Characterisation of industrial barks for their tannin contents for further green-wood based adhesives applications

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INTRODUCTION
Context and motivations

WOOD PANELS & FIBREBOARDS INDUSTRY

- France: 6.7 Millions m³ of wood panels produced in 2005 (2nd largest production in EU)
- 70-100 kg/m³ of adhesives in panels
  - ⇔ 5-12%, w/w (~500 000 T/y)
- Usually based on urea-formaldehyde mixture (amino resin UF & MUF)
- Recently, formol has been classified as a probable human carcinogen and its use could be limited in the near future

➤ Need to develop new and environmentally friendly adhesives
WOOD PANELS & FIBREBOARDS INDUSTRY

✓ Alternatives of formol-based adhesives
  ▪ Used of scavenger and lower the qty of formol in the formulation (molar ratio F/U ↓)
  ▪ Phenolic resin (phenol+ formol) => less formol released
  ▪ Isocyanate-based adhesives (pMDI) but costly and could also be restricted
  ▪ Partial substitution by green chemicals:
    Binder (protein) + Plasticizer (from bio-products)

⇒ Natural phenols: tannins already used in few panel & board productions
INTRODUCTION
Context and motivations

TANNINS

✓ Wood adhesives from condensed flavonoid tannins (*catechine*)
  ▪ Acacia (Mimosa), Quebracho, Pine (*pinus radiata*) tannins in South Africa, South America and Australia, Japan …
  ▪ Tannin-based adhesives: partial or total substitution of phenol in phenol/formol formulation,
    » tannin/hexamine or tannin/iso-cyanate
  ▪ World production: 200 000 T/year ➔ still too low for large industrial use

✓ Limitation:
  - not really industrial tannin extraction in Europe,
  - reactivity of tannin / nature (polymerisation duration, adhesive properties)
INTRODUCTION
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TANNINS

✓ Tannin from wood-bark residues from pulp mill
  ▪ Bark ~7-12 % w/w of the tree: std pulp mill (100 000 T/y pulp) → ~10 000 T/y barks
  ▪ In pulp mill: bark is used for energy recovering
  ▪ Softwood barks are especially rich in condensed flavonoid tannins

✓ Objectives
  ▪ Study the potential of several industrial wood barks wastes from pulp mills for tannin extraction, and further for their adhesive properties,
  ▪ Develop aqueous extraction of tannin, easy industrial scale-up
Tannin Extraction from pulp mill bark wastes

- Optimisation of aqueous extractions of condensed tannins
  - alkaline conditions or sulfite are the chemicals preferred for tannin extraction
  - urea as a nucleophile improves tannin extract quality
  - A too high temperature increases extraction yield but leads to worse adhesives properties
  - Therefore, extraction conditions, such as temperature, time, L/V ratio and bark pre-treatment need also to be set

- Analytical characterisation of tannin extracts using different spectrophotometric analyses and Pyr-GC/MS
MATERIALS AND METHODS

Tannin Extraction and characterisation

✓ Bark samples
  - 5 different barks were sampled in pulp mills:
    - spruce, maritime pine, aleppo pine, douglas fir and eucalyptus
  - Dryness of fresh wood barks was between 40% to 70%.
  - stored at −18°C, freeze dried and milled (particles Ø <1mm) before organic extraction.
  - In case of large aqueous extraction: air-dried and ground (particles <3 mm
MATERIALS AND METHODS

Tannin extraction and characterisation

✓ Extraction

- **Analytical organic extraction**
  - 250 mg of o.d. bark were extracted with 2x5 ml of acetone/water (70/30, v/v) in a ultra-sonic bath for 20 minutes at 20°C. After centrifugation, the supernatant was collected.

