LignoBoost Kraft Lignin
A New Renewable Fuel and a Valuable Fuel Additive

Per Tomani, Innventia

Co-authors:
Peter Axegård, Niklas Berglin, Daniel Nordgren, Innventia
Jonas Berghel, Karlstad University
Outline

• Background – Introduction
• Kraft lignin – process & product
• Trials in different combustion applications
• Summary
Driving forces

• Increased pulp production
  - By reduced thermal load in the recovery boiler

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

• Exporting revenue
  - Excess energy can be exported from market pulp mills to external users - energy, chemicals & materials
Oil price changes

Oil price
$/barrel

International Bioenergy & Bioproducts Conference
March 14-16, 2011 | Atlanta GA USA
The LignoBoost process

Liquor ~40%

Lignin lean liquor

CO₂

H₂SO₄

Wash water pH 2.5

- Na returned to the process
- Low Na content lignin
- Low was water consumption

Liquor from digester

Wash liquid ~2 m³/t lignin

pH ~10

pH 2 - 3.5
Kraft lignin properties & potential use?

26 - 27 MJ/kg
11 200 - 11 600 BTU/lb
Examples of potential products from kraft lignin
Pressfilter from Metso in our Demo plant in Bäckhammar, Sweden

VPA 1040
24 chambers
1-1.2 tonnes lignin/h
Process: comments & experiences

• First part of the LignoBoost-concept:
  – Product: 5-15% ash and 35% DS (waterslurry).
  – Continuous operation, one yearly maintenance stop.
  – Production of lignin on a level of 6 000 tonnes/year.
The second part of the LignoBoost-concept:

- Demonstration by Innventia on a level of 4 000 tonnes/year
- Product: 0.02-1 % ash, 65-70+% DS
- Operated 5 days a week 24 hours/day 2007-2008. Now focused on R&D.

The LignoBoost-concept have no new equipment but a key component - press filters:

- Well-proven equipment in the mineral industry. Fully automatic equipment.
Kraft lignin in our demonstration plant

Standard (bulk) lignin

HHV (dry ash free): 26-27 MJ/kg
However 30-35% moisture

95-98 % Lignin
Hydrophobic

C: 63 - 66 %
H: 5.7 - 6.2 %
O: 26 - 27.5 %
S: 2 - 3 %
N: 0.1 - 0.2 %

Ash (dry): 0.02 - 1 %

Normal operation
Ash (dry): 0.5-0.8 %
Na: 120 - 230 g/kg ash
K: 25 - 80 g/kg ash
# LignoBoost kraft lignin fuel characteristics

<table>
<thead>
<tr>
<th></th>
<th>Lignin</th>
<th>Coal</th>
<th>Wood chips</th>
<th>Bark pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (% Moisture)</td>
<td>30-40</td>
<td>9</td>
<td>50</td>
<td>10,3</td>
</tr>
<tr>
<td>Ash (% Ash)</td>
<td>0,02-1</td>
<td>11,7</td>
<td>2-3</td>
<td>3,6</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>26-27</td>
<td>29,8</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>LHV (MJ/kg)</td>
<td>17-19</td>
<td>25,9</td>
<td>7,7</td>
<td>17,7</td>
</tr>
<tr>
<td>Sulphur, S (% db)</td>
<td>2-3</td>
<td>0,4</td>
<td>0,05</td>
<td>0,04</td>
</tr>
<tr>
<td>Chloride, Cl (% db)</td>
<td>&lt;0,01</td>
<td>0,04</td>
<td>0,03</td>
<td>0,02</td>
</tr>
<tr>
<td>Bulk density (kg/m³)</td>
<td>500-600***</td>
<td>800</td>
<td>200-300</td>
<td>550-700</td>
</tr>
</tbody>
</table>

***Moist filter cakes. Dry lignin powder has a bulk density of 630-720 kg/m³
Energy density is a key issue for biofuels, $\text{MWh/m}^3$
Kraft Lignin Fuel

Successful energy applications tested by Innventia

- Lime kiln
- Co-firing with bio-fuels
- Co-firing with coal
- Kraft lignin pellets (100%) & additive (1-10%) in fuel pellets
- Kraft lignin powder suspended in oils
Full scale trial with kraft lignin as fuel in a lime kiln at the Södra Cell Mönsterås pulp mill

- April 15-17, 2008
- 275 tpd lime kiln
- 37 tonnes fired
- 32 hours
- 50 - 100 % oil replacement

Reference: Tappi Int. Chem. Rec. Conf. 2010, Williamsburg, USA
Kraft lignin fuel in lime kilns

Summary

• Stable and continuous operation of a lime kiln when lignin is used as fuel.

