A process concept to valorize industrial softwood bark to sustainable adhesives and coatings

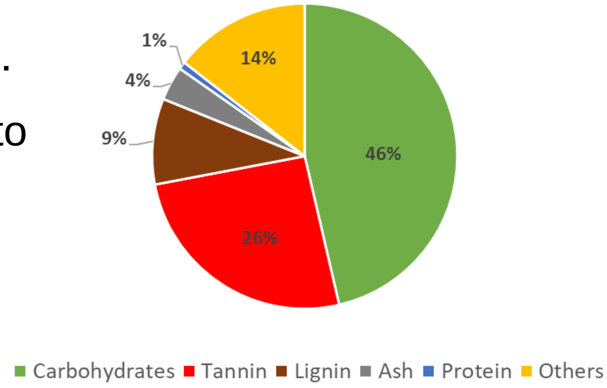
Kalliola, A., Kyllönen, H., Heikkinen, J., Rahikainen, J., Spönla, E., Widsten, P., Tuominen, L., Lahtinen, P, & Borrega, M.

NWBC 2024, Örnsköldvik 15-17.10.2024

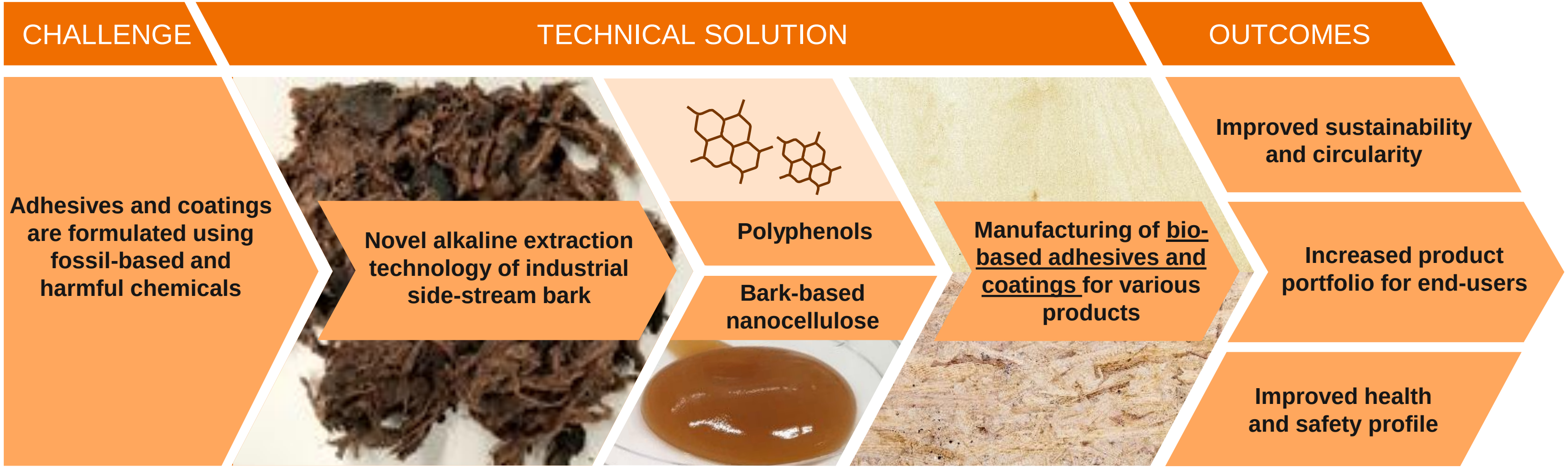
Industrial softwood bark

- More than **14 M tons of industrial softwood bark available in EU**, mostly in Sweden and Finland.
  - Currently industrial bark is combusted in the mills for energy.
- Softwood bark **contains valuable compounds such as tannins and other polyphenols** that can be exploited in a wide range of applications.
- With traditional hot water extraction, the polyphenol yield from European softwood bark is only ≤ 10% (on dry bark).
- Alkaline extraction of bark increases polyphenol yield up to ~25% on dry bark.

