Update on LignoBoost lignin and Applications

Per Tomani

SPCI
Stockholm, September 26 2013
LignoBoost – Production of kraft lignin
Lignin removal
- Driving Forces and Pulp Mill Manager Value

- Increase kraft pulp production
  By reduced thermal load in the recovery boiler

- Reduce fossil fuel oil consumption – Go Green
  Replacement of fossil fuel in the lime kiln with kraft lignin

- Export kraft lignin to create new revenues
  Kraft lignin can be exported to customers for use as a green raw material or product in application areas such as energy, chemicals & materials
LignoBoost installation in Domtar Plymouth

Source: Metso
LignoBoost installation in Domtar Plymouth

Domtar Plymouth, NC
• 444 000 t/y fluff pulp
• 25 000 t/y kraft lignin
• Start: Febr 2013
• USD 30 million*
• USD 7 million in funding from DOE & USDA*

*www.newsobserver.com

Source: Metso

http://www.newsobserver.com/2013/06/08/2946499/d Domtar unveils new technology.html#storylink=cpy
Press release from Stora Enso 19 July 2013

- Stora Enso invest **EUR 32 million** in a biorefinery at Sunila Mill in Finland, **replacing up to 90% of natural gas by lignin** extracted from the black liquor.

- The investment includes **a lignin extraction plant and dryer, lignin dust burners in the lime kilns, and a packing line**.
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- The first applications will be in, for example, the building, construction and automotive sectors, where lignin offers sustainable alternatives for phenols in plywood glues and other wood-based panels, and polyols used in foams.

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- Production is scheduled to start up during the **first quarter of 2015**.

- The investment is expected to generate **annual sales of EUR 80 million in 2017** and over time clearly exceed Stora Enso’s ROCE target of 13%.

- Technology also has **the potential for future scalability at other Group pulp mills**.
Laboratory scale equipment
~ 10g lignin per filtration-batch

Demonstration plant
~ 1 tonne lignin per hour

Pilot scale equipments in Europe
~ 0.5 - 1 kg lignin per filtration-batch
~ 5-15 kg lignin / 2 days

Pilot scale equipments in North America
~ 1.5-3 kg lignin per filtration-batch
~ 15-30 kg lignin / 2 days
Lignin quality & applications
Kraft lignin from our demonstration plant

Standard (bulk) kraft lignin

HHV (dry ash free): 25-27 MJ/kg
However 30-35% moisture

95-98 % Lignin
Hydrophobic

C: 63 - 66 % (dry ash free)
H: 5.7 - 6.2 %
O: 26 - 27.5 %
S: 1.5 - 3 % (normally 2-2.5%)
N: 0.1 - 0.2 %
Cl: 0.01 %

Ash (dry): 0.01 - 1 %

Normal operation
Ash (dry): 0.5-0.8 %
Na: 120 - 230 g/kg ash
K: 25 - 80 g/kg ash

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Kraft lignin in evaluated energy applications

- Lignin in oils
- Lignin fuel in lime kilns
- Lignin in pellets

Co-firing with bark

Co-firing with coal

www.innventia.com © 2013
Potential non-energy applications

- Kraft lignin
- Carbon fibre
- Activated carbon
- Dispersant
- Hydrophobic surfaces
- Binder in fibre boards
- Asphalt emulsions
Even a small lignin withdrawal can be interesting …

650,000 tonnes of pulp

Lignin withdrawal of 10% yields 33,000 tonnes

…converted to 16,000 tonnes of CF

…to support 160,000 cars with CF-composite (~40% replacement)
Carbon fibre production

Mainly based on petrochemicals
Process steps are tailor-made depending on raw material & target properties
Raw material accounts for 45-60% of the producing cost of CF composites

(Several filaments makes a fibre; a bundle of fibres makes a tow/yarn)
<table>
<thead>
<tr>
<th>Application</th>
<th>2011</th>
<th>2020</th>
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</thead>
<tbody>
<tr>
<td>Wind power</td>
<td>9.940 (2010)</td>
<td>54.270</td>
</tr>
<tr>
<td>Sports and leisure</td>
<td>7.790</td>
<td>11.820</td>
</tr>
<tr>
<td>Aerospace and defence</td>
<td>7.694</td>
<td>18.462</td>
</tr>
<tr>
<td>Civil engineering</td>
<td>4.050</td>
<td>8.905</td>
</tr>
<tr>
<td>Automotive</td>
<td>2.900</td>
<td>10.100</td>
</tr>
<tr>
<td>Pressure vessels</td>
<td>2.790</td>
<td>11.616</td>
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<tr>
<td>Other industrial</td>
<td>1.545</td>
<td>3.000</td>
</tr>
<tr>
<td>Off-shore oil and gas</td>
<td>1.100</td>
<td>4.000</td>
</tr>
</tbody>
</table>
## CFRP
### Examples of current projects and alliances

