Biofoambark

Bark Valorization into Insulating Foams and Bioenergy

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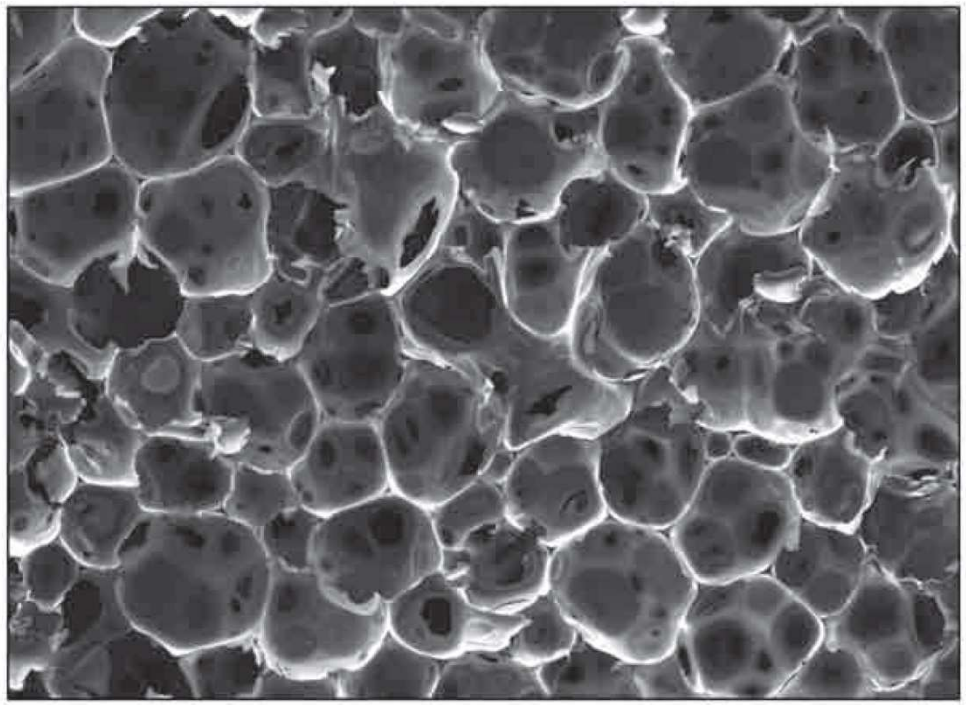
Biofoambark: Background

- Activities on tannin-based foams at ENSTIB-LERMAB (France, T. Pizzi):



SEM image of tannin-based foam (30x magnified)

Tannin-based foam

Source: Tondi et al., Maderas, 2008, 10, 219-217

Biofoambark: Background

- Properties of insulating rigid tannin-based foams:
  - Low thermal conductivity
  - Low density but good mechanical properties
  - Very low flammability
  - Mainly composed of renewable resources

- Raw material: **tropical** tannins (Mimosa, Quebracho…)

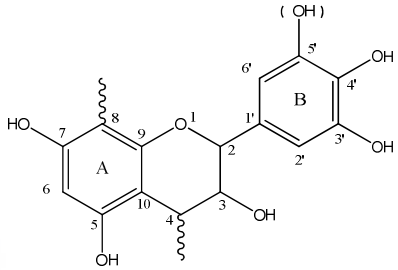
- Tannin-based foams as alternatives to insulating PUR or phenolic foams?

  →Core objective of Biofoambark:
  Development of insulating rigid foams based on **bark** tannins from **European softwood** species

Biofoambark: Objectives

Pine and spruce bark

Extraction and purification



Foam technology

Insulating foam

Syngas production for bioenergy (at end-of-life)

Life Cycle Assessment and techno-economic evaluation

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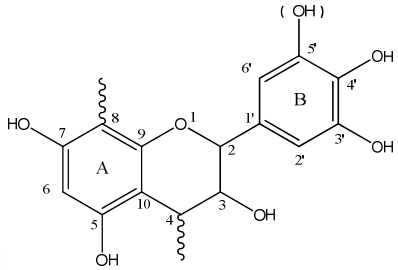
Extraction and purification



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WP2: Mapping of bark resources

- Partner:

  Chair of Forest Utilization
  University of Freiburg (Germany)
  (with input of further project partners)