Spruce bark composition

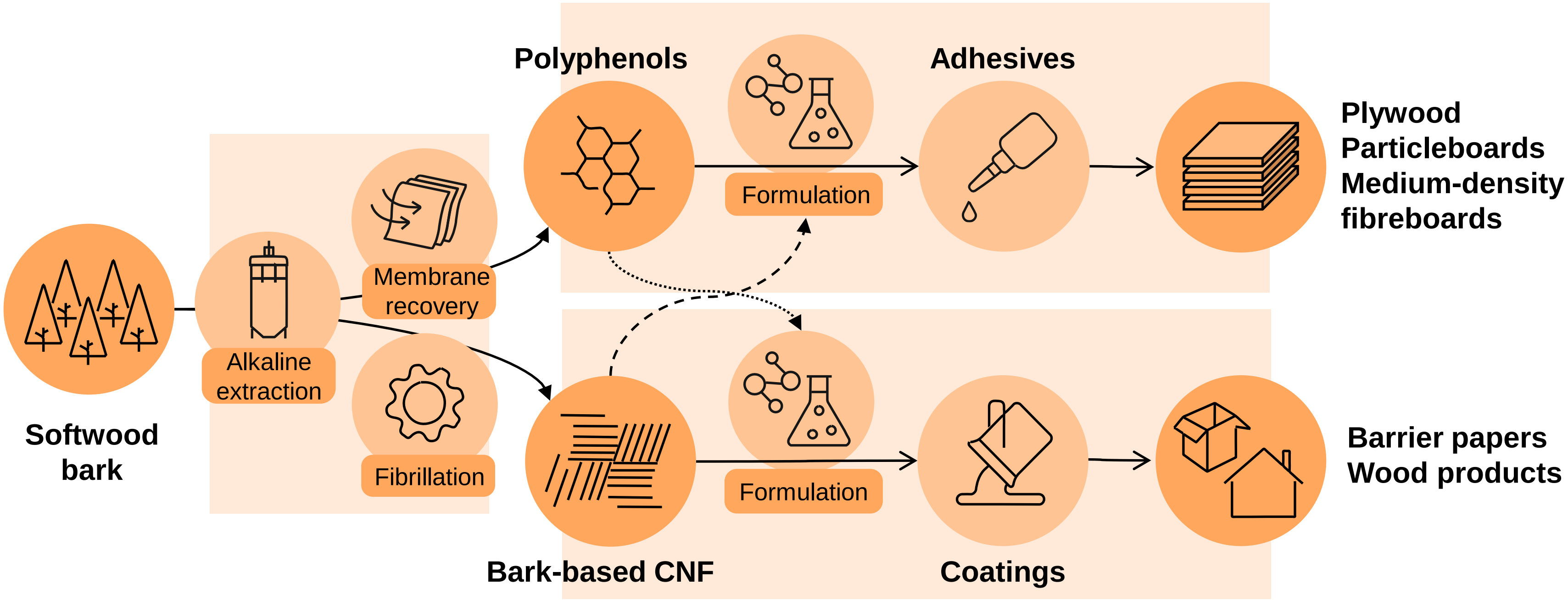


Towards sustainable adhesives and coatings

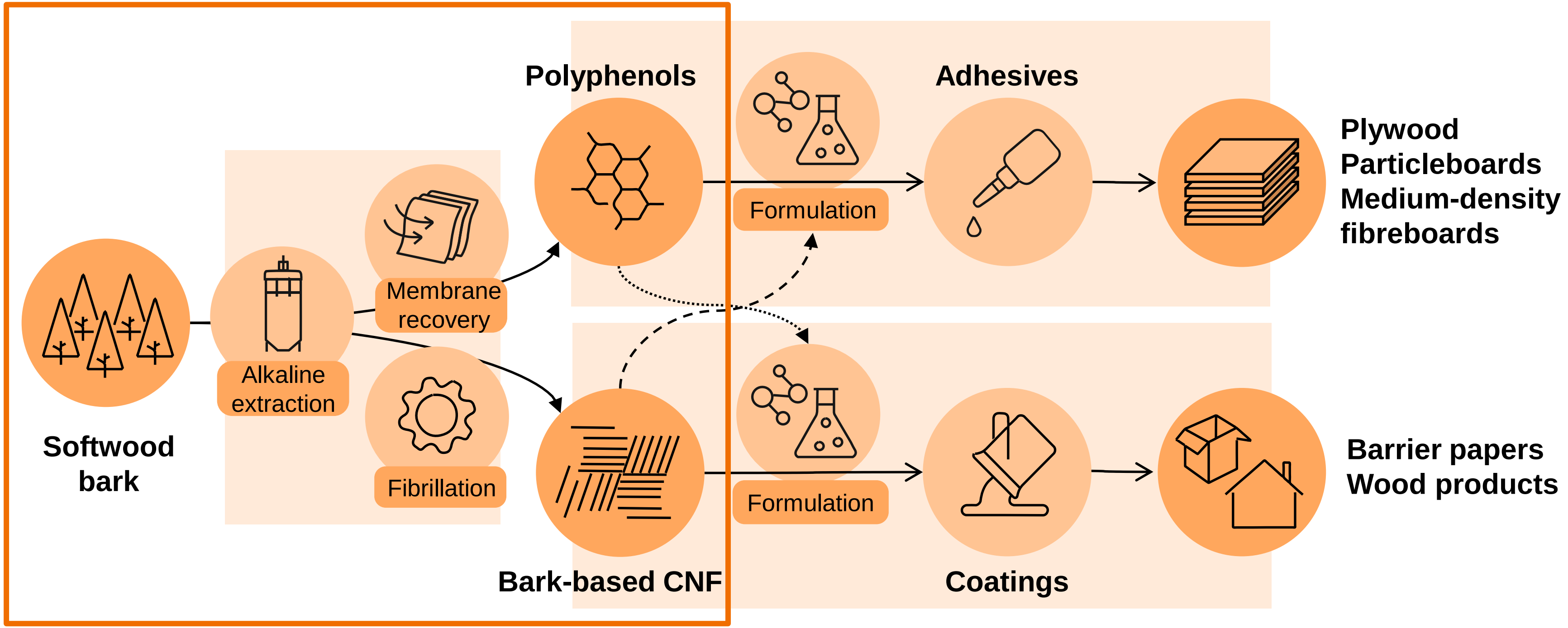


- SuperBark (2023-2027) aims to develop safe, sustainable, and high-performance **>95% bio-based adhesives and coatings** from industrial softwood bark.
- The project results will be applied in a range of industries, including **furniture, construction, transport, and packaging**.

Methodology



Methodology

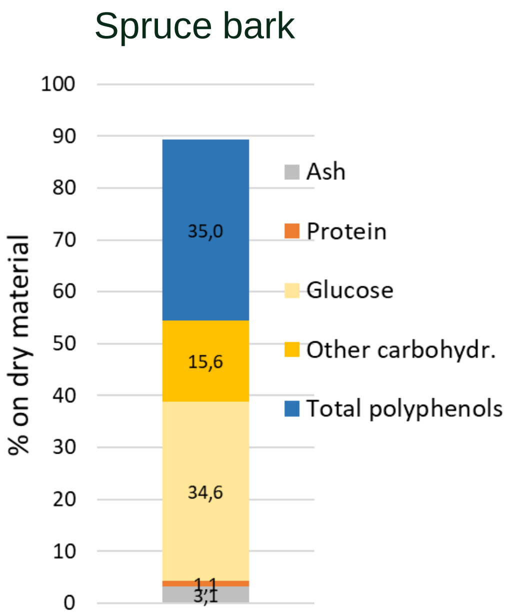


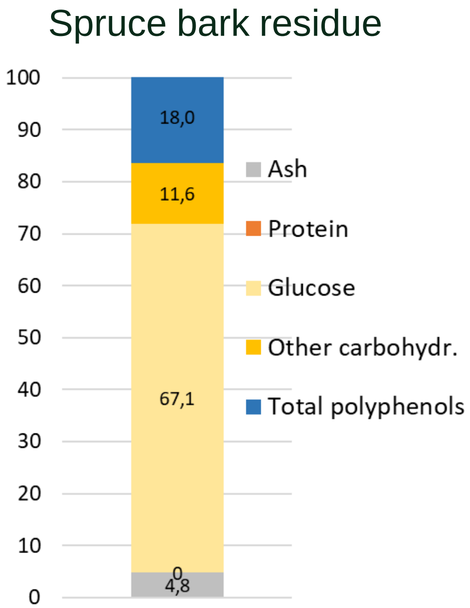
- Production of bark-based components (polyphenols and CNF) could be integrated into a pulp mill.
