Potential applications for different lignin sources based on experience from Borregaard and what about the future?

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Technology Director Business Development
Borregaard AS
Borregaard is the world’s most advanced biorefinery
Integrated production system serving diverse markets

<table>
<thead>
<tr>
<th>Specialty cellulose</th>
<th>Lignin</th>
<th>Vanilllin</th>
<th>Bioetanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Construction materials</td>
<td>Concrete additive</td>
<td>Food</td>
<td>Car care</td>
</tr>
<tr>
<td>Cosmetics</td>
<td>Animal feed</td>
<td>Perfumes</td>
<td>Paint/varnish</td>
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<tr>
<td>Food</td>
<td>Agrochemicals</td>
<td>Pharmaceuticals</td>
<td>Pharmaceutical industry</td>
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<td>Tablets</td>
<td>Batteries</td>
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<td>Bio fuel</td>
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<td>Textiles</td>
<td>Mining</td>
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<tr>
<td>Filters</td>
<td>Oil field chemicals</td>
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</tr>
<tr>
<td>Paint/varnish</td>
<td>Soil conditioning</td>
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Borregaard – Business areas
A global niche player with a market driven organisation

Performance Chemicals (46%)
Technology leader and largest supplier of lignin-based products with global market access

Specialty Cellulose (38%)
Leading global specialty cellulose Supplier. Significant producer of 2nd generation bioethanol

Other Businesses (16%)
Only producer of wood-based vanillin. Largest producer of C₃ aminodiols for X-ray contrast media

1050 Employees
NOK 4 billion turnover
Borregaard and Rayonier invest in new lignin operation

Letter of Intent ......The new company will be owned 55% by Borregaard and 45% by RYAM.

.....the project will be completed in two phases over 5 years.

... USD 110 million investment...

... capacity of 150,000 MTDS ......

The first phase starts production 2017.
Press release 21.10.2015

Borregaard acquires the lignin operation of Flambeau River

Flambeau River Papers LLC, Park Falls operations, Wisconsin, USA.

• .... long-term lignin raw material supply agreement.
• Agreement closing Q4 2015
• 40 000 MTDS/y
Global presence
An international business with global customers

Production facilities and sales offices in 16 countries provide a global platform

1. Intimacy with a global customer base through a fully controlled sales and marketing network
2. Earnings stability due to diversification
3. Strategically located manufacturing to supply customers efficiently
4. Well balanced between mature and emerging markets
5. Production and supply efficiencies
Significant environmental investments at Borregaard: Reducing CO2 footprint substantially

- New water purification unit, anaerobic only => biogas
  - Internal use
- Heavy fuel oil phased out
  - Replaced by biofuel, LNG and waste

Steam

Hydropower

Independent of heavy fuel oil for all purposes by 2013
Value creation through specialisation and innovation

- 12% of Borregaard’s revenues come from products launched in the previous five years
- 95 employees in R&D, of which 80 employees at the R&D centre in Norway – 34 are educated to PhD level
- R&D and innovation spending between NOK 150 and 200 million/year (3.5 – 5% or turnover)

Exilva Microfibrillar cellulose and Sensefi Advanced Texture Systems

Continuous specialisation and improved products

Utilisation of other biomasses for lignin products

"BALI"

Developing new process for 2G bioethanol
The BALI™ project
Borregaard value chains

Sarpsborg sulphite mill
- Cellulose
- Bioethanol
- Vanillin
- Lignin

External sulphite mills
- Lignin
- Lignin

BALI™ plant
- Cellulose

Sarpsborg biorefinery
- Bleached cellulose
- Specialty cellulose

Borregaard LignoTech production sites
- Lignin
- Sugar
- Bioethanol Biochemicals
Sugar platform and lignins
Biomass pretreatment, separation and hydrolysis processes

Hydrolysis processes
• Dissolving cellulose and hemicellulose leaving **hydrolysis lignins** undissolved
  – Strong acid (2 step)
  – Weak acid (1 step or 2 step)
  – Steam explosion (+ chemicals) & Enzymatic hydrolysis
  – Microbial

Modified pulping processes
• Dissolving lignin and (hemicellulose) leaving cellulose undissolved
  – Kraft (-> **kraft lignins**)
  – Soda (-> **soda lignins**)
  – Sulfite (-> **lignosulfonates**)
  – Solvent (-> **organosolv lignins**)
  – Extrusion

Lignin quality depending strongly on process and biomass source
Bagasse mass balance (only C/H/L shown)