• Standard powder burners and feeding equipment when firing lignin - OK.

• No sign of lignin stuck at the burner or in supply pipe system.

• The temperature levels in the kiln are of the same order of magnitude when firing lignin as when firing oil or wood powder.

• OK to keep the O\textsubscript{2}–level at normal values at the combustion of lignin, i.e. same as during bark and oil firing.

• Lime quality: not effected

• Increased SO\textsubscript{2} emission between 85-100% (kiln specific level?)
Co-firing of kraft lignin & bark in a CFB

- Co-firing of lignin and bark in a 12 MW research CFB-boiler at Chalmers University of Technology
- 3 tonnes of the lignin limited the trial to 3-days.
- The objectives were to study:
  - Fuel feeding properties in Chalmers feeding system
  - Effects on combustion conditions (CO, NOx, temp, etc)
  - SO₂-emissions
  - SO₂-reduction with limestone addition
  - Deposits on tubes
  - Effects on sintering properties of the bed material

Co-firing of kraft lignin and bark

- NO ppm
- SO₂ ppm
- (Na+K)Cl ppm

Lignin 15 % Lignin

International Bioenergy & Bioproducts Conference
March 14-16, 2011 | Atlanta GA USA
SO$_2$ capture by bark ash and limestone addition

SO$_2$, ppm at 6%O$_2$

82 % reduction
bark ash

99 % reduction
bark ash + limestone

Theoretical

Measured

<table>
<thead>
<tr>
<th>Reference Bark</th>
<th>85 % bark + 15 % lignin</th>
<th>85 % bark + 15 % lignin + Limestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>60</td>
<td>3,4</td>
</tr>
<tr>
<td>1,6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>332</td>
<td>327</td>
</tr>
</tbody>
</table>

International Bioenergy & Bioproducts Conference
March 14-16, 2011 | Atlanta GA USA
Co-firing in a CFB

Full scale

April 2010

International Bioenergy & Bioproducts Conference
March 14-16, 2011 | Atlanta GA USA
Co-firing in a CFB

Summary

• Feeding works well without any clogging problems
• A stable and continuous combustion is fully possible
• Sulphur content in kraft lignin can be used to reduce the alkali choride content in the deposits, thus reducing the risk for sticky deposits and high temperature corrosion
• Calcium in bark ash captured sulphur.
• Conventional sulphur capture with addition of limestone to the bed was also demonstrated.
• Kraft lignin addition had no measurable effect on the sintering properties of the bed material
Coal fired PFBC plant in Stockholm (Värtaverket)
(Pressurised Fluidised Bed Combined Cycle)

Facts year 2006
- Coal consumption: ~ 250 000 ton
- Energy production, power & heat: ~1,9 TWh
- CO2 emissions: ~ 650 000 ton
- Operation time: 5000 hours
Co-firing coal and kraft lignin

Demonstration scope

• Kraft lignin transported 300 km by trucks (40 ton lignin/truck) from the LignoBoost demo plant to Stockholm.

• The lignin was intermediate stored up to a year in 10 ton containers. No problems with biological activity or degradation.

• 4 000 ton of lignin 60 % DS (24 GWh) was co-fired with coal during 4 campaigns - totally 13 weeks (8 weeks continuous operation). The energy mix of lignin was 2 -15 %.

• Kraft lignin was added to coal, dolomite and water. This paste was pumped 300 m to the PFBC and injected with existing six burners.
Results co-firing coal & kraft lignin

• The fuel injection into the boiler and fluidized bed worked well and the distribution of fuel in the bed was very good.

• Compared to coal firing the centre of combustion shifted downwards due to the high reactivity of the lignin.

• No appeared changes in NO\textsubscript{x}, N\textsubscript{2}O, CO and HCl emissions were observed. The sulphur emission increased from 1-3 mgS/MJ to 12-13 mgS/MJ when co-firing with 15 % lignin (energy basis)

• Fortum Värme expect at least 30% coal substitution with optimal designed equipment.