- Bark is always generated as **by-product** in wood and pulp industry

  → Main current uses: Bioenergy and mulching

- 4 **European** softwood species of interest (focus at specific countries of the project partners)
  - *Pinus pinaster* (Maritime pine, France) → **quantitative potential**
  - *Pinus radiata* (Radiata pine, Spain) → **no potential**
  - *Picea abies* (Norway spruce, Finland) → **quantitative potential**
  - *Pseudotsuga menzisii* (Douglas fir, Germany) → **no potential**

- Cascade use of bark will probably be necessary for increasing the potential bark availability

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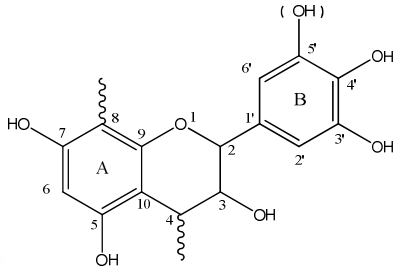

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WP3: Tannin extraction and purification

- Partner:

  Ledoga Srl
  (SilvaTeam, Italy)

VTT Technical Research Centre of Finland

Affiliated members connected to VTT:

- Savanaho Oy
- Chemigate Oy
- Finnish Wood Research Oy

- Objective:

  Develop extraction and purification of tannins from **spruce bark** at bench, pilot and industrial scale

WP3: Tannin extraction and purification

Bench and **pilot** scale spruce bark extraction with hot water:

- High temperatures increase extraction yield for both, tannin and carbohydrates

  → Extract contains always about 50 – 55 % tannins and 40 – 45 % carbohydrates

- Use of extraction chemicals ($NaHSO_3$ + Na_2CO_3) increases tannin extraction selectivity but results high ash content (26 %!)

  → WP4 shows that tannins with **high purity** are necessary in order to get tannin-based foams with good properties

    → extraction **without** additional chemicals favored

    → removal of carbohydrates (**purification**) necessary

- For **purification** by means of **enzymatic hydrolysis** of bound sugars followed by **ultrafiltration** there are indications that this is a potential new route but further development is required.

WP3: Tannin extraction and purification

Industrial scale spruce bark extraction with hot water at Ledoga Srl (Italy):

- 24 tons of spruce bark (1 truck) from Stora-Enso (Austria)
- Spruce bark can be chipped, sieved, conveyed and filled in the silo which feeds the extractor with the equipment adapted to chestnut wood.

WP3: Tannin extraction and purification

Industrial scale spruce bark extraction with hot water at Ledoga Srl (Italy):

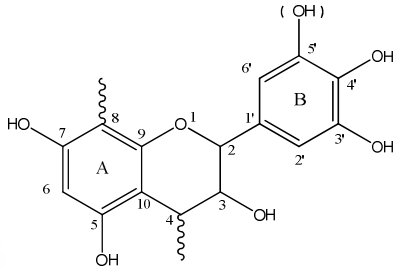
- Problems:
  - Bridging of bark in the silo and in the extractor complicates discharging by gravity
  - Additionally spruce bark acts like a sponge, so that the extract doesn't flow out
    - → Equipment for extraction of chestnut wood doesn't seem to be adapted to extraction of spruce bark

- Engineering problem:
  - → Commercial equipment suitable for tannin extraction from spruce bark is very likely available on the market
  - → Future projects should involve engineering companies and equipment manufacturers

Biofoambark: Objectives

Pine and spruce bark

Extraction and purification



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WP4: Foam technology

- Partner:

  ENSTIB-LERMAB
  Université de Lorraine (France)

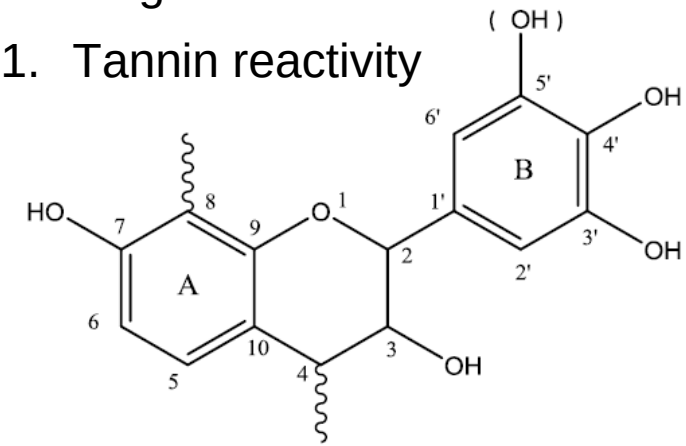
  Chair of Forest Biomaterials
  University of Freiburg (Germany)

