GREASE: A novel lipid platform to sustainable bio-based products from low-value forestry streams through multi-functional fatty acids

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Project Objectives and Main Tasks

Main tasks of GREASE-project

1) **Purification and chemical characterization** of fatty acid mixtures and mono-component fatty acids from tall oil and birch bark suberin
2) **Development of chemical and biotechnological routes** for conversion of fatty acid mixtures and monocomponent fatty acids to multifunctional fatty acid derivatives
3) **Further conversion** of multifunctional fatty acids **to polyester, polyamide, polyurea and polyurethane products** and testing them in coating, barrier, polyurethane resins/foams/elastomers and adhesives applications, and testing the semisynthetic fatty acid derivatives for their bioactivity
4) **Evaluation of techno-economical feasibility** of developed processes and products in end-use applications

Role of partners in value chain

Raw materials
(TOFA & Suberin FA)

Selection and chemical analysis: Stora Enso, Arizona Chemical, Anadolu, SP

Separation Fraunhofer, VTT, UHEL, SP

Conversion

Chemical functionalization: UHEL, Fraunhofer, VTT

Biotechnological oxidations: VTT

Bioactive fine chemicals

UHEL, Anadolu

Coatings & Adhesives

Polyamides and polyesters: VTT, SP

Crosslinkers: SP

Polyurethane materials

PU foams, casting resins, elastomers: Rampf, Fraunhofer

Bioplastics

Polyesters Novamont

Feasibility & sustainability

All partners

Case examples: Oleochemicals and products from wood-fatty acids

Pilot scale- reactor used for extraction studies

Isolated Suberin FAs and Tall Oil Fatty acids

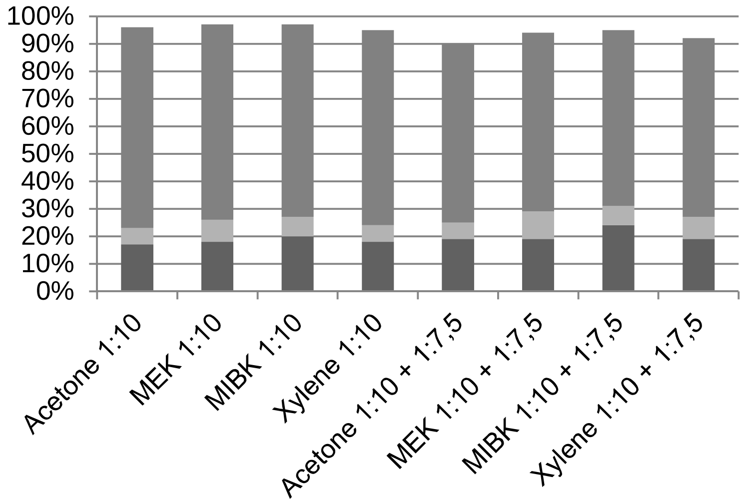
Rigid insulation foams from bio-based polyester polyol

Bioactivity testing of fatty acid derivatives

Laboratory scale pre-screening of extraction methods for isolation of Suberin fatty acids and Betulin

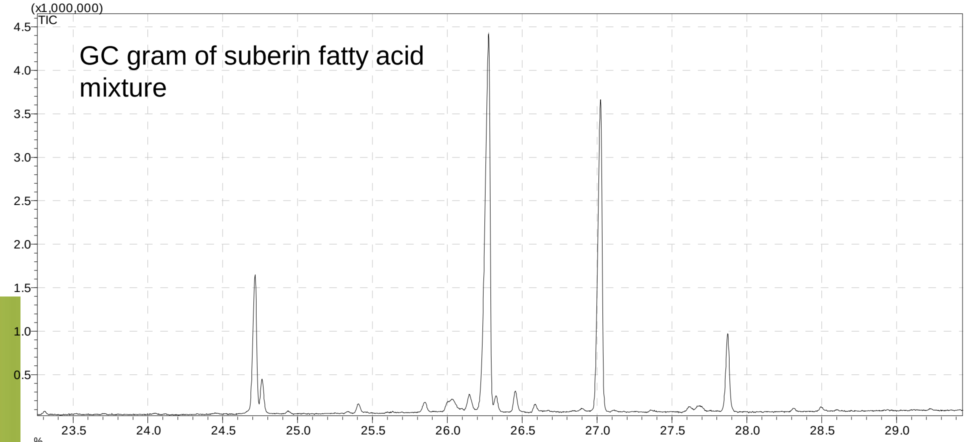
Birch outer bark of *Betula pubescens* or *Betula pendula*