Reference: Bioenergy 2009, Jyväskylä, Finland, 31 Aug- 4 Sept, 2009
Pellets, 100 % kraft lignin
Small and large scale pilot units from Amandus Kahl

10-100 kg scale

100-1000 kg scale
Kraft lignin as additive

- we use the softening properties

![Graph showing softening temperature vs. moisture content for various lignins](image)

- Kraft lignin, softwood
- Kraft lignin, hardwood
- Softwood lignin
- Hardwood lignin

Moisture content, %

Softening temperature, °C
Evaluation by single pellet pressings
Evaluation by single pellet pressings

Pellet strength / N

<table>
<thead>
<tr>
<th>Trial</th>
<th>125C</th>
<th>165C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reference Spruce

2 % kraft lignin liquid additive

Kraft lignin powder 5 %

International Bioenergy & Bioproducts Conference
March 14-16, 2011 | Atlanta GA USA
Pilot scale - pelletizing of fresh spruce

Lignin inblandning vs fines med 100% gran

Fines (wt-%)

0,00% 1,06% 2,12% 3,14% 0,00% 4,20%

Lignin (wt-% DS)

International Bioenergy & Bioproducts Conference
March 14-16, 2011 | Atlanta GA USA
Kraft lignin pellets & kraft lignin as additive

Summary

• Lignin can be pelletized when needed.
  – Normal energy input is needed
  – Correct handling system is important

• Moisture is an important softening agent

• Addition of lignin to biofuel pellets improves the strength and energy density

• Lignin is hydrophobic – pellets have good water resistance properties. Also other good storage properties
LignoBoost lignin mixed with fuel oil

30-50 % lignin (energy-%) in fossil fuel oil 5

We have also sucessfully mixed lignin with liquid bio-fuels like tall oil, tall oil pitch & glycerine from bio-diesel production
Summary

• Secure a continuous bulk production & use of lignin
• Substitute fossil fuel oil - sets the lignin value & should include potential green credits
• Do not forget applications where washed, moist lignin is accepted.
• Next generation applications: carbon fibers, etc

Successful demonstrations (a short term perspective):
• Moist lignin cakes co-combusted with bio-fuels (bark)
• Moist lignin cakes co-combusted with coal
• Moist lignin as additive in biofuel pellets (wood, straw etc)
• Dry lignin powder fuel in lime kilns/cement kilns
• Lignin pellets or new combinations
• Lignin slurries with fuel oil, tall oil, tall oil pitch, glycerine etc
Thank you for your attention!
Lignin removal

- Lignin IN
  - Replacement of fossil fuel in lime kilns
  - 50 L mineral oil ptp can be saved

Diagram:
- Wood → Wood Chips → Recovery Boiler → Lime Kiln → Digester → Bleaching → Pulp/Paper
- Lignin OUT
Biorefinery activities at Innventia

Energy
- Lignin
- Forest residues
- Bark

Material & Chemicals
- Lignin
- Hemicellulose
- Cellulose
- Extractives

International Bioenergy & Bioproducts Conference
March 14-16, 2011 | Atlanta GA USA
Energy situation in a pulp mill

Summary: General steam balance (2003)

Prod: Recovery boiler: 15.2 GJ/ADT

<table>
<thead>
<tr>
<th>Consumed</th>
<th>Average mill</th>
<th>BAT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporation:</td>
<td>5.1 GJ/ADT</td>
<td>4.0</td>
</tr>
<tr>
<td>Fibre line:</td>
<td>4.9 GJ/ADT</td>
<td>3.2</td>
</tr>
<tr>
<td>Pulp drying:</td>
<td>3.0 GJ/ADT</td>
<td>2.2</td>
</tr>
<tr>
<td>Others:</td>
<td>1.0 GJ/ADT</td>
<td>0.0</td>
</tr>
<tr>
<td>Total need:</td>
<td>14 GJ/ADT</td>
<td>10.8</td>
</tr>
</tbody>
</table>

LignoBoost Demonstration plant
Samples from the first year of operation

Dry solids in the final kraft lignin product, %

February 2007  One year of operation  February 2008

International Bioenergy & Bioproducts Conference
March 14-16, 2011 | Atlanta GA USA
LignoBoost Demonstration plant

Ash content in the final kraft lignin product, %

Ash content, mean value: 0.8 %
### Fuel content (weight-%)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Example</th>
<th>Median</th>
<th>Range</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>29.3</td>
<td>32.3</td>
<td>29.3</td>
<td>40.0</td>
</tr>
<tr>
<td>Ash (dry)</td>
<td>1.4</td>
<td>1.0</td>
<td>0.2</td>
<td>1.4</td>
</tr>
</tbody>
</table>

### Heat value (MJ/kg)

<table>
<thead>
<tr>
<th></th>
<th>Min</th>
<th>Max</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHV (dry ashfree)</td>
<td>26.7</td>
<td>27.1</td>
<td>5</td>
</tr>
<tr>
<td>HHV (moist)*</td>
<td>18.6</td>
<td>18.2</td>
<td>15.9</td>
</tr>
<tr>
<td>LHV (dry ashfree)</td>
<td>25.4</td>
<td>25.9</td>
<td>25.3</td>
</tr>
<tr>
<td>LHV (moist)*</td>
<td>16.9</td>
<td>16.6</td>
<td>14.2</td>
</tr>
</tbody>
</table>