- By using membranes and omitting the H2SO4 introduction for recovery, it is possible to recycle part of the inorganics (mainly sodium) into the pulp mill and reduce make-up chemical (NaOH) costs.

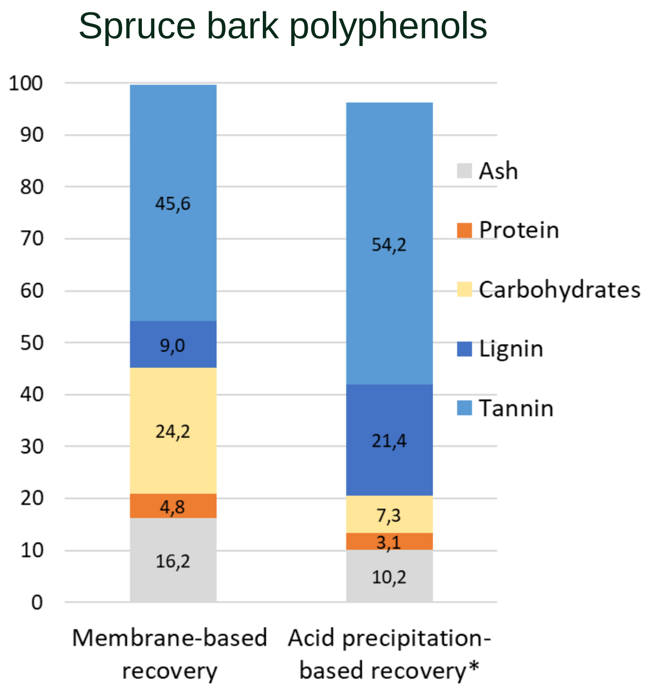
Production of bark-based components

- About 25% of spruce bark can be extracted as polyphenols by alkaline extraction.
- Composition of polyphenols depends somewhat on extraction conditions, also on the recovery method.
- Bark residue (30-50% of spruce bark) is enriched in cellulose, which allows its fibrillation to produce CNF.

