount of bark extracted (kg, dry)	114	243
Amount of wood impurities in bark (% DM)	21	10
Particle size	Shredded	Shredded at the sawmill and crushed
Extraction temperature (°C)	75	90
Solids content in extraction (%)	9	5
Extraction time (min)	120	120
Extraction chemicals	2% sodium bisulphite, 0.5% sodium carbonate	None
Solubilization yield	11.8	14.5
Practical yield	8.3	9.1
Amount of crude extract obtained (kg)	9.4	22.1
	Extract composition	
Water-soluble solids	100	80.1
Tannin (hide powder method)	49.7	57.6
Tannin (acid butanol method)	50.5	23.5
Carbohydrates	22.2	30
Ash	26.5	4.2
Acid insoluble material	34.5	46.8
Acid soluble lignin	12.3	9.4
Lipophilic extractives	0.9	2.6

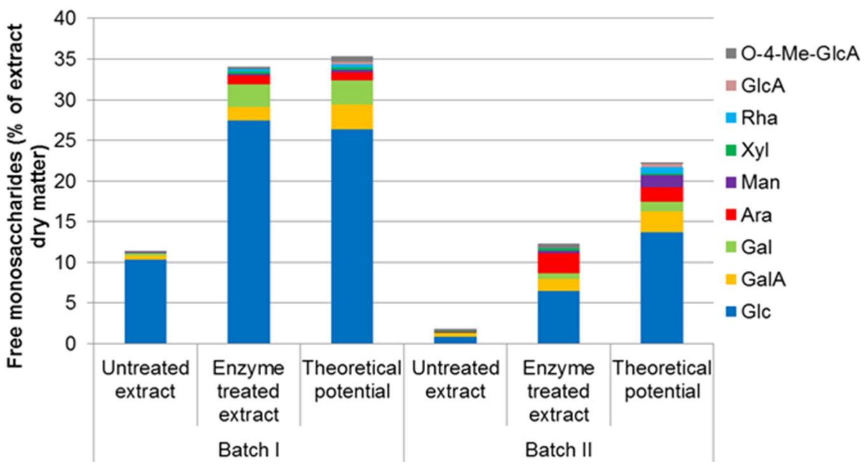

***Figure 3.** Release of monosaccharides during enzymatic hydrolysis of spruce bark extract produced in bench-scale from bark collected in the winter (Batch I) and extract produced in pilot-scale in similar conditions but from bark collected in the summer (Batch II).*

***Table 2.** Purification of enzymatically hydrolysed bark extracts by ultrafiltration in laboratory-, bench- and pilot-scale.*

	Lab	**Bench**	**Pilot**	**Unit**
Membrane pore size	10	5	5	kDa
Rate of filtration	27.3	30		$L/m^2/h$
Hydrolysis yield	56.7	68.9	67.4	%
Monosaccharide removal in filtration	74.0	85.8	38.5	%
Total sugar removal	42.0	59.1	25.9	%
Loss of tannin	31.7	32.1	9.3	%

Conclusions and outcomes

- Spruce bark composition
  - Spruce bark is a promising source of condensed tannins (11-12% tannin). Its composition is different from wood as it contains a significant amount of pectin and non-cellulosic glucose. Carbohydrate content and profile appears to have seasonal variation.
  - Dry debarked industrial spruce bark may contain significant amounts of wood as impurities.
- Storage of bark prior to extraction
  - Storage of bark in piles outside leads to a decrease in carbohydrate, acid soluble lignin and tannin content and an increase in the content of acid insoluble lignin. Apparently tannin condenses into insoluble matter (phlobaphenes) which shows up in analysis as acid insoluble lignin. Bark should not be stored but used as fresh as possible after debarking.
- Hot water extraction yields and extract composition
  - High temperature increased the extraction yield of both carbohydrates and tannin. It appears that selective extraction of tannins without carbohydrates is not possible.
  - Using extraction chemicals reduced the amount of carbohydrates, increases the amount of tannin and improved the stability of the extract in soluble form. Extracts produced with extraction chemicals contained a significant amount of ash.
  - Spruce bark hot water extracts produced in pilot scale contained 22-30% carbohydrates and circa 50-58% tannin according to the hide powder method. Carbohydrates were mostly in bound form (glycosides, polysaccharides, oligosaccharides), but in winter bark extracts monosaccharides amounted up to 30% of all carbohydrates.
- Purification of hot water extracts
  - Enzymes (betaglucosidases, pectinases, hemicellulases) can be used to hydrolyse bound sugars in the extract to monosaccharides, although the susceptibility of the extract to hydrolysis may have seasonal variation.
  - There is some indication that size-based separation of tannin from monosaccharides by ultrafiltration could be used to purify the extract.
  - Solvent based purification procedure carried out by a partner produced an extract with 80% tannin content and a lower carbohydrate content compared to the crude extract.
- Production of spruce bark tannin in pilot scale
  - Up to 22 kg of crude dried extract could be produced at VTT pilot facility with a 9% yield from raw material. With optimal industrial extraction equipment one could reach 12-16% yield.
  - Composition of the extract was similar to those produced in laboratory scale.
  - Spruce bark hot water extract, especially when it has been produced without extraction chemicals, should be dried as soon as possible, as storage in concentrated form may reduce its water solubility.

Publications

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2. Lacoste, C., Čop, M., Kemppainen, K., Giovando, S., Pizzi, A., Laborie, M.-P., Sernek, M., Celzard, A., 2014. Biobased foams from condensed tannin extracts from Norway spruce (Picea abies) bark. Submitted to Ind. Crops Prod.
3. Kemppainen, K., Grönberg, V., Siika-aho, M., Nakari-Setälä, T., Kruus, K., 2014. Valorization of spruce bark. 3rd Symposium on Biotechnology Applied to Lignocelluloses, October 26-29, Conception.
4. Kemppainen, K., Garcia Marrero, D.E, Grönberg, V., Sernek, M., Čop, M., Laborie, M.-P. 2014. Spruce bark biorefinery. Nordic Wood Biorefinery Conference, March 25-27, Stockholm, Sweden.
5. Kemppainen, K., Niemelä, T., Inkinen, J., Uusitalo, J., Kaijaluoto, S., Sorsamäki, L., Aaltonen, O., Suurnäkki, A., Peltonen, S., Mikkonen, H., Grönberg, V., Kruus, K., Nakari-Setälä, T., Siika-aho, M., 2013. Spruce bark biorefinery. Biomass Conference & Exhibition, June 3-7, Copenhagen, Denmark
6. Kemppainen, K., Grönberg, V. 2012. Extraction of hemicellulose and condensed tannin from spruce bark. Nordic Wood Biorefinery Conference, October 23-25, Helsinki, Finland.
7. Master thesis of Taru Niemelä: Removal of sugars from tannin-containing bark extract using hydrolytic enzymes and filtration technology, Aalto University, School of Chemical Technology, 2013.
8. PhD Thesis of Katariina Kemppainen: Production of sugars, ethanol and tannin from spruce bark and recovered fibres, Aalto University, School of Chemical Technology, 2015.