Bio-cascading of Heat Treated Wood After Service Life to Obtain Lignocellulosic Derivatives

Eduardo Robles, René Herrera, Oihana Gordobil, Jalel Labidi

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Aims
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Source: MAGRAMA (Spain)
Heat-treatment of wood is an effective method to enhance biological durability and physical stability of wood with a low environmental impact.

The target is promote native and non-durable wood by improving its properties, and therefore adding economic value to Pine wood.
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Wooden deck.
Façade, San Sebastián.
Building façade, Bilbao.
Hospital façade, Madrid.
Park floor, Bilbao.

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The heat-treatment was performed at 212 °C in an airtight chamber under reducing atmosphere (N₂) and steam for a period between 60 and 70 h, until all stages of the modification process were achieved according to the industrial standards (Termogenik®, Spain).
Heat-treated samples

Accelerated aging
Based on a modified EN 927-6:2007

15 hours submerged in distilled water at 20 kPa
9 hours dried in a convection oven at 75 °C
2.5 hours of UV-A lamp

40 cycles
1060 hours
## Physical Properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial</th>
<th>Artificial weathering</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ρ [g cm(^{-3})]</td>
<td>MC [%]</td>
</tr>
<tr>
<td>Pine</td>
<td>0.59 ± 0.02</td>
<td>11.02 ± 0.10</td>
</tr>
<tr>
<td>T-Pine</td>
<td>0.44 ± 0.01</td>
<td>6.07 ± 0.08</td>
</tr>
</tbody>
</table>

\(^1\)control time 0; \(^2\)Artificial weathering 40 cycles
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**Cellulose**

**Hemicelluloses**

**Lignin**

**Extractives**
Waxes, resins, fatty acids, etc...

*Pinus radiata* L  
Thermotreated
Chemical composition

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lignin [%]</th>
<th>α-Cellulose [%]</th>
<th>Hemicellulose [%]</th>
<th>Extracts [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine</td>
<td>27.65 ± 1.24</td>
<td>45.15 ± 1.36</td>
<td>23.61 ± 1.55</td>
<td>2.85 ± 0.24</td>
</tr>
<tr>
<td>T-Pine</td>
<td>40.20 ± 2.04</td>
<td>41.48 ± 2.04</td>
<td>12.89 ± 1.06</td>
<td>4.77 ± 0.88</td>
</tr>
</tbody>
</table>

- Lignin content to be valorized over 40 %
- High cellulose content → Cellulose platform valorization
- Lower hemicelluloses → Degradation
- Higher extracts content due to chemical reconfiguration
Considerations
Hydrothermal treatments of wood can be considered an autohydrolysis process, since different cycles varying temperature and humidity inside an inert (N₂) atmosphere induce the degradation of arabinose and the cleavage of acetyl groups of hemicelluloses (Rangel et al., 2016).

The degradation of wood by fungi has been studied intensely for many years due to its importance in preservation of in-service wood and nutrient cycles of forest ecosystems. Nowadays, the reasons for the improvements in the resistance of hydrothermal wood against fungal decay are discussed and are focused on the fact that pyrolytic degradation of material involves a decrease of thermally unstable components of the wood such as the polyoses present in the hemicellulosic fraction, in addition to the volatilization of some extractive compounds (Herrera et al., 2015).

Since the solid phase from autohydrolysis can be subjected to further processing (for example, delignification to separate cellulose and lignin), mild autohydrolysis can be conceived as the first step of a possible multi-stage process for LCM utilization (Garrote et al., 2002).
Pathway
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Pulping

Process
Sodium carbonate
Sodium hydroxide
Sodium sulfite
Kraft
Sulphite
Soda
Ethanol
Methanol
Acetone
Butanol
Formic acid

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World Bleached Chemical Pulp Production

![Graph of World Bleached Chemical Pulp Production](www.aet.org)
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Bleaching Stages

Process
Chlorine
Sodium hypochlorite
Chlorine dioxide
Extraction with sodium hydroxide
Oxygen
Alkaline hydrogen peroxide
Ozone
Chelation (metal removing)
Enzymes (xylanase)
Peracids (peroxy acids)
Sodium dithionite (sodium hydrosulfite)

