

## Publishable Final Activity report

### Background

Wood is a significant raw material in Europe and is exploited to a range of primary products, e.g. pulp, paper, timber and cork products. A modern kraft pulp mill produces considerable amounts of organic by-products, *Table 1*. The cork industry also produces large amounts of by-products containing interesting wood-derived substances.

These residual streams are mainly used as fuel at the pulp/cork mill, to a large extent ending up as low-value heat with no practical use. The broad spectrum of organic compounds in these streams could instead be processed to valuable chemical products within "biorefineries", utilising the energy surplus of the wood/cork-processing for the manufacture.

Table 1. The main organic residual products from the production of kraft pulp and cork. The production in Europe amounts to ca 22.5 Mt of kraft pulp and 0.28 Mt cork.

kg /t pulp or cork	produced	in Europe											
Black liquor organic material*	1 2 0	0	0	2	7	0	0	0	0	0	0	0	0
Bark	1 9	0	4	3	0	0	0	0	0	0	0	0	0
Cork powder	2 2	0	5	0	0	0	0	0	0	0	0	0	0
Cork black condensates	7	0	1	3	0	0	0	0	0	0	0	0	0
Solid residues from cork cooking waters	0.5	120											

\*Mainly consisting of lignin (ca 45 %), hemicellulose and other carbohydrate degradation products (ca 35 %), aliphatic acids (ca 10%), extractives (ca 5%) and methanol (ca 1%).

### Project objectives

The **overall objective** of WaCheUp was to upgrade low-value residual products from pulp and cork manufacture into value-added bio-based chemicals, with methods that can be efficiently integrated with the pulp/cork mills, *Figure 1*. Novel chemical and biotechnical conversion technologies have been applied with special emphasis on kraft black liquor and bark/cork.

#### More detailed objectives:

- Novel technologies for valorisation of pulp and cork mill residual products without negatively affecting the overall energy economy or quality of the primary products.
- Novel value-added products from current low-value energy streams (pulp mill black liquor, bark and cork residues)
- A method for separation and upgrading of lignin suited for non-fuel purposes.
- A method for separation and upgrading of non-degraded hemicelluloses from black liquor.
- A method for separation and upgrading of aliphatic suberin (a natural polyester) from bark.

# WaCheUp

- Evaluation of the applicability of producing phenols from lignin.
- Valorisation of hemicelluloses (polysaccharides) into e.g. paper additives, thickeners, food additives, emulsifiers, gelling agents, adhesives or adsorbents.
- Chemical and biotechnical valorisation of bark/cork suberin and extractives – hitherto undeveloped natural resources – into “green” polymers, composites and specialty chemicals.
- Principles for the integration of the above technologies with the pulp/cork mill.
- Economical and environmental evaluation of the developed processes and products.

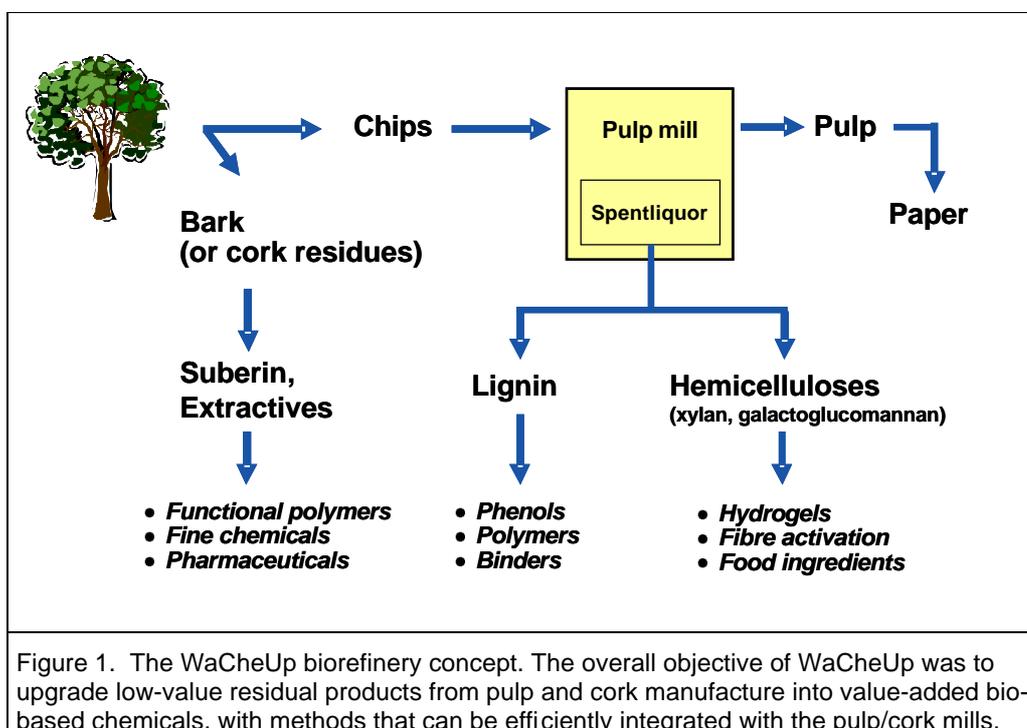


Figure 1. The WaCheUp biorefinery concept. The overall objective of WaCheUp was to upgrade low-value residual products from pulp and cork manufacture into value-added bio-based chemicals, with methods that can be efficiently integrated with the pulp/cork mills.