  University of Ljubljana
  (Slovenia)

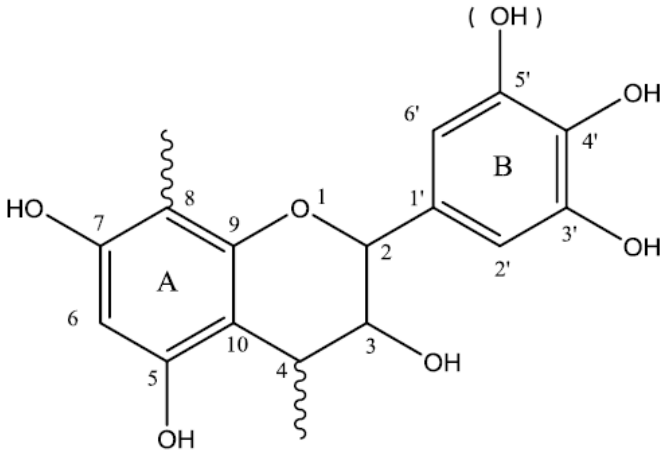
- Objectives:
  - Design of tannin foams: base and nanocellulose modified formulations
  - Establishment of kinetics for foam preparation
  - Establishment of structure/property relationships

WP4: Foam technology

- Challenges:
  1. Tannin reactivity



Quebracho tannin
Gel time (pH = 5.6): 495 s
→ Lower reactivity



Pine tannin
Gel time (pH = 5.6): 77 s
→ Much higher reactivity

→ Original (tropical) tannin formulations and kinetics have to be adapted

  2. Tannin heterogeneity

Source: Pizzi und Stephanou, J. Appl. Polym. Sci., 1994, 51, 2109-2124

WP4: Foam technology

- **New formulations** of tannin-based foams:
  - Foams can now be produced from bark tannins of Radiata pine, Maritime pine and Norway spruce
  - At tannin purities > 80 % foam formulations show good transferability between the 3 softwood bark tannins resulting in foams with comparable properties
  - Crude tannins not suited for foam production
- Empirical knowledge on **control** of foam morphology (cell size, density …) and properties (thermal and acoustic insulation) by addition of additives created
- Many alternative aldehydes for formaldehyde as cross-linker tested

  → **Glyoxal** as the most promising route resulting in comparable foam properties
- **Nanocellulose** modification of tannin-based foams investigated

  → High **heterogeneity** within the nanocellulose modified foams

WP4: Foam technology

- Tannin-based foam formulations use toxic furfuryl alcohol
- Emissions (e.g. VOCs) from foams unknown
- Industry very interested, but not willing to take investment risk so far

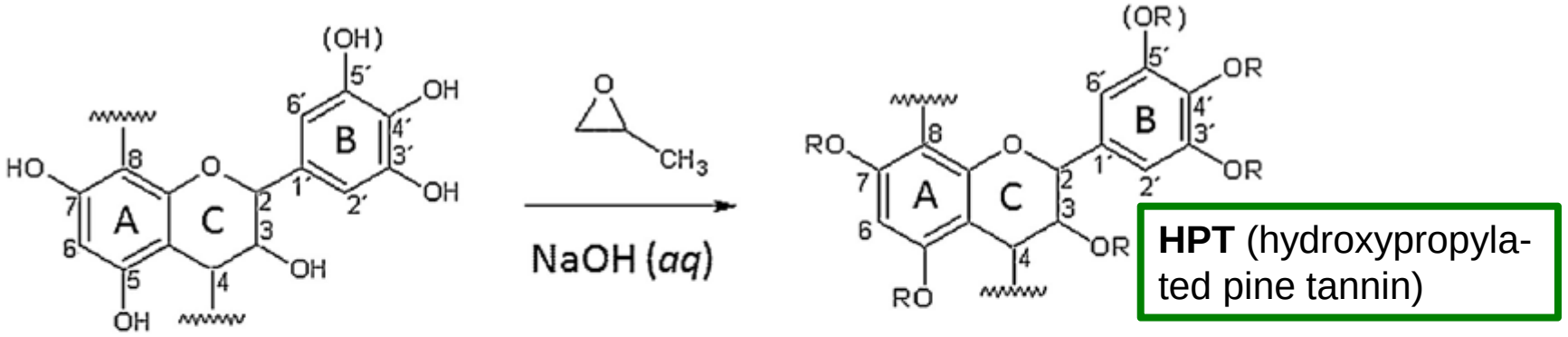
- Up to now only experiments at laboratory level
  → Applicability at a larger scale remains unknown