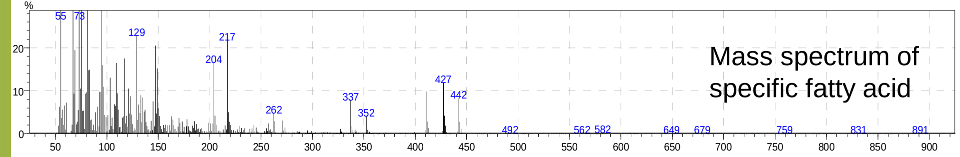
Grinded outer bark and Soxhlet extraction



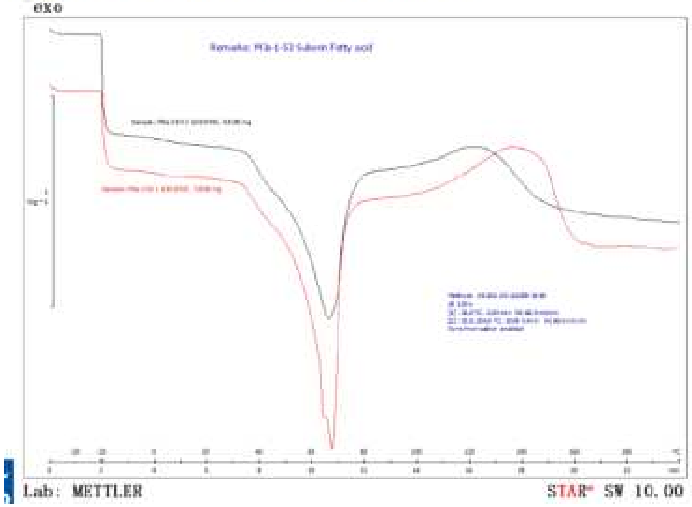
Extracted betulin

Analytics for wood components and derivatives





DSC of Suberin fraction obained

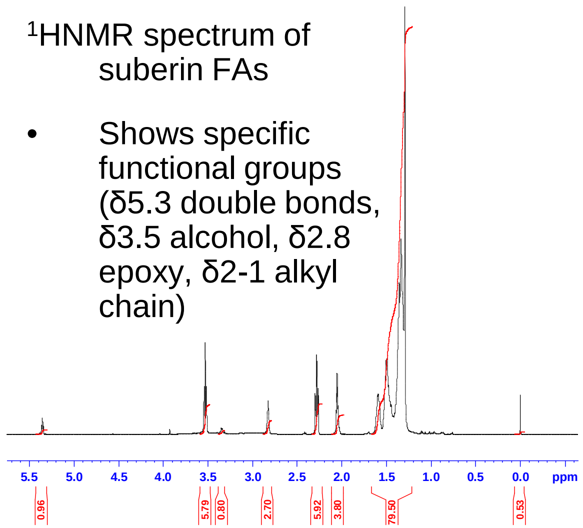


Shimadzu 2D-GC-MS QP 2010 Ultra

Major suberin fatty acids identified:

- 9,10-epoxy-18-hydroxy-octadecanoic acid **~40%**
- 9,10,18-hydroxyocta-decanoic acid **~25%**
- 9,10-ene-18-hydroxy-octadecanoic acid **~10%**
- 22-hydroxydocosane-dioic acid **~5%**