## Project participants

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## Project execution and results

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### Lignin

#### Work performed

Technique for separation of lignin from softwood (SW) and hardwood (HW) pulping black liquors has been developed by STFI PF, CUT and LU in close co-operation: precipitation with carbon dioxide, ultrafiltration and combinations thereof have been used. The target product has been value-added chemicals from lignin while fuel applications have been excluded.

Separation/upgrading of lignin through precipitation with carbon dioxide (LignoBoost) was studied at CUT. Special focus has been on filtration characteristics and further purification through washing of the lignin.

Separation/upgrading of lignin through membrane filtration was studied at LU. Lignin from liquors withdrawn at various positions (from the digester, before the evaporator unit and from the evaporator) in a Swedish kraft pulp mill was isolated, fractionated and concentrated by ultrafiltration (UF). The UF permeate was further treated by nanofiltration (NF) in some experiments. The performance of ceramic and polymeric membranes was studied. How purity and concentration of the lignin fraction are governed by membrane cut-off and operating parameters during membrane treatment was investigated. The lignin-rich UF fractions were investigated at CUT regarding precipitation and filtration characteristics. The hemicellulose-rich samples were analysed at STFI-PF.

The different developed process solutions were evaluated with the help of theoretical model mills, regarding process economy and integration with the pulp mill. (STFI-PF)

A literature survey was made on possible applications of phenols produced from lignin. (STFI-PF)

### Results

#### *Separation and upgrading of lignin*

Lignin with good quality, i.e. low sodium content, was successfully precipitated from black liquor. The filtration resistance for both hardwood and softwood lignin could be improved through a lower precipitation pH.

Precipitated HW lignin showed to be more difficult to filter than SW lignin, however, which was presumed to be due to the higher hemicellulose content. In order to improve the filtration resistance, three different pre-treatment techniques for decreasing the hemicellulose content were investigated: heat-treatment, ultrafiltration and a combination of ultrafiltration and nanofiltration. All of the three pre-treatment techniques tested were successful in decreasing the filtration resistance of the thereafter precipitated HW lignin. The molecular mass was, as expected, lower for lignin precipitated from UF permeate. The molecular mass was lower for the heat treated lignin as well, indicating a degradation of lignin into smaller parts during the heat treatment, in addition to the degradation of hemicelluloses.

The initial separation of lignin from hemicelluloses in HW black liquor was successfully performed with membrane technique: UF using a 15 kDa ceramic membrane at low transmembrane pressure and high cross-flow velocity. Hemicelluloses are preferentially retained, whereas lignin to a large amount passes through the membrane.

The combination of ultrafiltration and nanofiltration (*Figure 2*) resulted in a hemicellulose-poor permeate with an increased lignin concentration. The filtration resistance of the finally precipitated lignin was still low despite the fact that not only lignin, but also (smaller) hemicellulose molecules were concentrated in the nanofiltration permeate.

Lignin from UF permeate contain more phenolic hydroxyl groups than retentate lignin, which is an advantage if the lignin is to be used as raw material for phenols. The phenolic content could also be increased by a lower precipitation pH.

The sulphur content is also higher in permeate, which might be a drawback for some product applications. Washing of the lignin did not decrease the sulphur content, indicating that the sulphur is covalently bound to the lignin and cannot be washed out with acidified wash water.

The developed method for separation of hemicelluloses before the lignin precipitation gives a solution to the problem with the dewatering of hardwood (especially birch) lignin. It will also produce a lignin with thermal properties suitable for spinning – the first process step in the production of carbon fibres. The results provide a valuable starting-point for the design and optimization of future plants designed to extract and refine lignin from various liquors in kraft pulp mills.