Chemical compositions

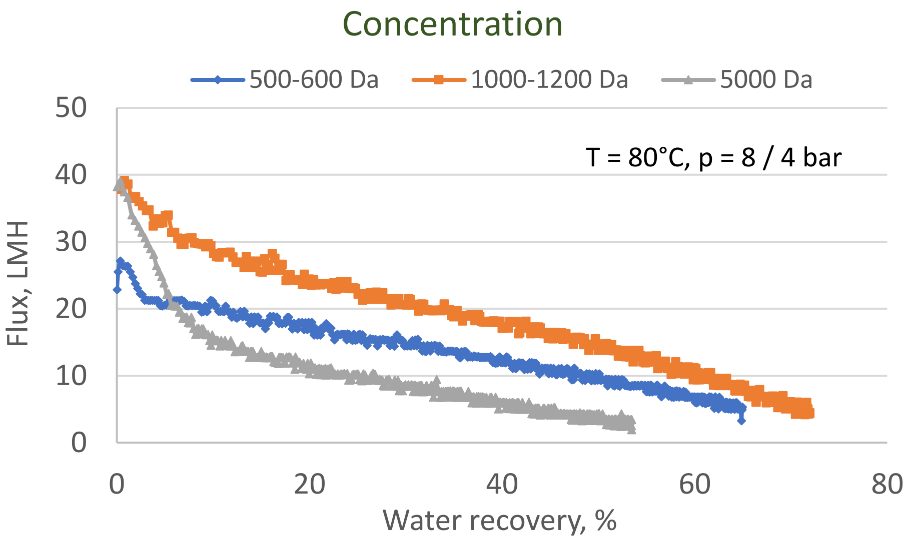


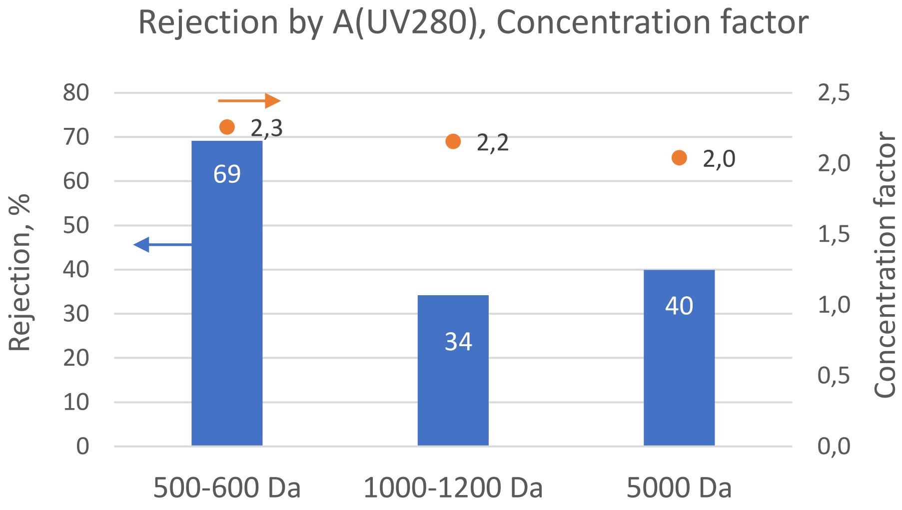




- Alkaline extraction of spruce bark: 160ºC, 25% NaOH on bark.
- Higher purity in polyphenol material by acid precipitation-based recovery.

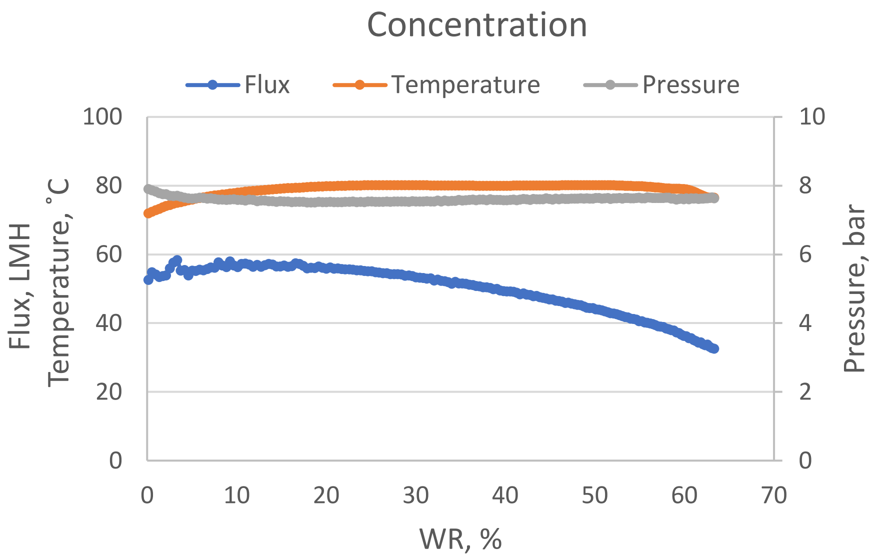
Membrane-based recovery of polyphenols – Membrane screening