- **Aqueous extraction**
  - 100 g of o;d. bark were extracted by 500 ml of aqueous solution at 75°C during 1h, under reflux. The extract was filtrated on sintered glass N°1 before analysis.
  - Four different aqueous solution were tested:
    - aqueous solution: tap water,
    - urea solution containing 2% of urea
    - urea/sulphite solution containing 2% urea and 2% sulphite
    - sulphite/carbonate solution containing 2% sulphite and 0.5% carbonate
MATERIALS AND METHODS

Tannin extraction and characterisation

✓ Spectroscopic analyses
  - **Phenolic compounds**: Folin-Ciocalteu method
    Tannic acid was used as standard. 0.5 ml of 1N Folin-Ciocalteu reagent and 2.5 ml of 2% sodium carbonate solution are added to 0.05 – 1 ml of extract. Absorbance is measured at 725nm after 40 min of reaction.
  - **Total phenols content**: UV measurement at 280nm as described by Antoine et al. (2004) using mimosa tannin as standard.
  - **Condensed tannins** were determined according to butanol/HCl method, using catechine and mimosa tannin as standards.

✓ Pyr-GC/MS analysis
  - 0.1 – 0.3 mg of dried extract
  - PyroLab 2000, 500°C/4s,
  - GC/MS: HP1 (30 m x 0.25 mm, film thickness 0.25 µm), Temperature prog: 50°C (1min) – 5°C/min – 300°C
### RESULTS: Tannin Extraction

#### ANALYTICAL EXTRACTION & CHARACTERISATION

Characteristic of acetone/water (70/30, v/v) extracts of wood barks

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<tr>
<th>(g/100g of o.d. bark)</th>
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\(^1\) eq. mimosa tannin, \(^2\) eq. tannic acid, \(^3\) eq. catechine
\(^*\) after 0.45µm glass membrane filtration
RESULTS: Tannin Extraction

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Highest extraction yields for **aleppo pine, spruce** and **douglas fir** barks
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* after 0.45μm glass membrane filtration

Highest extraction yields for **aleppo pine**, **spruce** and **douglas fir** barks

Highest phenol/phenolic contents in **aleppo pine**, **spruce** and **douglas fir**
## RESULTS: Tannin Extraction

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\(^*\) after 0.45µm glass membrane filtration

Highest extraction yields for **pine, spruce** and **douglas fir** barks

Highest phenol contents in **spruce, douglas fir** and **allepo pine**

1/3 to 1/2 of bark extracts were constituted of condensed tannins (maritime pine and eucalyptus contain much less condensed tannins)
RESULTS: Tannin extraction

OPTIMISATION OF AQUEOUS EXTRACTION

Highest extraction yield (10-15%): Aleppo pine & Douglas fir
Urea/sulphite
RESULTS: Tannin extraction

OPTIMISATION OF AQUEOUS EXTRACTION

Urea/sulphite extracts: high total phenol contents

Highest phenolic contents: **aleppo pine** and **douglas fir**
RESULTS: Tannin extraction

OPTIMISATION OF AQUEOUS EXTRACTION OF INDUSTRIAL BARKS

Urea/sulphite in favor of condensed tannins extraction
RESULTS: Pyr-GC/MS

Pyr-GC/MS: structural elucidation of tannins

Condensed Tannin

Condensed Tannin

Extender Unit "ACB":
- Epicatechin: R₁=OH, R₂=H
- Epigallocatechin: R₁=R₂=OH
- Epicatechin: R₁=H, R₂=OH
- Terminal Unit "DFE":
  - Catechin: R₁=OH, R₂=H
  - Gallolatechin: R₁=R₂=OH
  - Afzelechin: R₁=R₂=H

Condensed Tannin

Condensed Tannin

Flavanol

Flavanol

R₁=OH, R₂=H, R₃=OH:
- Catechin (FC)
- Epicatechin (FC)

R₁=OH, R₂=OH, R₃=OH:
- Gallolatechin (PD)
- Epigallocatechin (PD)

R₁=H, R₂=H, R₃=OH:
- Afzelechin (PF)
- Epiafzelechin (PF)

R₁=H, R₂=H, R₃=H:
- Guibourtinidol
- Epiguiibourtinidol

R₁=OH, R₂=OH, R₃=H:
- Fisetinidol
- Epifisetinidol
RESULTS: Pyr-GC/MS

Pyr-GC/MS of a reference sample

3. Mimosa

(1) catechol ⇔ A ring
(2) Resorcinol ⇔ B ring
(3) pyrogallol ⇔ A ring

Tannin structures:
as Catechine et/ou Epicatechine (catechol B ring and resorcinol A ring)
and Epigallocatechine (pyrogallol B ring and resorcinol A ring).
RESULTS: Pyr-GC/MS