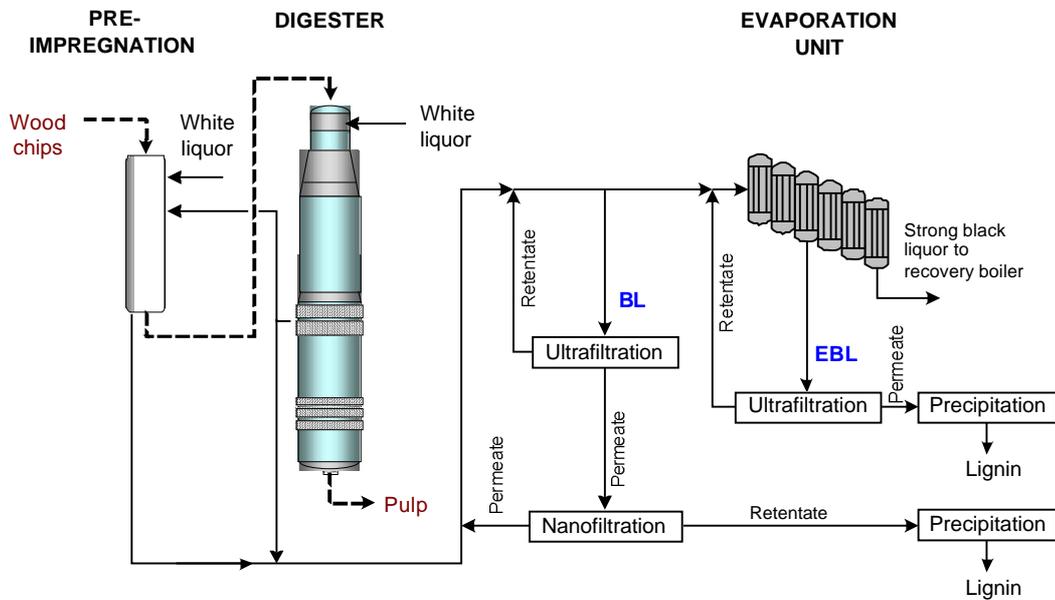


Figure 2. Concept for separation and upgrading of black liquor lignin through a combination of ultra filtration and precipitation. If the liquor is withdrawn before the evaporation (BL), a nanofiltration step needs to be added in order to concentrate the lignin further before precipitation.

### Process economy

In the calculations, it has been assumed that the alternative to lignin extraction is more production of electric power from incineration of black liquor, meaning that the decreased power production and green certificates are important cost items in lignin production.

The cost for extracting lignin from hardwood black liquor is ca 30% higher than in the softwood case, due to the lignin's poorer filterability and lower yield. The investment cost is almost twice as high in the hardwood case. The three pretreatment methods described above make hardwood lignin easier to dewater, but results in an even higher total production cost.

This result implies that hardwood lignin should preferably be used for high-value applications. One suitable application might be production of carbon fibre, where the UF pretreatment described in figure 2 would be an advantage, since lignin from UF permeates has better thermal properties than lignin from unfractionated black liquor.

### Lignin applications

Phenols are an important group of base chemicals used in e.g. polycarbonate plastic materials, *Figure 3*. Since crude oil is the main feedstock today, the price has increased significantly during recent years. Lignin may serve as a "green" feedstock for production of phenol. One possible way is catalytic hydrocracking of the lignin into monomers, followed by catalytic hydrogenation, giving a mix of several phenols.

Many of the phenol applications require, however, either pure phenol, as in the production of bisphenol A, aniline and nylon, or a mix of cresol or xylenol. The

phenol mixtures that are produced during hydrocracking of lignin seem to have a quite limited area of application. One solution can be to transform the mixture into pure phenol through dealkylation, preferably through a catalytic process.



Figure 3. Phenols are a widely used raw material for e.g. fibre glass boats and CD discs, and could be produced from lignin in pulping black liquors.

## Hemicellulose from chemical pulping

### Work performed

In hardwoods, the hemicellulose is composed of an O-acetyl-(4-O-methylglucurono)-xylan together with a small amount of an O-acetylated glucomannan.

Technical conditions suitable for recovering and processing of xylans from birch and eucalyptus spent kraft cooking liquors have been developed. Xylans with good purity with respect to lignin were produced by employing a process chain involving redrawing of xylan-rich spent liquor early in the cook and isolation and upgrading of the xylan through ultrafiltration with diafiltration followed by precipitation and drying. (STFI-PF)

The developed process was evaluated with the help of theoretical model mills, regarding process economy and integration with the pulp mill for different cases. (STFI-PF)

### Results

#### *Birch and eucalyptus black liquors*

Black liquor from the initial heating-up phase in birch kraft cooking exhibits a high xylan and low lignin content. An optimal point of xylan extraction was identified: after ca 80 minutes (i.e., in the heating-up phase), *Figure 3a*. At this point, the xylan concentration had reached its maximum, while the concentration of lignin was still low.