- **Variability** remains a main problem
  - Source variability
  - Spatial variability within the foam
  - Control of foam properties has still some limitations

WP4: Foam technology

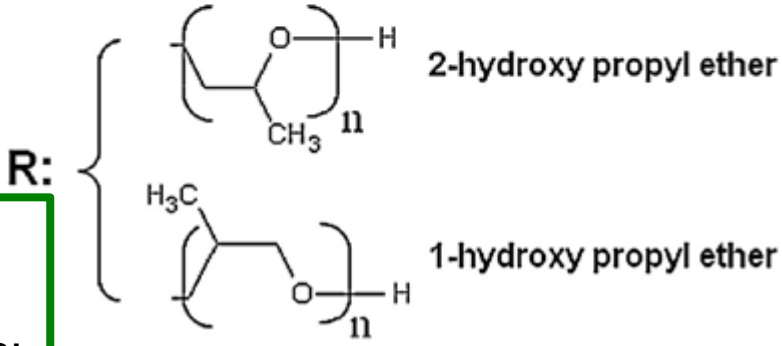
- Hydroxypropylation as route to tailor tannin characteristics**?**

Reaction of *Pinus pinaster* bark tannin with propylene oxide (RT, 30min):



HPT (hydroxypropylated pine tannin)

R:

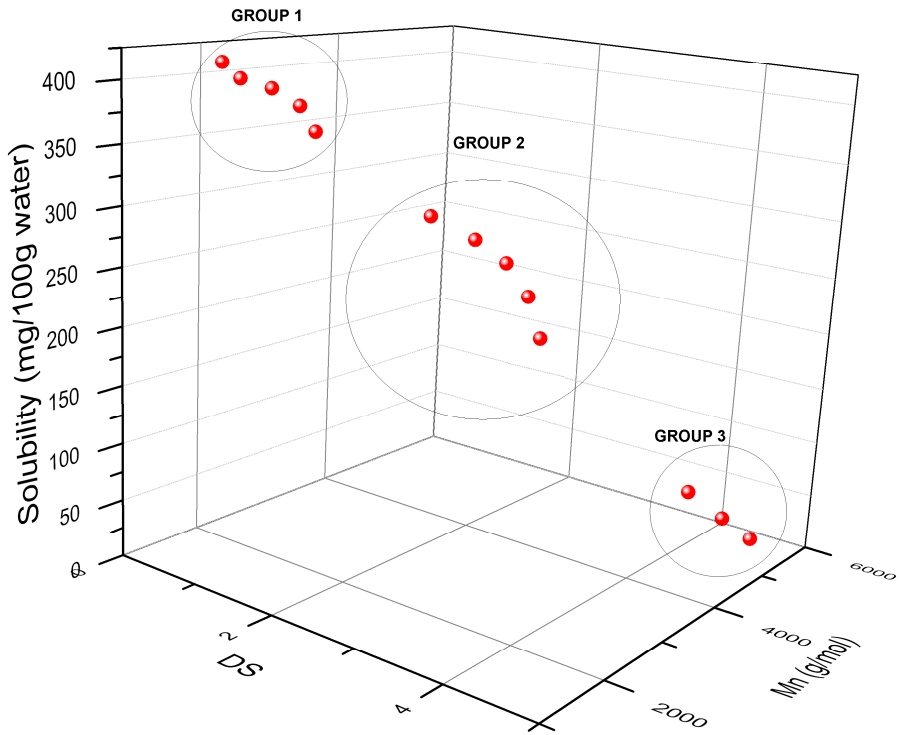


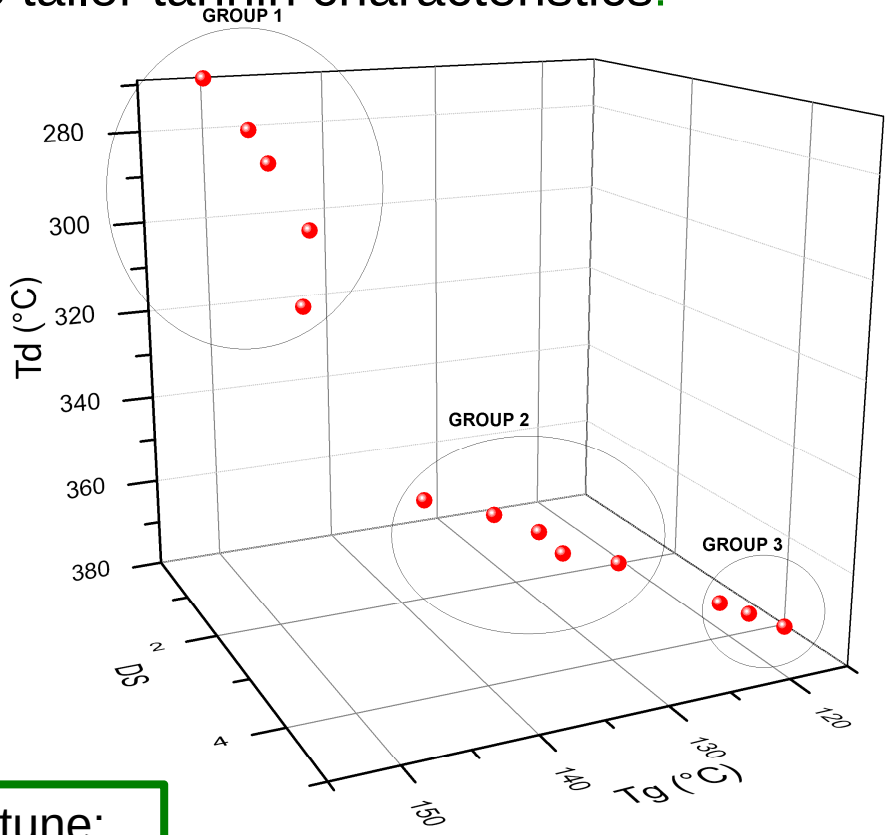
Stoichiometric control of degree of substitution (DS):
Different PO/C15 molar ratios:
0.1:1 to 5:1 → DS 0.1 to 4.7

Source: Garcia et al., Ind. Crops Prod., 2013, 49, 730-739; Garcia et al., Holzforschung., 2014, 68, 411-418

WP4: Foam technology

- Hydroxypropylation as route to tailor tannin characteristics!





Hydroxypropylation as a solution to tune:
- Reactivity and solubility
- Thermal properties and heterogeneity

3 groups (cluster) of HPTs

Source: Garcia et al., Holzforschung., 2014, 68, 411-418

WP4: Foam technology

- Two potential groups of HPTs

  – HPTs with **low DS** (0.1 – 0.7)

    → More adapted for polycondensation with aldehydes (“classical” tannin foaming)

    → Important drawback: low water solubility of HPTs

  – HPTs with **high DS** (4.0 – 4.7)