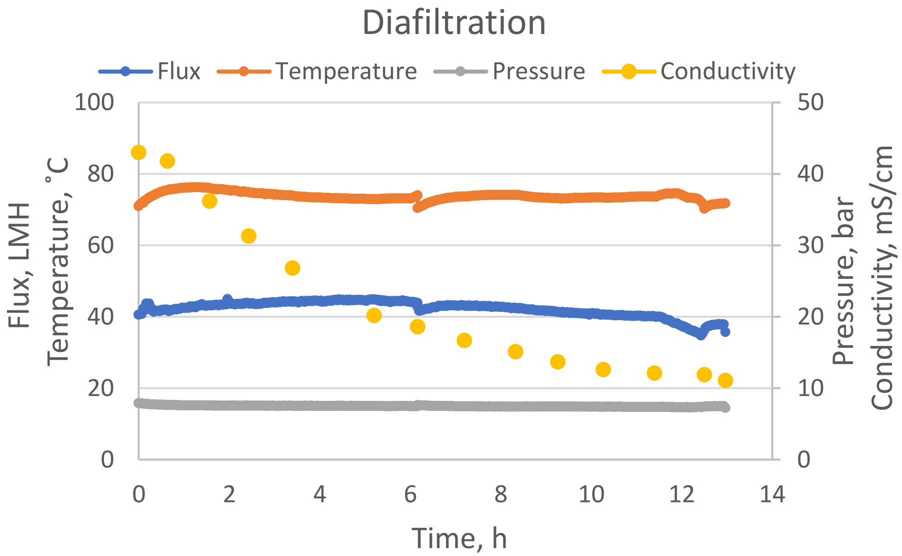




- Polyethersulfone (PES) membranes were screened in small scale (Sterlitech, HP4750X Stirred Cell) for PP recovery from bark alkaline extract (160ºC, 25% NaOH on bark).
- PP recovery yield of 70% was obtained using the tightest membrane with cut-off range of 500-600 Da.

Membrane-based recovery of polyphenols – Large scale trial

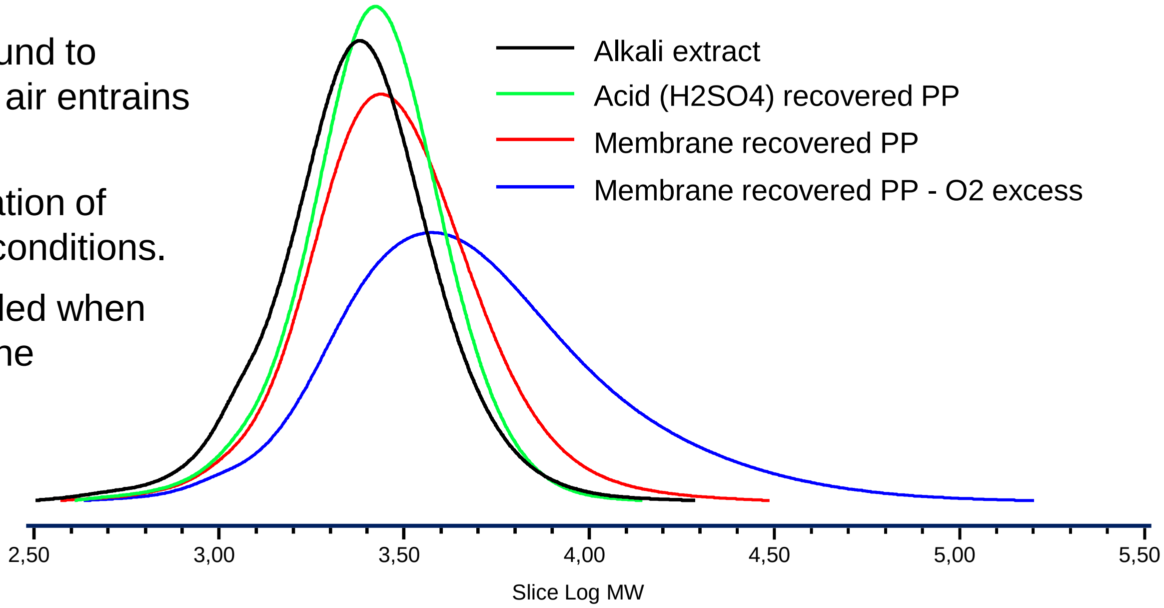




- Large scale polyphenol recovery was done using CR250-filter with membrane cut-off of 500-600 Da.
- Fluxes were in good range.
- CR250 filter set-up allows feeding of excess air into the alkaline extract during the concentration.