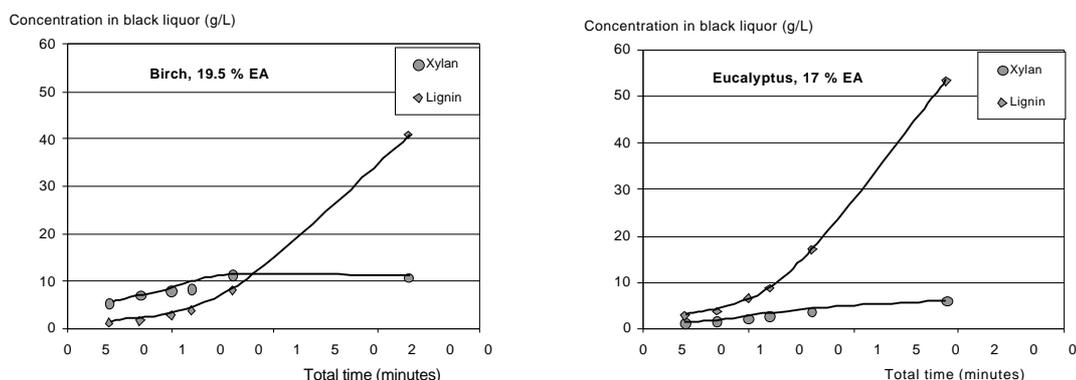


Figure 3. The xylan and lignin concentrations (g/L) in black liquor samples collected after different times in birch (3a) and eucalyptus (3b) kraft cooks.

In the case of eucalyptus cooking, the concentration of lignin was always higher than that of xylan, throughout the cook, and the highest xylan concentration was observed at a much later cooking phase, *Figure 3b*. Moreover was the xylan concentration in the spent eucalyptus liquors much lower than that of the corresponding birch liquors. This was partly due to the fact that the eucalyptus wood chips contained only half as much xylan (~15 %) as the birch wood chips (~30 %).

An ultrafiltration/diafiltration process sequence was developed for the isolation and upgrading of xylans from the spent black liquors *Figure 3*. Xylan is isolated through ultrafiltration with a ceramic membrane at elevated temperature. Diafiltration is applied in order to improve the purity of the xylan.

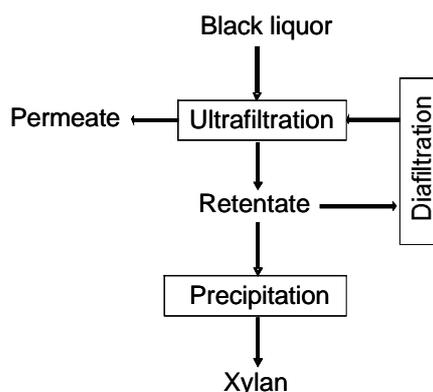


Figure 3. Schematic presentation of the developed process for isolation of xylans from birch and eucalyptus black liquors.

Xylan is concentrated in the UF retentate, *Table 2*. More than 90 % of the polymeric xylan could be recovered in the retentate. In contrast, a substantial quantity of the lignin (~60 %) was removed from the product streams together with the inorganic cooking chemicals through the permeate streams.

**Table 2.** Concentration of xylan and lignin in the process streams from ultrafiltration and subsequent diafiltration of birch and eucalyptus black liquors.

Stream	Birch liquor		Eucalyptus liquor	
	Xylan (g/L)	Lignin (g/L)	Xylan (g/L)	Lignin (g/L)
Black liquor	10.4	7.9	7.9	35.9
Permeate	0.3	3.5	0.7	28.2
Retentate	40.6	11.1	36.6	65.0
Diafiltrate	53.1	7.9	34.0	41.5

Finally, the xylan is isolated in solid form through acidic precipitation in the presence of methanol, which prevents the remaining lignin to precipitate as well.

In conclusion; on a lab scale, a process has been developed for producing birch and eucalyptus xylans with good purity with respect to lignin from pulping black liquor.

### *Process economy*

Eucalyptus xylan is more expensive to produce than birch xylan, due to lower concentration in the liquor and lower yield during the ultrafiltration. Diafiltration increases the production.

It has been assumed that the alternative to xylan extraction is more production of electric power from incineration of black liquor, meaning that the decreased power production and green certificates are important cost items in xylan production. The steam needed for methanol regeneration also adds to the lost income from power and green certificate.

The main production cost is related to the use of methanol in the precipitation. Several possibilities to improve the economy by process optimizations have been identified. The possibility to dewater the product more efficiently should be investigated, as there are large losses of methanol with the product corresponding to a significant part of the operating cost.