    → Shows potential as building block for materials based on (poly-) urethane chemistry

    → Newly developed formulation for production of tannin-based foams not applicable

  – For both groups polymerization and cross-linking are being explored

    → Foaming has not been investigated yet

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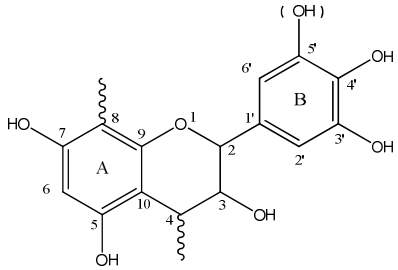

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WP5: Feasibility of syngas production

- Partner:

  Fraunhofer ISE (Germany)

- Objective:
  Asses the feasibility of small scale fixed-bed gasification of tannin-based foams for the production of a tar-free synthesis gas

- Major outcomes:
  - Pyrolysis products from tannin-based foams show similarity to pyrolysis products of wood

    → gasification should be comparable to wood gasification

  - Restriction:
    - Presence of sulphur (corrosion, emissions …)

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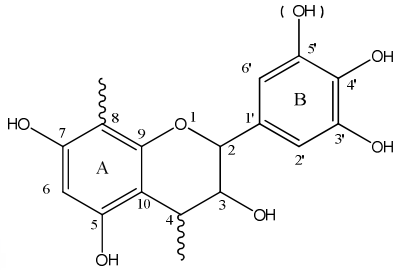
Extraction and purification



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WP6: LCA and techno-economic evaluation

- Partner:

  University of Santiago de Compostela (Spain) → LCA

  nova-Institute (Germany)
  → Techno-economic evaluation

- Objective:

  Assess the environmental performance and techno-economical feasibility of tannin-based foams for use as insulating materials and syngas production

WP6: LCA

LCA follows a “Cradle to grave” perspective (from raw materials to end of life):

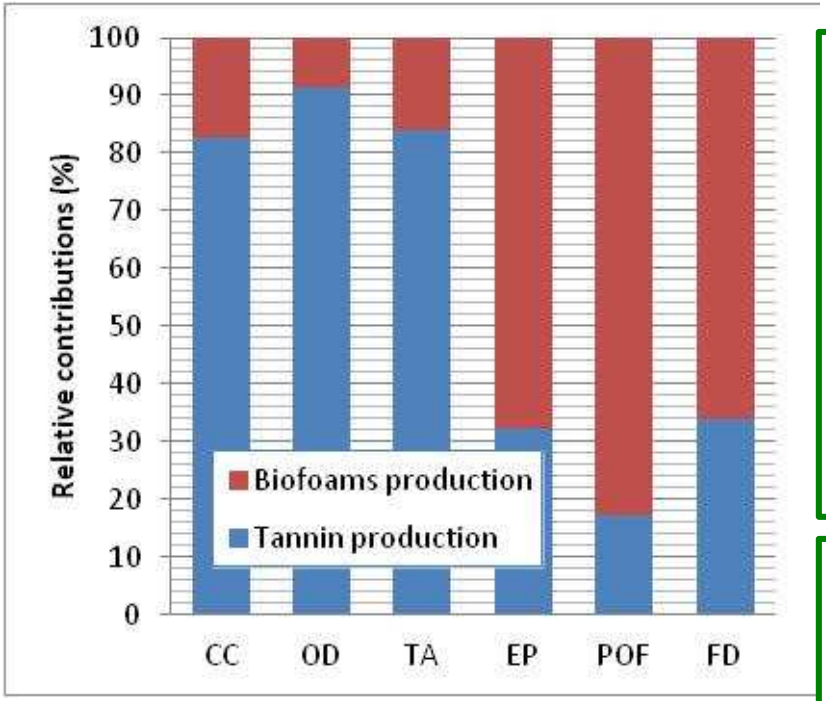
WP6: LCA

A selection of environmental impact categories:

Impact category	
Climate Change	CC
Photochemical oxidant formation	POF
Ozone depletion	OD
Terrestrial acidification	TA
Eutrophication	EP
Fossil fuel depletion	FD

WP6: LCA

Environmental profile corresponding to *Pinus pinaster* based foams



Tannin production:
→ SS1 + SS2 + SS3.1 (large scale)

Main hotspot:

→ Production of **electricity** for the tannin extraction process (extraction, evaporation and tannin drying)