<table>
<thead>
<tr>
<th>Fiber producer</th>
<th>Part manufacturer</th>
<th>OEM</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dow/Aksa</td>
<td>Ford</td>
<td>BMW</td>
<td>Co-op with ORNL on alt. precursors</td>
</tr>
<tr>
<td>SGL</td>
<td>BMW</td>
<td>BMW</td>
<td>Co-op MRC 50K, 3000 t/y</td>
</tr>
<tr>
<td>TohoTenax</td>
<td>GM</td>
<td></td>
<td>One part per rmin. for CFRP car parts</td>
</tr>
<tr>
<td>Toray</td>
<td>Toyota</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toray</td>
<td>Daimler</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zoltek</td>
<td>Magna</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voith</td>
<td>Audi</td>
<td>VW</td>
<td>VW XL1 169 kg CFRP/car</td>
</tr>
<tr>
<td>Johnson</td>
<td></td>
<td></td>
<td>Own prod. method for CFRP parts</td>
</tr>
<tr>
<td>Zoltek</td>
<td></td>
<td>VW</td>
<td>JV with Weyerhaeuser lignin/PAN</td>
</tr>
</tbody>
</table>
Automotive
- Huge potential for cost efficient CF

- Large tow PAN based carbon fiber starts at 15 - 20 $/kg
  - Energy 10% of variable cost
  - PAN fiber 50 % of variable cost

- $/kg CF target for automotives
  - 11 (Ford)
  - 11-15 (DOE)

- Potential: 20% cost savings in CF process with lignin because:
  - SW lignin crosslinks faster than PAN
  - Complicated solvent spinning potentially avoided
  - Lignin can be stabilized in inert atmosphere
Specifications
- Lignin raw material for melt spinning, Oak Ridge

> 99 % lignin
< 500 ppm residual carbohydrates
< 5 weight-% volatiles
< 1000 ppm ash
< 500 ppm non-melting particles larger than 1 micron in diam.

Why these numbers?
What more to specify?
We need more work on specifications!
## Normal alkaline black liquors
- Example of chemical composition of LignoBoost lignin

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SW kraft</th>
<th>SW/HW kraft</th>
<th>HW kraft</th>
<th>HW soda</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of different mills</td>
<td>9</td>
<td>2</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Number of samples analysed</td>
<td>13</td>
<td>3</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td><strong>High heating value (MJ/kg)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Mean value</td>
<td>27.2</td>
<td>27.0</td>
<td>25.7</td>
<td>25.6</td>
</tr>
<tr>
<td>Min</td>
<td>26.8</td>
<td>26.8</td>
<td>24.8</td>
<td>-</td>
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<tr>
<td>Max</td>
<td>28.0</td>
<td>27.2</td>
<td>26.4</td>
<td>-</td>
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<tr>
<td><strong>Klason lignin (% of dry solids)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean value</td>
<td>91.7</td>
<td>89.3</td>
<td>85.8</td>
<td>76.7</td>
</tr>
<tr>
<td>Min</td>
<td>88.8</td>
<td>87.0</td>
<td>82.7</td>
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</tr>
<tr>
<td>Max</td>
<td>96.3</td>
<td>92.3</td>
<td>90.1</td>
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<td><strong>Acid soluble lignin (% of dry solids)</strong></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Mean value</td>
<td>6.0</td>
<td>9.8</td>
<td>13.6</td>
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<tr>
<td>Min</td>
<td>4.1</td>
<td>7.8</td>
<td>10.3</td>
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<tr>
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<td>9.0</td>
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<tr>
<td><strong>Carbohydrates (% of dry solids)</strong></td>
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<tr>
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<td>2.2</td>
<td>1.6</td>
<td>2.2</td>
<td>9.6</td>
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<tr>
<td>Min</td>
<td>1.5</td>
<td>0.7</td>
<td>0.8</td>
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<td>1.6</td>
<td>2.2</td>
<td>9.6</td>
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<tr>
<td>Min</td>
<td>1.5</td>
<td>0.7</td>
<td>0.8</td>
<td>-</td>
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<tr>
<td>Max</td>
<td>2.8</td>
<td>2.7</td>
<td>4.6</td>
<td>-</td>
</tr>
</tbody>
</table>
Differences in kraft cooking result in different lignin purity – With & without pre-hydrolysation

