Biolignin™, a renewable and efficient material for wood adhesives

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In wood and lignocellulosic plants, cellulose is today the only valuable component.

Sugars from hemicelluloses and lignin are used today for energy purposes with a low calorific value for a very simple reason: chemical and thermochemical pulping, steam explosion, mineral acid hydrolysis degrade this macromolecules.

Impossible to be competitive with oil for biofuels and biosourcing for chemical industry.

The CIMV process™ solves this very old problem and Lignin...becomes Biolignin™
CIMV PROCESS

Raw Material
(wood, straw, bagasse, …)

Mechanical conditioning

Organic refining

Sugars & Lignin

CIMV 3

Organics acids recycling

Cellulose

Delignification

Deacidification

Washing

Enzymatic hydrolysis

CIMV 2

CIMV 6

Separation lignins / sugars

BIOLIGNIN™

C₅ SUGARS SYRUP

CIMV 8, 9, 10

CIMV 4 & 5

CIMV 1

10 worldwide Patents

CIMV 1

CIMV 2

CIMV 3

CIMV 4 & 5

CIMV 6

CIMV 7

CIMV 8, 9, 10

GLUCOSE

CELLULOSIC PULP
CIMV PROCESS™ ADVANTAGES:

- FEEDSTOCK FLEXIBILITY (straws, hardwood, bagasse...)
- ~ 100% SOLVENT RECYCLING
- NO DEGRADATION BY-PRODUCTS
- PURITY AND SPECIFIC PROPERTIES OF THE COMMERCIAL PRODUCTS
CIMV BIOREFINERY

1 ton

- Forest residual
- Wheat straw
- Sugar cane
- Corn straw
- Rice straw

CIMV process

Products

Yield / purity

- 270Kg Biolignin™
  - 90% lignin

- 490Kg cellulose pulp
  - 89% C₆ + 9% C₅

- 220Kg Sugars syrup
  - 48% C₅

- 220Kg Stillage/ Others
  - 2% others

products

- 270Kg Biolignin™

- 280Kg 2G ethanol

Applications

- 2G biofuels
- Phenolic resins
- Elastomers
- Carbon fibers
- Bioplastics
- Chemical intermediates

*(79% C₆ et 21% C₅)*
CELLULOSE PULP/GLUCOSE

- Paper
- 2G Biofuels
- Chemical intermediates

C6 pulp composition

- Glucan
- Xylan
- ashes
- lignin

90% Glucan
High purity Glucose

- TCF Pulp (printing and domestic paper).
- Non-food origin glucose
- 2G Biofuels.
Xylan: 28%  
Arabinan: 4.5%  
Mannan: 1.5%  
Galactan: 3%  
Glucan: 10%  
Salts: 20%  
Proteins: 6.5%  
Tannins and phenolic compounds: 7.5%  
Waxes: 3.2%  
Furfural: 0.005%

Other: 13.8%

Additives for animal feed  
2G Biofuels  
Xylitol  
Furanic chemistry
Molecular Weight:
Mw = 1500  Mn = 1000

Hydroxyl groups (mmol/g of DM):
1.2 mmol aliphatic OH
1.8 mmol phenolic OH
0.9 mmol esterified aliphatic OH

Wheat straw Biolignin™ has H, G and S units.

R = H or OCH₃
R₁ = H, formyl or acetyl
R₂ = H or aliphatic ketone
R₃ = H, quinone or LIGNIN
R₄ = COOH or -COOH
IN A MORE SIMPLY WAY

R = H or OCH₃

BIOLIGNIN™
BIOLIGNIN™

Applications

- Phenolic resins
- Reinforcing agent for Rubbers
- Polyurethanes,
- Epoxy resins…

Advantages

- substitution of phenol (50 to 80% substitution rate)
- Substitution of polyols (40 to 60%)
- Substitution of carbon black (50 to 100%)
- Direct use for the Industry.
- A product for the green chemistry.
### BIOLIGNIN™ based Resoles