Letter designation
C
H
D
E
O
P
Z
Q
X

TCF ECF
Process Design

Total Chlorine Free Bleaching

Spent Black Liquor

Bleaching side-streams

Bleached pulp
Potential valorization

2 vol water pH:2

Acidification to pH:2

Precipitation

Lignin
Potential valorization

Cellulose

Low valuable chemicals
Results
Untreated pine sample
Treated pine sample
Treated pine sample (weathered)
Treated pine sample (weathered) + Organosolv
Organosolv + Bleaching sequence
Cellulose and lignin after bleaching sequence

- Precipitated lignin
- Bleaching side-stream
- Refined cellulose
- Precipitated lignin

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<table>
<thead>
<tr>
<th>Raw material</th>
<th>$Y_0$ (%)</th>
<th>$Y_{B1}$ (%)</th>
<th>$Y_{B2}$ (%)</th>
<th>$Oy^1$ (%)</th>
<th>$Ry^2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine</td>
<td>13.30</td>
<td>5.57</td>
<td>1.95</td>
<td>20.82</td>
<td>75.32</td>
</tr>
<tr>
<td>Pine Th-202</td>
<td>22.54</td>
<td>9.22</td>
<td>4.94</td>
<td>36.71</td>
<td>91.32</td>
</tr>
</tbody>
</table>

$1$ $Oy$ corresponds to overall yield, the amount of lignin obtained related to the biomass used.

$2$ $Ry$ corresponds to relative yield, the obtained lignin compared to the lignin content as obtained from TAPPI methods.

- High recovery yield for Th-202 Pine: ~90%
- In the 2$^{nd}$ bleaching step, lignin recovery was considerably low
- Cascade process: The lower amount is available, the more difficult is extracted, as it can be seen for both pine samples

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# Bio-cascading of Heat Treated Wood After Service Life to Obtain Lignocellulosic Derivatives

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## Table of Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>AIL (%)</th>
<th>ASL (%)</th>
<th>Sugars (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine O</td>
<td>85.19 ± 0.88</td>
<td>2.51 ± 0.51</td>
<td>6.03 ± 0.32</td>
</tr>
<tr>
<td>Pine B1</td>
<td>81.49 ± 2.74</td>
<td>1.46 ± 0.19</td>
<td>10.47 ± 1.24</td>
</tr>
<tr>
<td>Pine B2</td>
<td>76.19 ± 1.87</td>
<td>2.83 ± 0.74</td>
<td>11.67 ± 2.11</td>
</tr>
<tr>
<td>Th-212 Pine O</td>
<td>89.63 ± 2.73</td>
<td>2.85 ± 0.92</td>
<td>2.67 ± 1.32</td>
</tr>
<tr>
<td>Th-212 Pine B1</td>
<td>84.79 ± 2.68</td>
<td>2.87 ± 0.07</td>
<td>8.97 ± 2.75</td>
</tr>
<tr>
<td>Th-212 Pine B2</td>
<td>79.99 ± 1.87</td>
<td>2.16 ± 0.29</td>
<td>12.32 ± 2.34</td>
</tr>
</tbody>
</table>

AIL: Acid Insoluble Lignin  
ASL: Acid Soluble Lignin
Conclusions
The initial chemical composition of Monterey pine (*Pinus radiata* L) as well as its availability makes this biomass waste capable to be valorized into high value-added product by biorefinery processes, not only based on its high cellulose content, but also the lignin, which is neglected through the cellulose purification process.

High recovery yields for lignin can be achieved. The extraction in the 1st bleaching stage supposed 36% and 20% of the total lignin extraction for Th-212 pine and untreated pine respectively, justifying the lignin extraction even in the bleaching stages.

Higher purity lignin was obtained for Th-212 pine than untreated pine, which presented greater sugar impurities.

As summary, Th-212 pine presented higher lignin content, that is easier to extract, with higher purity and better properties for its further valorization.
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Current Status

✓ Chemical characterization of wood samples.
✓ Procedure design for wood revalorization after accelerated weathering.
✓ Lignin and cellulose valorization after pulping-bleaching train sequence.
Upcoming analysis

- Polysaccharide quantification (HPLC)
- Inorganic content quantification (TGA)
- Molecular size comparison (GPC)
- Lignin monomer quantitation (Py–GC–MS)
- Cellulose crystallinity (XRD/CP-MAS $^{13}$C NMR)
References

Thank you!

Eskerrik asko

Děkuji
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