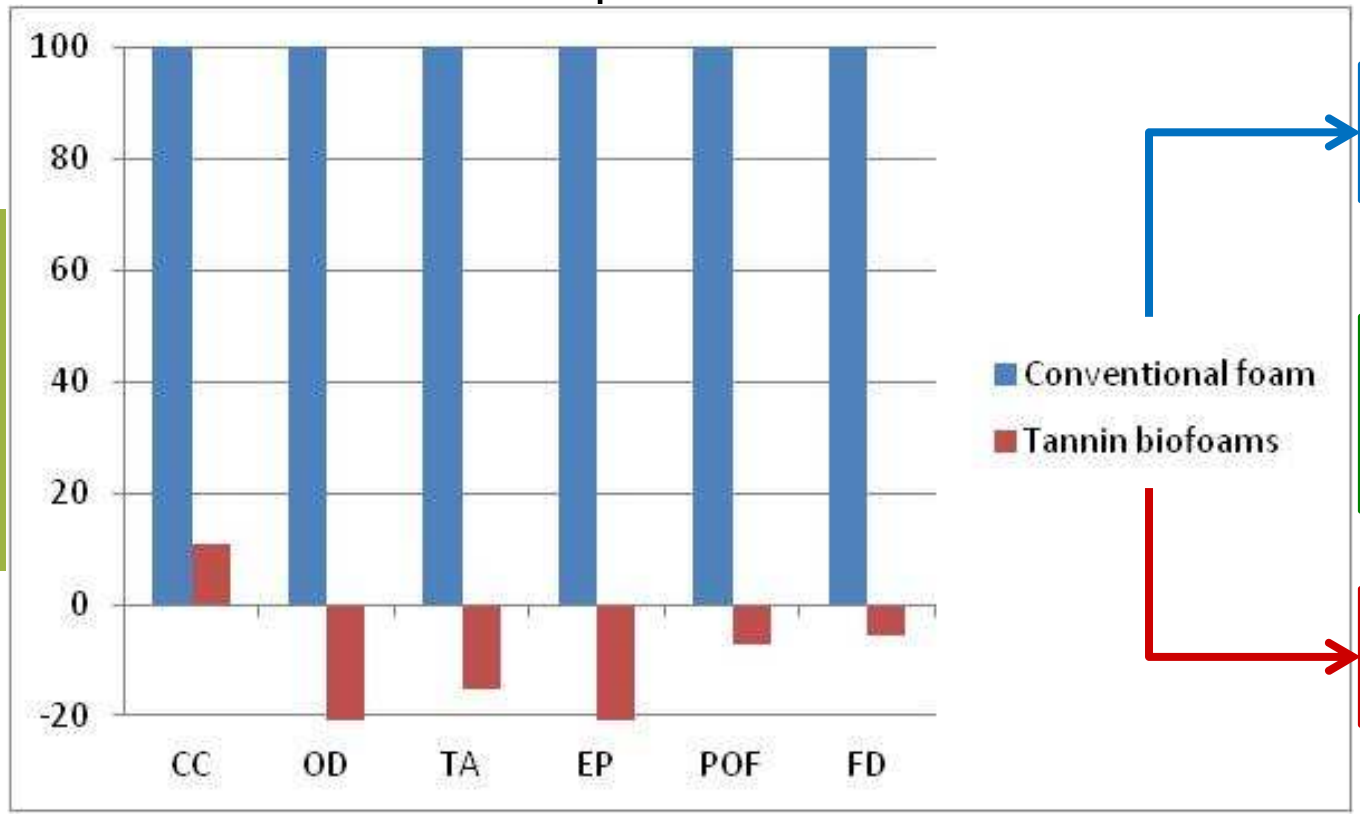
Tannin foam production: SS3.2 (laboratory scale → not optimized)

Major hotspots:

→ Production of **chemicals** for foaming
→ **Emissions** during foaming process (blowing agent)

WP6: LCA

Comparative environmental profile between conventional (PUR) and tannin-based foam production



disposal: **landfill**

Only valid for certain circumstances !

disposal: **bioenergy**

Reductions on environmental profile in all categories due to the use of renewable resources (tannin from bark and furfural) and different disposal.

WP6: Techno-economic evaluation

- **Economic feasibility** of tannin production (still ongoing)
  - → The gap between feedstock price (bark) and target prize for tannin will be determining
  - → Target prize will depend on refinement, quality and application of the tannin

- "**Green premium**"
  - → For the tannin-based foams an opportunity for "green premium" might be given → 10 – 20 % higher prices

WP7: Dissemination activities

- Around 15 reviewed publications until now and presentations at various conferences and exhibitions
- "German High Tech Champion" (GHTC) award 2012 in Green Buildings from the Fraunhofer organization
- 2nd place of the "Innovationspreis Schaumstoffe 2013" from the Fachverband Schaumkunststoffe and Polyurethane e. V.

- **Final workshop** for interested stakeholders planed in May 2015 (Ljubljana, Slovenia)
  - → Presentation of detailed results of the Biofoambark project
  - → Proposition of a strategy for softwood bark and tannin valorization in Europe
  - → Panel discussion with stakeholders
  - → In case of interest contact Prof. Milan Šernek: milan.sernek@bf.uni-lj.si

Conclusions

- Softwood bark as by-product in Europe available but strong competitors (bioenergy)
- Industrial tannin extraction only needs engineering input but purifications methods require further development
- Foam production and modification based on softwood bark tannins successful, but only tested at lab scale
- HPT as new more homogeneous and tunable building block introduced
- Tannin-based foams show potential for syngas production
- LCA indicates environmental credits in comparison to conventional foams
- Work on Techno-economic feasibility not finalized yet

Acknowledgement

- All project partners for enthusiastic participation
- National Funding (Germany):

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aufgrund eines Beschlusses des Deutschen Bundestages

FACHAGENTUR NACHWACHSENDE ROHSTOFFE e.V.

- European framework:

WoodWisdom-Net

ERA-NET Bioenergy

Thank you for your attention

and

see you in Ljubljana!