## **Hemicelluloses from mechanical pulping**

### **Work performed**

TMP process waters from four mechanical pulp mills were sampled and analysed. Two CTMP waters from laboratory refining of spruce and aspen CTMP were also analysed. (AAU)

Partially acetylated galactoglucomannan (AcGGM) was recovered during a 4-week pilot-scale trial using ultrafiltration at a Finnish TMP mill using spruce wood. The concentrate was further purified with various techniques, *Figure 4*. The physicochemical properties of different GGM qualities were determined. Kinetics of acid hydrolysis of Ac-GGM was also investigated. (AAU)

Purified AcGGM was substituted by various amounts of carboxymethyl (CM) groups. In this process, the acetyl groups were removed. The sorption to cellulose (bleached softwood kraft pulp) was studied. The surface active properties of Ac-GGM and CM-GGMs were studied through their sterical stabilization of spruce TMP pitch droplets.

# WaCheUp

Finally, the emulsification power of GGM preparates was studied with rapeseed oil / water mixtures. (AAU)

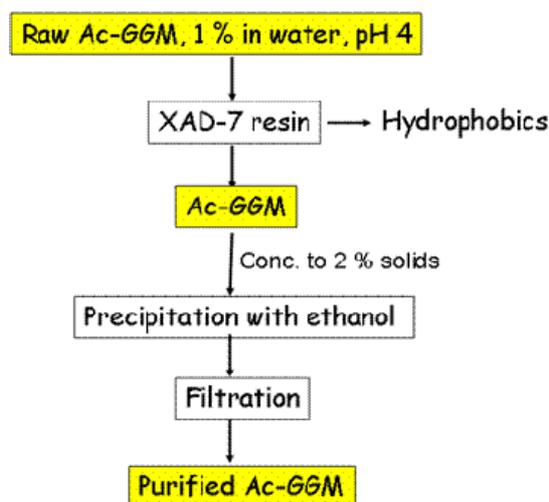


Figure 4. Schematic presentation of glucomannan (Ac-GMM) purification, starting from crude galactoglucomannan concentrate.

## Results

Effluents from TMP mills are a potential rich source of AcGGM. Conventional ultrafiltration techniques can provide a concentrate containing about 70% of GGM. The spruce TMP waters were a richer source of AcGGM than the CTMP waters. The pilot-scale isolation of AcGGM at the TMP mill was successful and about 20 kg technical grade AcGGM concentrate was produced and purified. Removal of lignin with XAD sorption followed by precipitation with ethanol addition increased the hemicellulose purity to over 90%.

The physicochemical properties of AcGGM were assessed. Acid hydrolysis was extensive at pH 1 at 90 °C, but was insignificant at human stomach conditions (pH2, 37°C), a valuable property in some pharma and food applications.

Carboxymethylation of GGM was rather straight-forward, but did not provide any advantages over the original AcGGM regarding stabilization of TMP pitch. However, one CM-GGM preparate gave superb stabilization of oil-water emulsions, implying that CM-GGM preparates have promising applications in food and feed applications, as well as in non-food applications such as cosmetics.

The results have raised an industrial interest in recovering AcGGM and in finding high-value applications for this natural polysaccharide.

## Extraction of bark/cork compounds

### Work performed

Inner and outer bark were separated from fresh birch bark and industrial birch bark. Extractives in birch inner bark were analysed. Kinetics of leaching of water-soluble compounds from inner bark was also assessed. The birch outer bark was analysed and compared with cork samples. The suberin part, *Figure 5*, was of particular interest as a source of fatty acids with an epoxy group in the chain. (AAU)

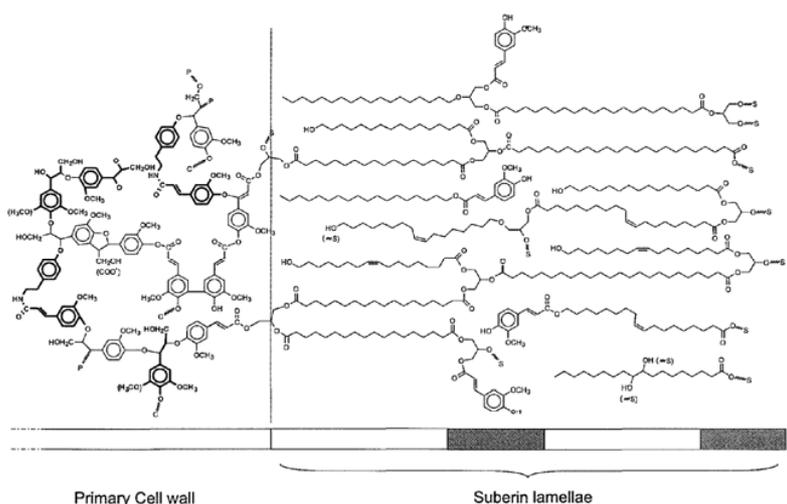


Figure 5. Postulated structure for suberin (Bernards, M., *Can. J. Bot.* **2002** 80 227)

A simple and direct NMR method was developed, which made it possible to analyse suberin acids from different kind of bark material as well as to study the reactivity of different functional groups and their changes in various reactions. (VTT)