### Elementary analysis (% dry ashfree)

<table>
<thead>
<tr>
<th>Element</th>
<th>C (carbon)</th>
<th>H (hydrogen)</th>
<th>O (oxygen)</th>
<th>S (sulphur)</th>
<th>N (nitrogen)</th>
<th>Cl (chlorine)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (carbon)</td>
<td>63.6</td>
<td>65.1</td>
<td>63.6</td>
<td>66.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H (hydrogen)</td>
<td>6.2</td>
<td>5.8</td>
<td>5.7</td>
<td>6.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O (oxygen)</td>
<td>27.5</td>
<td>26.1</td>
<td>25.9</td>
<td>27.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S (sulphur)</td>
<td>2.54</td>
<td>2.5</td>
<td>1.8</td>
<td>3.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N (nitrogen)</td>
<td>0.15</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl (chlorine)</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Ash analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>mg/kg DS</th>
<th>mg/kg ash</th>
<th>mg/kg ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (aluminum)</td>
<td>364</td>
<td>26 000</td>
<td>17 824</td>
</tr>
<tr>
<td>As (arsenik)</td>
<td>15</td>
<td>14</td>
<td>16</td>
</tr>
<tr>
<td>Ba (barium)</td>
<td>31</td>
<td>2 200</td>
<td>2 000</td>
</tr>
<tr>
<td>Ca (calcium)</td>
<td>1 085</td>
<td>77 500</td>
<td>4 037</td>
</tr>
<tr>
<td>Cd (cadmium)</td>
<td>10</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td>Co (cobalt)</td>
<td>10</td>
<td>8</td>
<td>11</td>
</tr>
<tr>
<td>Cr (chromium)</td>
<td>257</td>
<td>108</td>
<td>500</td>
</tr>
<tr>
<td>Cu (cupper)</td>
<td>157</td>
<td>59</td>
<td>800</td>
</tr>
<tr>
<td>Fe (iron)</td>
<td>270</td>
<td>19 300</td>
<td>4 036</td>
</tr>
<tr>
<td>Hg (mercury)</td>
<td>2</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>K (potassium)</td>
<td>543</td>
<td>38 800</td>
<td>38 800</td>
</tr>
<tr>
<td>Mg (magnesium)</td>
<td>116</td>
<td>8 300</td>
<td>1 996</td>
</tr>
<tr>
<td>Mn (manganese)</td>
<td>71</td>
<td>5 100</td>
<td>2 835</td>
</tr>
<tr>
<td>Mo (molybdenium)</td>
<td>484</td>
<td>353</td>
<td>614</td>
</tr>
<tr>
<td>Na (sodium)</td>
<td>1 666</td>
<td>119 000</td>
<td>151 500</td>
</tr>
<tr>
<td>Ni (nickel)</td>
<td>69</td>
<td>59</td>
<td>79</td>
</tr>
<tr>
<td>P (phosphorous)</td>
<td>66</td>
<td>4 700</td>
<td>2 484</td>
</tr>
<tr>
<td>Pb (lead)</td>
<td>16</td>
<td>11</td>
<td>21</td>
</tr>
<tr>
<td>Si (silica)</td>
<td>979</td>
<td>69 900</td>
<td>13 071</td>
</tr>
<tr>
<td>Ti (titanium)</td>
<td>25</td>
<td>1 800</td>
<td>969</td>
</tr>
<tr>
<td>Ti (thallium)</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V (vanadium)</td>
<td>820</td>
<td>769</td>
<td>871</td>
</tr>
<tr>
<td>Zn (zinc)</td>
<td>500</td>
<td>443</td>
<td>954</td>
</tr>
</tbody>
</table>
One driving force to avoid fossil fuels in lime kilns

Use of 50 liter oil (13.2 gallon) in the lime kiln/ADt pulp

Example: In a pulp mill producing 350 000 ADt/year, without a production increase:
- means 110 000 bbl / year (17 500 m3 / year)
- corresponds to 25 000 tonnes of lignin on energy basis

Avoided oil cost* in the lime kiln, US$/year

Savings: US$ 8-9 million/year

*corresponds directly to the x-axis (no taxes etc)
Typical installation

- 2 or 3 VPA pressure filters
- Precipitation equipment
  - CO₂ storage tanks – optional
- Process pumps and tanks
- Heat exchangers
- Scrubber, vacuum pump and fan
- Belt conveyors
- Piping and valves