**Substitution of phenol by unmodified BIOLIGNIN™**

<table>
<thead>
<tr>
<th>Substitution rate</th>
<th>Reaction time (min)</th>
<th>pH</th>
<th>Viscosity P (25°C)</th>
<th>Dry Matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>0%</td>
<td>52 min</td>
<td>11,8</td>
<td>3,1 P</td>
</tr>
<tr>
<td>BPF1</td>
<td>30%</td>
<td>35 min</td>
<td>11,7</td>
<td>4,7 P</td>
</tr>
<tr>
<td>BPF2</td>
<td>50%</td>
<td>15 min</td>
<td>11,4</td>
<td>4,1 P</td>
</tr>
<tr>
<td>BPF3</td>
<td>60%</td>
<td>12 min</td>
<td>11,5</td>
<td>4,8 P</td>
</tr>
</tbody>
</table>

Due to the length of BIOLIGNIN™ chain: when the substitution rate increases, the reaction time decreases. All the resins synthesized reached the viscosity, dry matter and pH requirements.
# Characterisation of Biolignin™-based Resole

<table>
<thead>
<tr>
<th>Substitution rate</th>
<th>F/(P+L)</th>
<th>Reaction time</th>
<th>Dry matter</th>
<th>Viscosity (20°C)</th>
<th>pH</th>
<th>Residual formaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BPF 10</strong></td>
<td>50%</td>
<td>47%</td>
<td>21 min</td>
<td>48%</td>
<td>3.4 P</td>
<td>11.9</td>
</tr>
<tr>
<td><strong>BPF 11</strong></td>
<td>60%</td>
<td>43%</td>
<td>14 min</td>
<td>43%</td>
<td>3.5 P</td>
<td>11.5</td>
</tr>
</tbody>
</table>

Resins with 50% and 60% of Biolignin™ reach the specifications.
BIOLIGNIN™ based Resoles

Commercial product characteristics:

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry matter</td>
<td>&gt;42%</td>
</tr>
<tr>
<td>pH</td>
<td>11-12</td>
</tr>
<tr>
<td>Viscosity 25°C</td>
<td>300-800 cP</td>
</tr>
<tr>
<td>Residual free formaldehyde content</td>
<td>≤ 0.2%</td>
</tr>
</tbody>
</table>

Unmodified Biolignin™ can substitute at least 60% of phenol in PF resins
Thermomechanical analysis of BPF resins:

**DLTMA (Dynamic load thermomechanical analysis) of Biolignin based Resol (BPF) and standard PF**

Young modulus of the substituted resin were very close to standard PF resin
**BIOLIGNIN™ based Resols**

Wood panels (particle boards) manufactured with Biolignin-based Resole

<table>
<thead>
<tr>
<th>% dry resin</th>
<th>pressing temperature °C</th>
<th>Density N/mm²</th>
<th>Traction N/mm²</th>
<th>Flexion N/mm²</th>
<th>Module MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>9%</td>
<td>190°C</td>
<td>681</td>
<td>0,39</td>
<td>13,8</td>
<td>2337</td>
</tr>
</tbody>
</table>

Specifications

<p>| | | | | | |</p>
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<tbody>
<tr>
<td></td>
<td>0,3</td>
<td>13</td>
<td>2050</td>
<td></td>
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</tbody>
</table>
Pilot plant (51, France): capacity 2.5 T/day feedstock, operating since 2007.

Process validation

Samples for R&D and commercial validation of the products

Central partner for 3 big R&D European Union programs gathering 40 universities and companies working on CIMV cellulose, hemicelluloses and biolignin™:

- www.biocore-europe.org
- www.biomimetic-eu-project.eu
- www.innobite.eu
Biocore

Varied biomass Fractionation → Intermediates → Chemistry Biotechnology

Final products
2\textsuperscript{nd} generation fuels
- Ethanol

Thermoplastics
- PVC, polyolefins, polyurethanes, polyesters

Application sectors
- Energy
- Materials
- Packaging
- Building
- Adhesives and paints

Materials
- Resins/Adhesives
- Food additives
- Detergents
- Wood panels

CIMV

Hemicellulose
Cellulose
Biolignin\textsuperscript{TM}

Chemistry

INRA
The European Biocore program brought together 16 universities and research organizations as well as eight European companies that worked on the development of cellulose, C6 and C5 sugars and biolignin™ provided by CIMV between 2010 and 2014.

It validated the technology that provides excellent profitability without subsidy and urges the construction of a European demonstration plant.

The final report is publicly available on the website: www.biocore-europe.org
we start to built with Technip as EPC contractor

2 demonstration plants:

- Toulouse, France, focused on industrial biosourcing, first half of 2015:

- Shanghai, China, focused on bioéthanol second half of 2015

In partnership with big oil and agroindustrial Companies
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