NMR Bruker Avance III 500 MHz

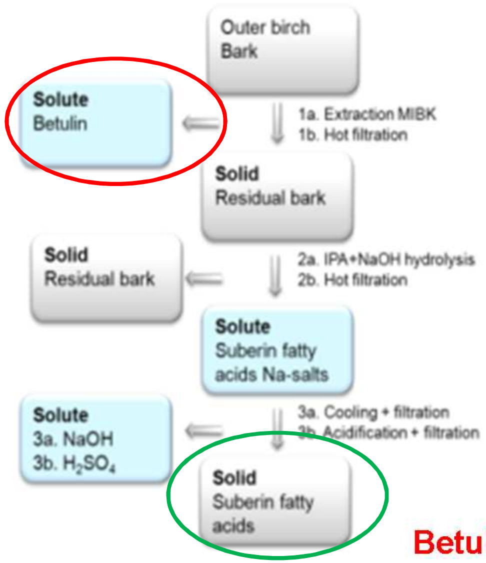


^{1}HNMR spectrum of suberin FAs

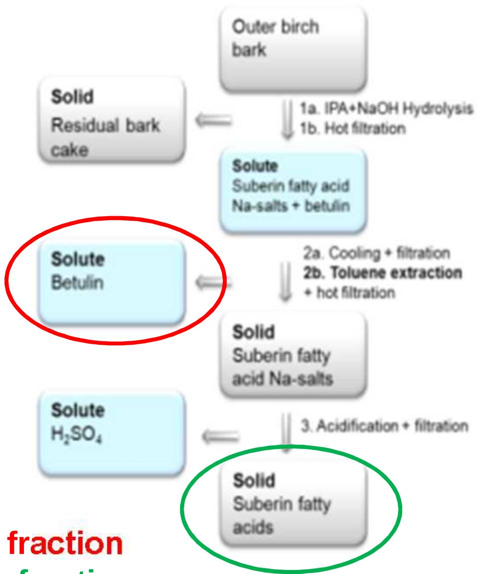
- Shows specific functional groups (δ5.3 double bonds, δ3.5 alcohol, δ2.8 epoxy, δ2-1 alkyl chain)

Development of extraction and hydrolysis methods

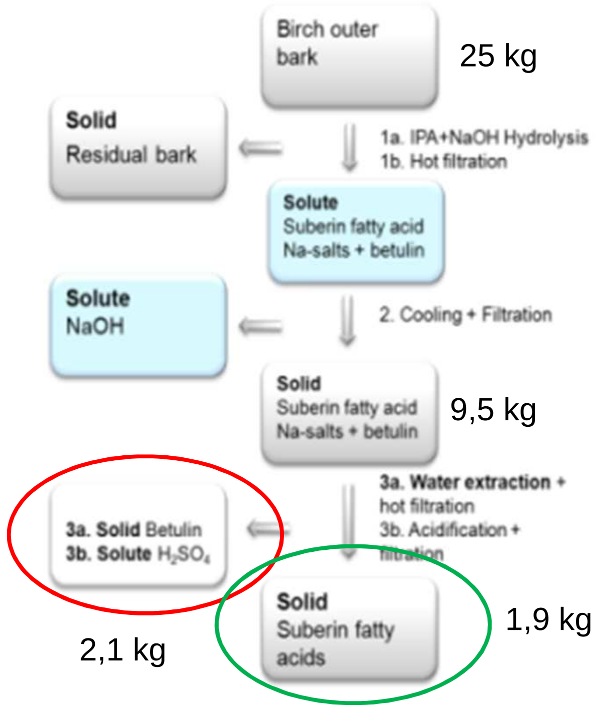
Conventional process



Krasutsky's process



Improved process



Betulin fraction
Suberin fraction

<u>VTT's lab experiments:</u>

Suberin 3% (inc. betulin 54%)
Betulin 28%

<u>Frauhofer's pilot experiments:</u>

Suberin ~6%
Betulin 37% (85-97%)

<u>VTT's lab experiments:</u>

Suberin 15% (inc. betulin 12%)
Betulin 9% (purity ~96%)