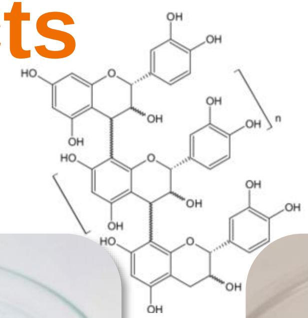
Membrane-based recovery of polyphenols – Molar mass

- Membrane-based recovery was found to increase polyphenol molar mass if air entrains the system during concentration.
  - Oxidative coupling *i.e.* condensation of polyphenols by O2 under alkali conditions.
- Molar mass increase is likely avoided when operating using industrial membrane installations.



Yang, X., et al. (2023), Oxygen mediated oxidative couplings of flavones in alkaline water, https://www.nature.com/articles/s41467-022-34123-w

Polyphenols in adhesives for wood products



Spray-dried polyphenols from spruce bark

Polyphenol-hexamine adhesive

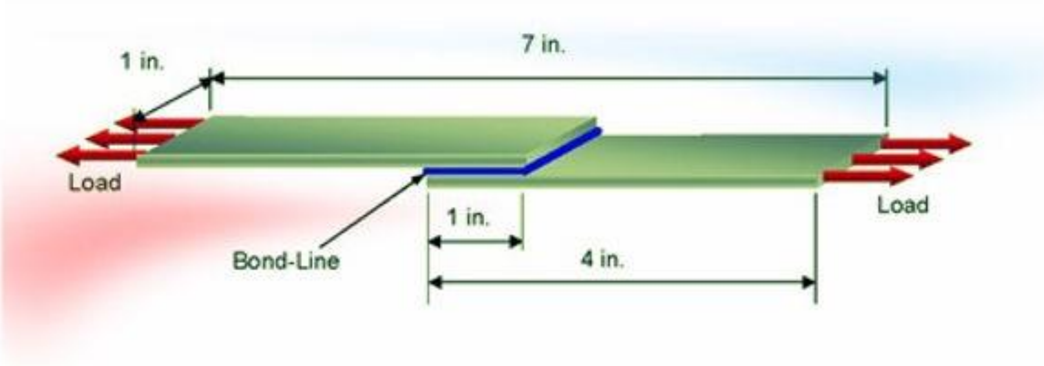
Birch veneer joints (lab)

Birch plywood

- Adhesive formulation with ≥ 95% bio-based content to replace current fossil-based solutions (e.g., PF and UF resins) in plywood, particleboard, and MDF.
- Several bio-crosslinkers to be tested.

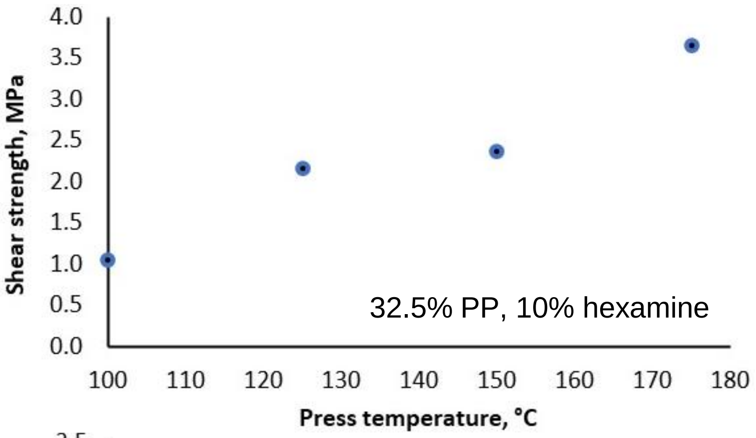
PP-based plywood adhesives

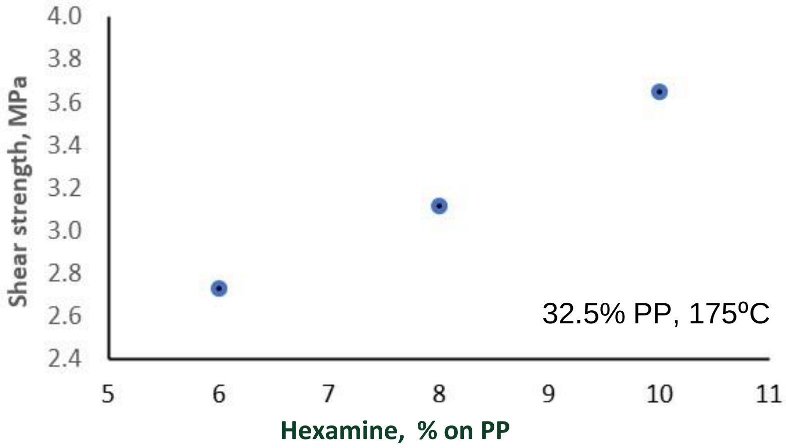
- Polyphenol-hexamine adhesives were formulated with acid recovered PPs dissolved in alkali.
  - PPs extracted from spruce bark at different temperatures (100°C, 160°C, 180°C) were tested.
- The main challenge was the high viscosity that negated solids contents higher than 35%.
- The lowest viscosity and highest solids content were obtained with PPs from alkali extraction done at 160°C.
- Birch veneer lap joints were prepared by hot pressing and tested for dry shear strength (goal is high wet strength after boiling to comply with the EU standards for class 3 plywood).