Different fractions of cork extractives were obtained by using solvents of different polarities and a scheme of direct and sequential extractions, *Figure 6*. The solubilized material was recovered in the solid form after solvent removal under vacuum. (UM)

The chemical composition of cork, cork industrial residues and birch (*Betula pendula* L.) outer bark was determined in detail. (UAVR)

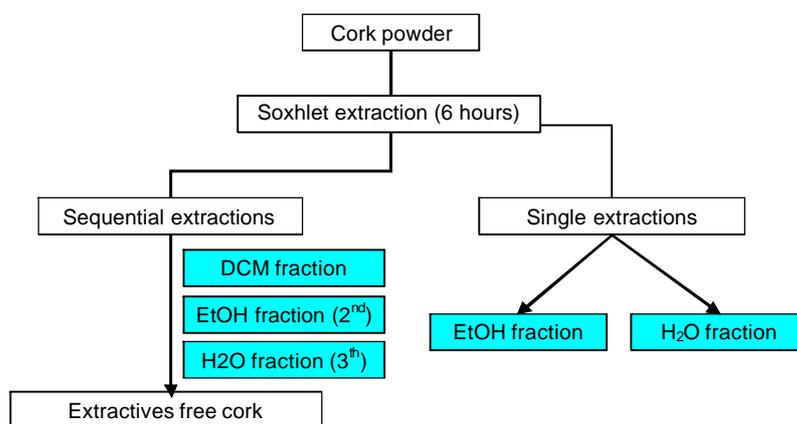


Figure 6. The sequential extraction procedure used for obtaining different fractions of cork extractives.

A method for separation of suberin and betulinol from birch outer bark has been suggested and evaluated regarding operating costs. (VTT, STFI-PF)

## Results

Cork oak samples have lower extractives contents (6-9%) and higher contents of carbohydrates and lignin (23-27% and 33-38% respectively) than those found for birch outer bark (40, 6 and 9%, respectively). Suberin contents accounted for around 30% of cork, 11% of industrial cork powder and 45% of birch outer bark.

A conclusion is that industrial cork by-products can be considered as abundant sources of triterpenic compounds, particularly betulinic acid and friedeline, which are known to have promising applications as bioactive substances. Lipophilic extracts of cork and cork by-products were quite rich in triterpenic compounds (Figure 7 and Table 3). Industrial cork powder (ICP) is particularly rich in betulinic acid (~12 g/kg), whereas in natural cork (QsC) the major component was cerine (4.6 g/kg), followed by friedeline and betulinic acid. This can be partially due to the fact that ICP is mainly composed by the outer (ONC) and inner (INC) fractions of cork planks, whose composition is quantitatively different from that of the whole cork, and also because of the boiling treatment and the natural variability of cork.

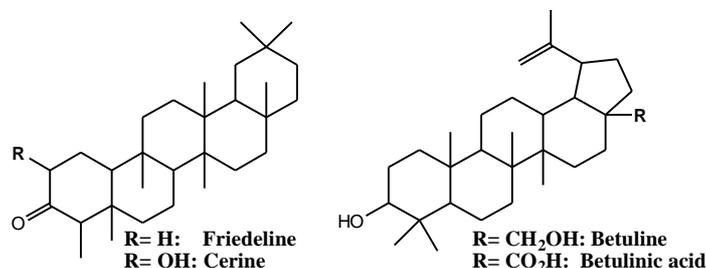


Figure 7. The major triterpenes identified in the cork samples

	ICP	BC	QsC	INC	ONC
Betulinic acid	11.7	12.1	2.2	5.2	1.6
Cerine	2.1	-	4.6	7.5	2.7
Friedeline	2.0	95.3	2.3	3.8	1.4
Ellagic acid	1.3	-	1.2	2.8	1.2
Betuline	0.9	13.3	0.3	0.5	0.5
□-Sitosterol	0.3	-	0.5	0.7	0.3
Ursolic acid	0.1	-	0.1	0.03	0.04
Lupeol	0.06	-	0.07	0.07	0.07
<b>Triterpenes</b>	<b>17.1</b>	<b>1185.6</b>	<b>10.3</b>	<b>17.8</b>	<b>6.5</b>

Table 3. Major components (g/kg) of lipophilic extracts of industrial cork powder (ICP), black condensate (BC), natural cork (QsC) and its inner (INC) and outer (ONC) fractions

Black condensate (BC) is particularly rich in the high-value compound friedeline (95 g/kg), which is not surprising, considering that this by-product is obtained by condensation of a volatile fraction of cork by thermal treatment.