<u>VTT's lab experiments:</u>

Suberin 15% (inc. betulin 3%)
Betulin 40% (purity ~78%)

<u>VTT's pilot experiments:</u>

Suberin 8,3% (inc. betulin <5%)
Betulin 8,4% (purity ~85%)

Production of suberin FAs and betulin in pilot scale

Grinding of the outer birch bark

Filtration off residual cake

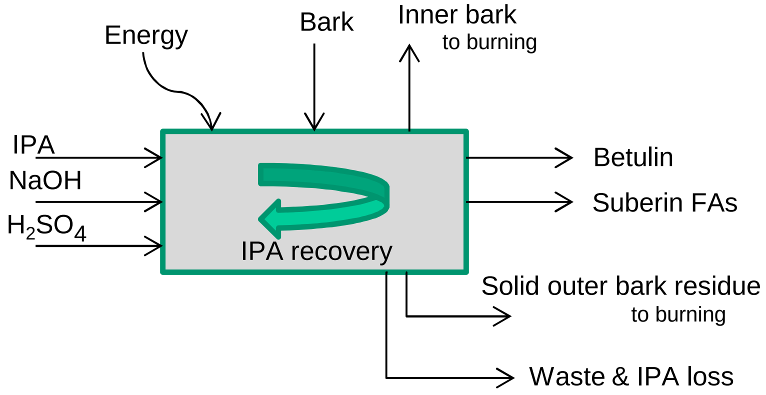
Sentrifugal separation of products

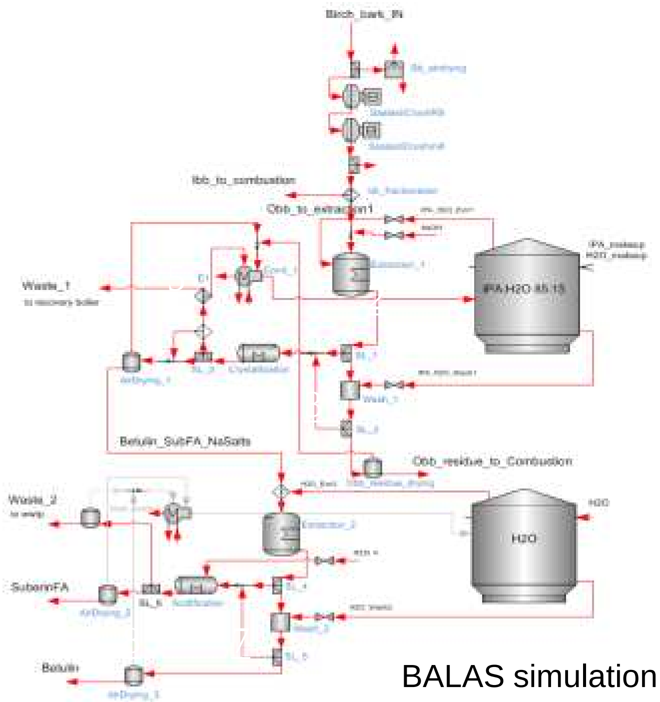
Solvent extraction at VTT

Freeze drying of suberin FAs

Fraunhofer’s pilot Soxhlet extraction

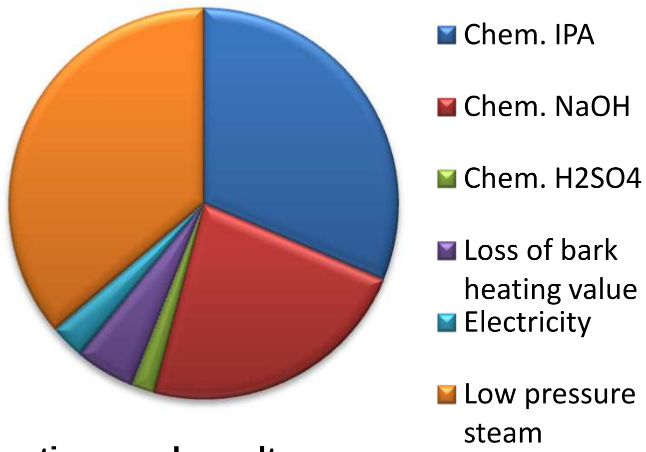
Modelling of the process to evaluate production costs