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Birch Ref</th>
<th>Birch Pre-Hydrolysed</th>
<th>Euca Ref</th>
<th>Euca Pre-Hydrolysed</th>
<th>Spruce Ref</th>
<th>Spruce Pre-Hydrolysed</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS (%)*</td>
<td>36.1</td>
<td>34.9</td>
<td>46.0</td>
<td>33.3</td>
<td>42.4</td>
<td>34.0</td>
</tr>
<tr>
<td>Acid insoluble lignin,(%-w**)</td>
<td>61.9</td>
<td>89.0</td>
<td>78.9</td>
<td>86.5</td>
<td>91.7</td>
<td>89.1</td>
</tr>
<tr>
<td>Acid soluble lignin,(%-w**)</td>
<td>22.0</td>
<td>9.5</td>
<td>17.9</td>
<td>13.2</td>
<td>7.2</td>
<td>7.1</td>
</tr>
<tr>
<td>Carbohydrates (%-w**)</td>
<td>16.2</td>
<td>0.3</td>
<td>3.6</td>
<td>0.3</td>
<td>1.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Lignin purity is important according to specifications
Lignin is modified/degraded in a kraft cook

Native lignin
Heterogeneous, amorphous and branched macromolecule built up with phenylpropane units

Lignin properties are of course formed already in the forest but also in the kraft process

<table>
<thead>
<tr>
<th>Measure</th>
<th>HW Kraft lignin (ca 90 %)</th>
<th>SW Kraft lignin (ca 98 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tg</td>
<td>148</td>
<td>119</td>
</tr>
<tr>
<td>Td</td>
<td>267</td>
<td>254</td>
</tr>
<tr>
<td>Mw</td>
<td>4470</td>
<td>1600</td>
</tr>
<tr>
<td>Mn</td>
<td>1000</td>
<td>440</td>
</tr>
<tr>
<td>PD</td>
<td>4.5</td>
<td>3.6</td>
</tr>
<tr>
<td>Phenolic OH, mmole/g</td>
<td>4</td>
<td>4.3</td>
</tr>
<tr>
<td>Aliphatic OH, mmole/g</td>
<td>2.3</td>
<td>1.7</td>
</tr>
<tr>
<td>Carboxylic groups, mmole/g</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Lignin for CF
- Important progress by Innventia since 2010

Softwood lignin

2010: “Not possible to melt spin”
New: Innventia can melt spin SW lignin

Hardwood lignin

2010: Only possible to melt spin with additives or by chemical modification
New: Innventia can melt spin pure HW lignin
Innventia
- New investment for controlled fibre spinning

Vertical melt extruder with possibility to control:

• Temperature
• Screw speed
• Melt viscosity
Innventia
- New investment for post-treatment studies

Stabilisation unit - controlled tension & atmosphere
Melt spinning
– General observations in our new equipment

- More flexible equipment
  - Historical conditions cannot be applied without adjustments
  - Improved possibilities for optimisation

Both softwood and hardwood-based fibres can be made. CF strength is the challenge!

- Melt viscosity
  - HW kraft lignin-based: stable
  - SW kraft lignin-based: instable
Co-operation 1
- Prize to develop new knowledge on the production of carbon fibre from the wood raw material lignin

- Innventia’s Hannah Schweinebarth has been awarded this year’s Skills Prize by the Gunnar Sundblad Research Foundation.

- 6 months research at Oak Ridge National Laboratories (ORNL) and University of Tennessee in Knoxville to collaborate, network and bring home new knowledge & contacts
First commercial application for lignin-based carbon fibres (CF)

- GrafTech International Holdings Inc, US
- High temperature thermal insulation prototypes from lignin-based CF:

Source: ORNL
Sept 2013
Lignin-based CF for a insulator application

Source: Oak Ridge National Laboratory
Co-operation 2
- University of Tennessee, Knoxville Center for Renewable Carbon
Center for Renewable Carbon  
- Importance of glass transition temperature, $T_g$

Relationship between:

Potential fiber $T_g$ and maximum permissible rate of oxidative stabilization without fusion/adhesion (left)

Carbon fiber yield and rate of oxidative stabilization of lignin fibers (right)

Both relationships are lignin chemistry/purity specific but all give similar trends.

Source: University of Tennessee, Knoxville, Center for Renewable Carbon
Modification of lignin production  
– Control of the glass transition temperature, Tg

We can also modify lignin properties in the process where lignin is separated
Use of carbon fibres
BMW electricity & hybrid cars (commercial production 2013)
Built in carbon reinforced plastics. Partnership with SGL.

Thank you for your attention!