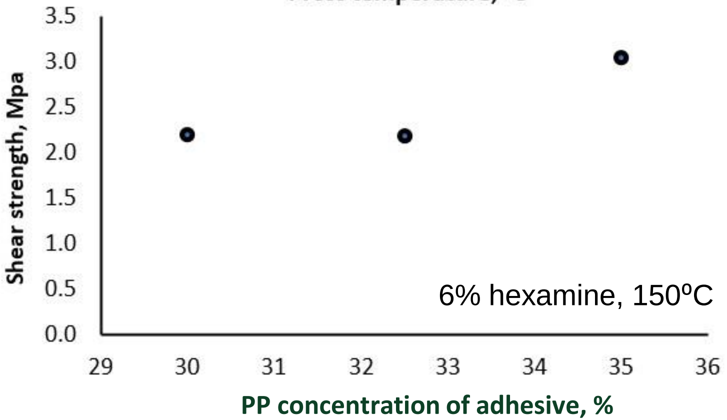


Shear strength testing of veneer lap joint

Shear strength of veneer lap joints bonded with PP-hexamine adhesive







Dry shear strength increases with an increase in

- Press temperature
- Bio-crosslinker (hexamine) dose
- Polyphenol concentration

Effects of press time and pressure to be investigated.

Bark CNF in coatings for wood products and packaging paper (barrier)

Bark CNF paste

Bark CNF based coating formulation

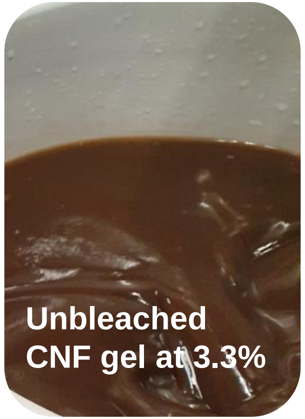
Plywood coating by

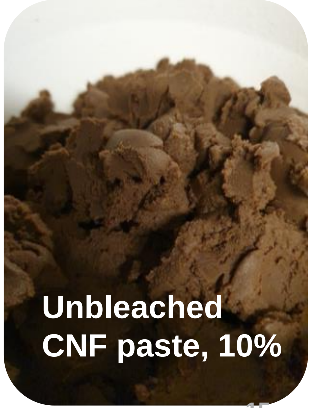
HOLZ FORSCHUNG AUSTRIA

- Coating formulations with ≥ 95% bio-based content to replace current fossil-based solutions.

Production of CNF from bark residue

- Both delignified and unbleached bark pulp was successfully fibrillated to CNF.
- Process included mechanical pre-refining and fibrillation by microfluidizer.
- Bark pulp could be processed at higher consistency (3%) compared to wood pulp.