BALAS simulation

Variable production costs

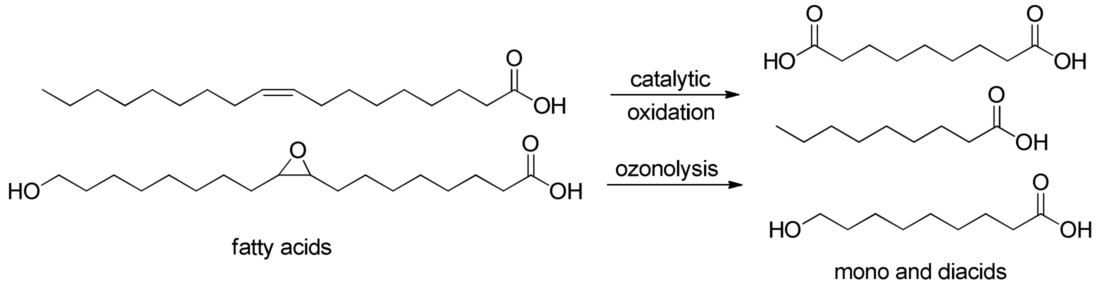


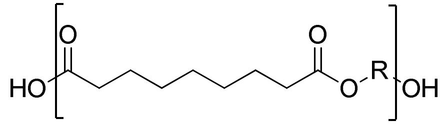
Main assumptions and results

- Extraction with 85 w-% of 2-propanol (IPA) and 15 w-% of water
- IPA recovery rate 98 % (loss 2 %)
- Yields: Betulin 12 w-% and SFAs 15 w-% (moderate values used in calculations)
- Solid residues combusted for energy
- Variable costs includes: chemicals and energy
- Fixed costs i.e. capital costs or labour are not included
- Variable production costs total ~2200 €/t (betulin and suberin FA yield 27 %) and 1500 €/t with yield of 40 %
- Efficient solvent recovery is crucial for economical process
- Betulin and suberin yields are also important parameters

To polyurethanes

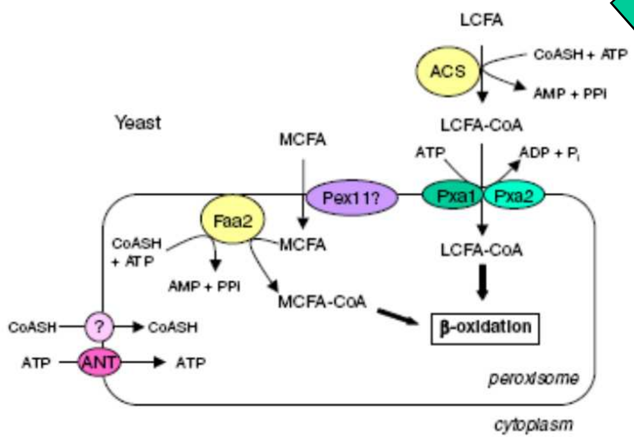
Chemical conversion





Polyesterpolyols

Biotechnological conversion



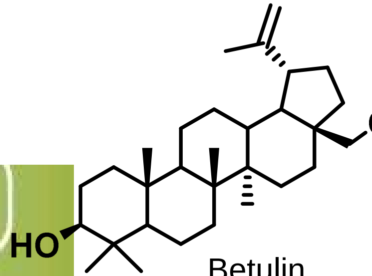
Biochemical ω-oxidation by blocking β-oxidation pathway