Both birch outer bark and oak cork contain the epoxy-hydroxy stearic acid "HEPA" (18-hydroxy-9,10-epoxy-octadecanoic acid) that is an interesting starting material for specialty polymers. Especially birch bark is rich in both total suberin and HEPA. Birch outer bark can be separated by rather simple means, and constitutes a rich source of suberin as well as betulinol and other related triterpenols. New components with interesting bioactive properties were identified in birch inner bark.

The developed NMR technique for suberin analysis was proved to be fairly quantitative compared to a typical GC-MS method. Suberin acid distributions in birch bark and cork are compiled in *Table 4*.

Whereas in the case of birch suberin HEPA is clearly predominant, which might justify its isolation for further exploitation, cork suberin samples do not have a dominant component. The approach for valorization of cork suberin should therefore be using the entire depolymerization mixture rather than isolated components.

The method studied for for isolation of betulinol and suberin from birch outer bark, *figure 8*, showed to have high operating costs, implying that the products has to be used for high-value applications like pharmaceutical and cosmetics applications. Each step could be optimized more, though. The possibility to dewater the product more efficiently should be investigated, as there are large losses of solvent with the product, corresponding to a significant part of the operating cost.

M O N O M E R N M R ( m o l - % ) <sup>VTT</sup>	Birch		outer bark		suberin		Cork		suberin	
	GC-MS(mol-%) <sup>*1</sup>	NMR(mol-%) <sup>VTT</sup>	GC-MS(mol-%) <sup>*1</sup>	NMR(mol-%) <sup>VTT</sup>	GC-MS(mol-%) <sup>*1</sup>	NMR(mol-%) <sup>VTT</sup>	GC-MS(mol-%) <sup>**4</sup>	NMR(mol-%) <sup>VTT</sup>	GC-MS(mol-%) <sup>**4</sup>	NMR(mol-%) <sup>VTT</sup>
<chem>HOOC(CH2)7CH=CH(CH2)7C</chem>	0	0	1	3	4	0	9	7	0	1
<chem>HOCH2(CH2)7CH=CH(CH2)7C</chem>	0	0	1	3	1	3	2	4	6	4
<chem>HOCH2(CH2)7CH-CH(CH2)7C</chem>	0	0	4	0	4	0	3	7	0	9
<chem>HOOC(CH2)7CH-CH(CH2)7C</chem>	4	0	2	n	3	d	2	1	0	1
<chem>HOCH2(CH2)6CH(OH)CH2C</chem>	0	0	1	3	1	3	6	1	1	4
<chem>HOCH2(CH2)7CH-CH(CH2)7C</chem>	0	0	8	0	8	0	2	6	0	9
<chem>HOOC(CH2)7CH-CH(CH2)7C</chem>	0	0	1	0	1	0	5	7	0	0
<chem>HOCH2(CH2)9CH-CH(CH2)7C</chem>	0	0	n	0	n	0	0	0	0	9
Other monomers without secondary functionalities										
nd=notdetermined										
*=calculatedfromw/w-%values,alkalinehydrolysis										
**=calculatedfromw/w-%values,alkalinemethanolysis										

Table 4. Suberin monomers in birch outer bark and cork, quantified with GC and the new NMR method. The second section shows the epoxy activated monomers (HEPA).

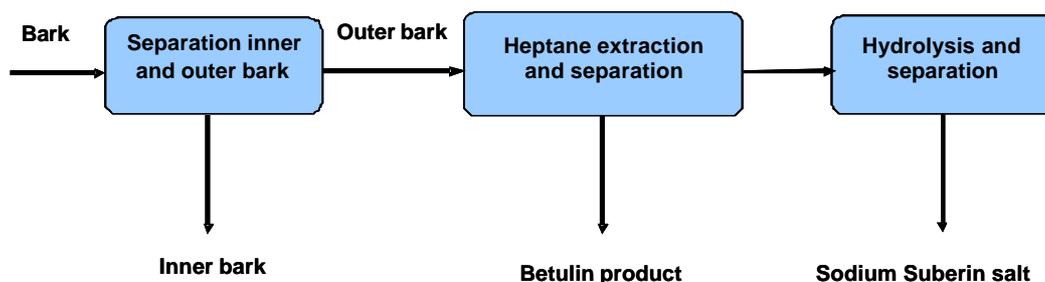


Figure 8. Simplified process scheme for the separation of inner and outer bark, betulinol and suberin.

## Depolymerisation of bark/cork suberin

### Performed work

Different polyesterase enzymes were tested for their ability to depolymerise suberin, with the aim to obtain suberin fragments with functional fatty acids. (VTT)

## Results

It was soon noticed that suberin matrix is recalcitrant to enzymes. Various pre-treatments were tested and the traditional steam exposure was found to be efficient in opening up the suberin structure prior to enzyme treatment.