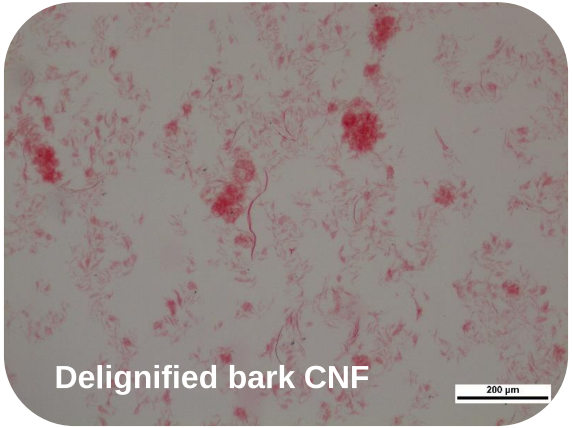


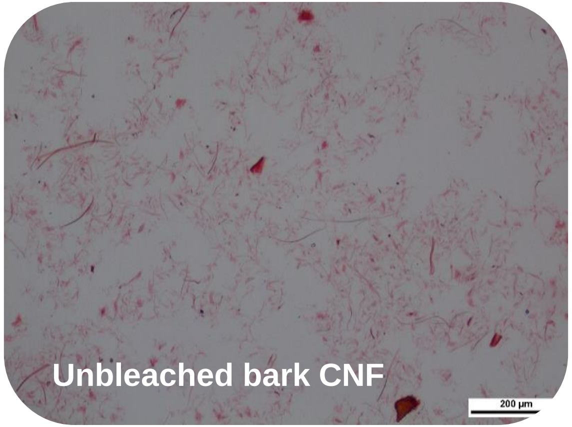


Characteristics of bark CNF grades

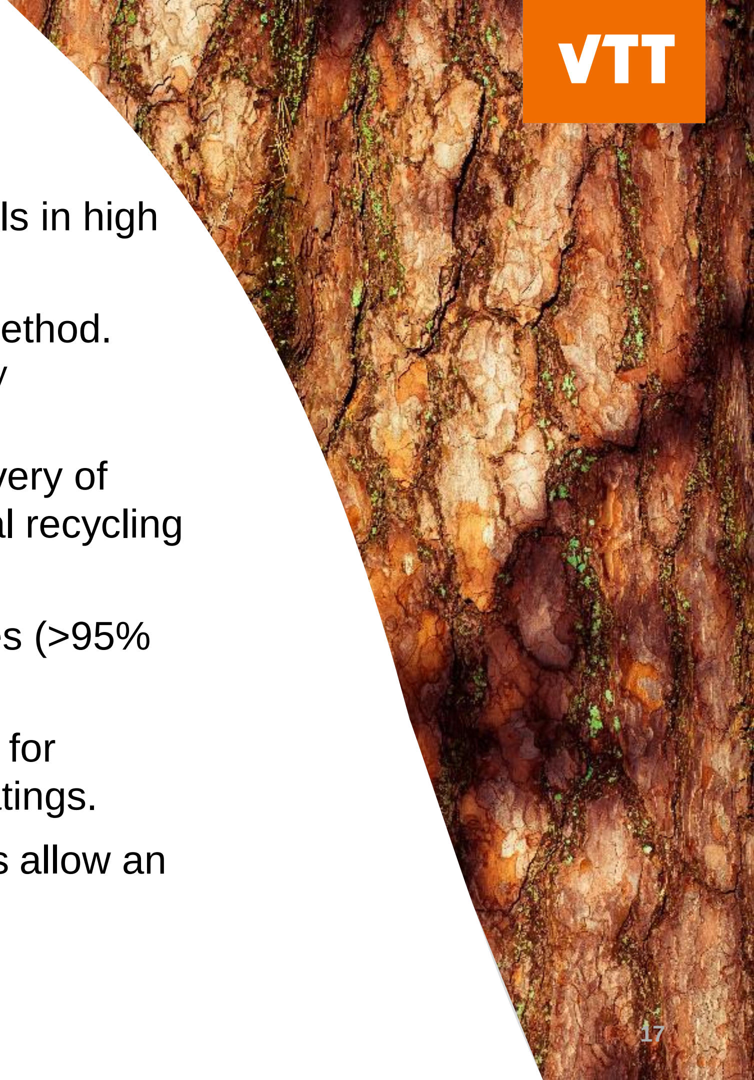
- Delignified bark CNF was more homogenous and had better water holding capacity than unbleached CNF.
- Unbleached CNF contained more flakes, pieces of bark.
- Delignified CNF contained less residual micron-sized fibres (higher degree of fibrillation) and had higher gel strength (yield value) than unbleached CNF.

Bark CNF	Cons. %	Residual fibres pcs/mg	Fines %	Yield value Pa	Visc., 0,5 rpm mPas	Visc., 10 rpm mPas
Unbleached	3,3	2080	99	19	44400	6770
Delignified	1,7	110	100	33	88700	4680





Conclusions



- Alkaline extraction of softwood bark provides polyphenols in high yield (~25% on dry bark).
- Composition of polyphenols depends on the recovery method.
  - Higher purity is reached with acid precipitation-based recovery
  - Membrane-based recovery retains carbohydrates
- Alkaline extraction coupled with membrane-based recovery of polyphenols omits H2SO4 introduction and allows partial recycling of sodium if being integrated in a pulp mill.
- Initial results of polyphenol-hexamine plywood adhesives (>95% bio-based) show potential.
- Bark residue from the extraction is a viable raw material for production of CNF which can be used for bio-based coatings.
- Full utilization of bark as well as smart process concepts allow an economic process and cost competitive products.

Acknowledgements

VTT

SuperBark – Safe and sustainable adhesives and coatings from industrial softwood bark

Super Bark

The project is supported by the Circular Bio-based Europe Joint Undertaking and its members.

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or CBE JU. Neither the European Union nor the CBE JU can be held responsible for them.

Circular Bio-based Europe Joint Undertaking

Co-funded by the European Union

Bio-based Industries Consortium

beyond
the obvious

anna.kalliola@vtt.fi
+358 40 5885748