Betulin

Betulin based prepolymer

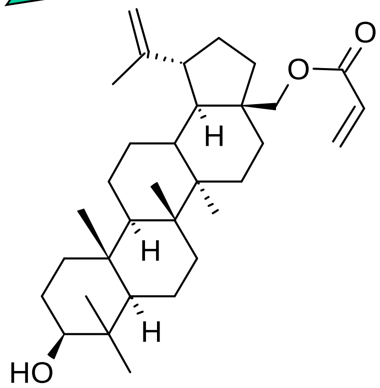
Bio-based rigid polyurethane foam

To tires and tackifiers



Betulin

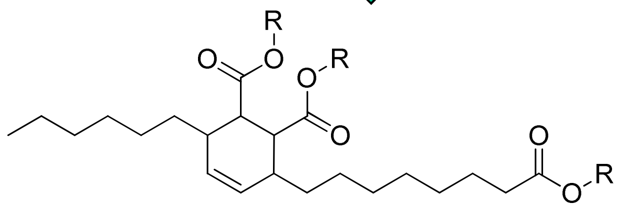
Chemical modification



Betulin esters such as acrylates

Rubber applications

Tackifiers or Crosslinkers

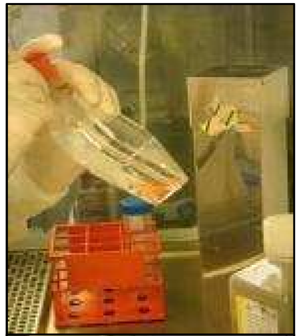


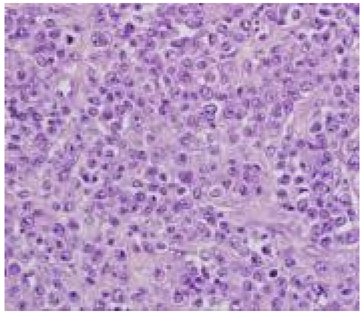
Diels-Alder adduct of linoleic acid

To pharmaceuticals and cosmetics

Conclusion of bioactivity test results

- Abietanes: good activity, some even for pharma use (some cytotoxicity observed)
- Betulins: medium activity, interesting in cosmetics
- Suberin FAs: low activity, interesting in cosmetics





MTT cytotoxicity

Bioactivity assays tested

- Antibacterial
- Antifungal (Anticandidal)
- Cholinesterase Activity (Ache – Buche)
- Antioxidant
- Cytotoxicity & safety

Microdilution

Agar diffusion

Material testing

Elastomers from dicarboxylic acid

T3	T4	T5	T6
o	+	-	+

Testing of hydrolysis resistance

Rigid polyurethane foam from suberin FAs based esterpolyol

- Excellent properties even with 50 % suberin FA content

Bending strength

Compressive strength

Major achievements

- Effective separation method developed and up-scaled for isolation of suberin FAs from outer birch bark with minimized solvent usage. Moreover, variable production costs were computed (VTT, Fraunhofer, Stora-Enso)
- For wood-based FAs conversion techniques such as hydrothermal techniques, oxidative cleavage and biotechnological ω-oxidation with modified yeast strains were developed for production of difunctional FA derivatives (VTT, Fraunhofer, UHEL)
- Use of Suberin FAs as pharmaceutical additives was studied. Suberized cellulosic films were excellent as pharmaceutical moisture barrier (VTT, UHEL).
- Antimicrobial activities of fractionated wood-based chemical components and derivatives were determined with antimicrobial assays. Some compounds are potential for cosmetics application (UHEL, ANADOLU)
- Ester polyols based on 100 % biomonomer have been developed and PU polymers with promising characteristics have been produced (Rampf).
- Usability of Suberin FA, TOFA and betulin derivatives for tackifiers, tire resin and polyester-based barrier films have been studied (Arizona Chemical, SP)

Co-operation with partners

- The international co-operation has provided complete set of complementary experimental methods to address technological challenges and the best methods could be found for each value chain in the project.

- Engaging industrial partners is a good way to get feedback on various project activities and results. Beneficial is, if the industry partners have an active research role and share their results. This all adds to the relevance of the activities and also helps in building of potential future development spin-outs.

Thank You!