Natural polymers, birch outer bark and cork suberin and apple cutin were treated with various esterase preparations in different conditions. *Coprinus* cutinase CcCUT1 and the commercial Optimyze preparations provided the most promising suberin depolymerisation results.

The amount of enzyme had a clear effect on the degree of suberin/cutin hydrolysis. Addition of HFBII hydrophobin improved clearly the hydrolytic effect of CcCUT1 on suberin and cutin while having no advantage for the efficiency of Optimyze. Both fatty acid monomers and oligomers were released by the enzymes.

## Valorisation of bark/cork suberin

### Work performed

Polyesters have been synthesised by polycondensation and by polytransesterification (starting from depolymerized suberin obtained by alkaline hydrolysis). (UAVR)

Epoxy-activated co-polyesters and cyclic macromonomers have been synthesised from HEPA and  $\epsilon$ -caprolactone by use of a commercial enzyme as catalyst. (STFI-PF)

Isolated HEPA has been grafted on bacterial cellulose cellulose by ring-opening of the epoxy group. (STFI-PF)

Suberin-based poly/oligoesters were synthesised in order to obtain surface-active products for use as e.g lubricants or specialty coatings. (VTT)

Novel composite structures were prepared with modified polymer (polyethylene) combined with cork particles and grafting agents prepared from suberin. Physical and mechanical characterization required for a deeper evaluation of the potential of the novel "green" composites were performed. (Amorim)

### Results

It was shown that suberin monomers, especially HEPA, are useful polyester precursors. This opens up a new research/development field for new renewable materials based on bark suberin. The synthesized polymers show unique characteristics, differing from the original suberin macrostructure.

Cellulose can be surface-modified (grafted) by use of HEPA in combination with catalysed ring-opening of the epoxy group.

It was shown that it is possible to refine suberin into reactive co-polyesters by use of "green" enzyme catalysis without the use of organic solvents. HEPA was successfully co-polymerized with  $\epsilon$ -caprolactone into epoxy-functionalized linear polyesters and cyclic oligomers (polymer precursors).

Suberin-based hemi esters were prepared from suberin with e.g. maleic, succinic, phthalic and acetic anhydrides, *figure 9*,

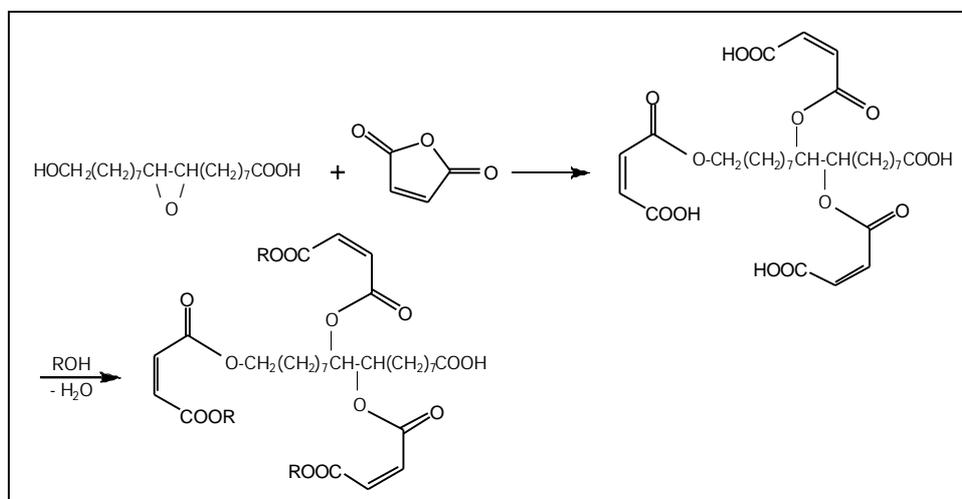


Figure 9. Surface active compounds were produced from suberin acids together with different anhydrides (here: maleic anhydride) and alcohol.

Some of the synthesis products showed very good surface-tension decreasing properties in their salt form, making them interesting as e.g. components in cosmetics and potential monomers for oligo/ polyesters to be used as binders and lubricants. The surface activity of birch suberin acid Na-salt has nearly identical values with the commodity surfactant, sodium dodecyl sulphate (SDS). The worldwide usage of anionic surfactants is about 4 Mt/a and alkyl sulphates count for about 10 % of this market.

The prepared cork-polyethylene composites (*Figure 9*) showed high dimensional stability and show promise to be developed into novel "green" composite materials with tailored properties. In fact, it was proven that the incorporation of cork as reinforcements of thermoplastic matrices can be achieved without the incompatibility problems that are usually present when hydrophilic ligno-cellulosic materials are used. The results open up for new lines of research for the natural-based composites field, where the combination of the properties of the thermoplastic and cork can be substantially exploited due to their significant complementarities.