Aleppo pine extracts

Water extract

Phenol A ring
Catechol B ring

Extr H2O Alep 150mcg sur HP1
500 deg 4 s

04-Dec-20
500 deg 4
PC1208: 17

15:52:36
Extr H2O Alep 150mcg sur HP1
500 deg 4 s

15:5
Scar
1.
RESULTS: Pyr-GC/MS

Aleppo pine extracts

- Water
- + sulfite/carbonate
- + urea
- + urea/sulfite
RESULTS: Pyr-GC/MS

Douglas fir extracts

04-Dec-2008
Extr H2O Douglas 20mg sur HP1
500 deg 4 s

02-Apr-2009
Douglas extr. H2O 5CB
500 deg 4 s

COST FP0904_29 - 07-Apr-2009 - F.BERTAUD (21)

02-Apr-2009
Douglas extr. H2O 5CB
500 deg 4 s

COST FP0901 - 20.08.2010 - F.BERTAUD (21)

08-Dec-2008
Extr water Douglas 20mg sur HP1
500 deg 4 s
RESULTS: Pyr-GC/MS

Summary

In all aqueous extracts, but especially urea+sulfite

**Douglas bark tannin** ()
phenol type A ring \((R_1 = H)\)
catechol type B ring \((R_1 = OH)\) rich

**Aleppo pine bark** (all aqueous extracts)
phenol type A ring \((R_1 = H)\)
catechol type B ring \((R_1 = OH)\) rich
ADHESIVE PROPERTIES (LERMAB)

Water: Euca, spruce, douglas fir
Urea: Aleppo pine
Urea/sulphite: spruce, douglas, aleppo pine
Sulphite/carbonate: aleppo pine, maritime pine
RESULTS: Adhesives properties

ADHESIVE PROPERTIES (LERMAB)

Water: Euca, spruce, douglas fir
Urea: Aleppo pines
Urea/sulphite: spruce, douglas, aleppo pine
Sulphite/carbonate: aleppo pine, maritime pine
LARGE-SCALE EXTRACTION

✓ Large Aqueous Extraction
  ▪ 10 kg eq.sec, L/V = 5 L / 1 kg
  ▪ coarse milled bark + extraction 2% urea + 2% sulphite
  ▪ agitated thermo-regulated reactor 75°C/1h
  ▪ centrifugation : tannin extract + extracted barks

✓ Aleppo pine, spruce and ‘mill blend’ (20% black pine + 20% maritime pine + 30% norway pine + 10% aleppo pine + 15% spuce + 5% douglas fir)

→ tannin extracts for the preparation of adhesive formulations and production of wood panels at pilot-scale
LARGE SCALE STUDY
## LARGE SCALE STUDY: Preliminary results

<table>
<thead>
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<th>Extract Yield (%)</th>
<th>Prepared extract (kg)</th>
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<tbody>
<tr>
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<td>95.6%</td>
<td>27%</td>
<td>2.8</td>
</tr>
<tr>
<td>Aleppo pine</td>
<td>83.5%</td>
<td>46%</td>
<td>2.5</td>
</tr>
<tr>
<td>Mill Blend</td>
<td>84.7%</td>
<td>33%</td>
<td>2.8</td>
</tr>
</tbody>
</table>

- Higher amount of extract at large scale
  - >> Lab-scale
  - ≥ Acetone/water extraction

?? Quality and Reactivity
CONCLUSIONS

BARK EXTRACTION : TANNIN UTILISATION in ADHESIVES

- Aqueous extraction are well suitable and easily to up-scale
  Water + 2% urea + 2% sulphite

- Softwood species : Spruce, Allepo pine, Douglas fir
  Extraction yield of 10-15%

=> An aqueous extraction of softwood barks in pulp mill before heat recovering can be realistically foreseen

- Economical Evaluation
  - Adhesives 300 $/ T, Tannin extract 600 $/ T
  - Bark / Heating recovery : 20 €/T
  => Tannin recovery =10 % of initial bark => 1 000 T/y tannin
ACKNOWLEDGEMENTS

- ADEME financial support (French Environment and Energy Management Agency)
- TEMBEC R&D Kraft (now FIBRE EXCELLENCE)
- ENCE-Pontevedra