Steam explosion

Bagasse

BALI™ acid pretreatment

Solid fraction

Cellulose

Solid fraction

Hemicellulose

Liquid fraction

Lignin

Solid fraction

Liquid fraction

Lignosulfonate market today

- Global commercial market 1 – 1.2 million tons DM of lignosulfonates
  - 1 manufacturer using feed stock from Kraft pulping
  - Others using spent sulfite liquor as feed stock
  - Some small suppliers using feed stocks from soda pulping
  - Mainly softwood and hardwood based, small amounts from annual plants
- Lignosulfonate market only partly consolidated,
  - leading supplier supplying 50+% of world supply,
  - many smaller independent suppliers
- Market largely in balance – main supplier takes on the responsibility to buffer capacity to changing demands
- Short term: Expected growth with GDP, no room for substantially more capacity unless new applications are developed
- Long term: Potential growth for green chemicals
Need at least one $SO_3^-$ for every four C9 units to be water soluble
Intrinsic properties of lignosulfonates

In frequent use
- Binder
- Dispersing agent
- Emulsifier
- Complexing metal ions

Under exploration commercially
- Corrosion reduction
- Plant growth stimulation
- Anti oxidant

Not in commercial use
- Flame retardant
- Resins (stopped)
- UV-absorption/UV-protectant
- Protein precipitation (stopped)
- Bioplastics

Old idea of lignosulfonate structure

New lignosulfonate structure by Bernt O Myrvold, Borregaard Surfaces – scaling laws
Physical properties of Lignosulfonates

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>20,000 – 80,000 Da</td>
</tr>
<tr>
<td>Polydispersity</td>
<td>6-8</td>
</tr>
<tr>
<td>Sulfonate groups</td>
<td>0.6-1.2 per monomer</td>
</tr>
<tr>
<td>Organic sulfur</td>
<td>4-8%</td>
</tr>
<tr>
<td>Solubility</td>
<td>soluble in water at all pH</td>
</tr>
<tr>
<td></td>
<td>insoluble in most organic solvents</td>
</tr>
<tr>
<td>Color</td>
<td>very light to very dark brown</td>
</tr>
<tr>
<td>Delivery</td>
<td>powder or liquid form (40-50% DS)</td>
</tr>
<tr>
<td>Non-toxic:</td>
<td>LD$_{50}$ &gt; 5 g/kg</td>
</tr>
</tbody>
</table>
Decreased viscosity in mortar and concrete

Flow table test
Lignosulfonate
- emulsifier and dispersing agent

Disperse color pigments
Disperse pesticides

Stabilize emulsions

Future use:
Disperse carotenoids and fat soluble vitamins
Lignosulfonates and oxylignins in lead acid batteries

crystal growth modifier =>
better discharge/charge performance

Particles size distribution of lead sulphate grown from dilute suspensions of lead oxide in sulphuric acid. The original lead oxide is shown together along with the results of the test with and without lignosulphonates present.
Reduction of corrosion from strong acids

- Products from spruce lignosulfonates can reduce corrosion from strong acids
- Applications
  - Replacement of preventive antibiotics - control of bacterial activity
  - Ensilage – reduced corrosion, reclassification of acids
  - Acid conservation – reduced corrosion, reduced skin irritation.

After 7 days in 15% HCl:

15% HCl
15% HCl + SoftAcid

Formic acid + SoftAcid
Properties of Kraft lignins and Borregaards experience

- Borregaard constructed and operated the Kraft lignin plant at Bäckhamar, 10 000MTDS/y (Now LignoBoost)
- MeadWestvaco only commercial supplier of Kraft lignins
  - Sulfonated kraft lignins used as dispersing agents in pesticides and fabric dying
- Sulfonated kraft lignins
  - Limited applications, mostly not performing as well as lignosulfonates
  - World market 40 – 50 000 MTDS/y
  - More costly to produce (feedstock cost = energy value, additional chemical treatment needed)
Lignin based plastics

- Kraft lignin (and others) has been used. Forms plastics with acceptable mechanical properties which can be extruded and injection molded.
- Smell and colour limiting potential markets
- Potentially large volume market
- Hydrolysis lignin less suited
- Need further development

LignoPol, Borregaard

Arboform, Technaro
Properties of hydrolysis lignins and Borregaards experience

NOT A GOOD STARTING POINT FOR CHEMICALS

- Low Mw – high polydispersity
- Reach temp. > 180 – 200 °C -> Strongly condensed
- Very few β-O-4 bonds left – mainly C-C bonds
- Few –OH groups left
- Generally low O content relative to other lignins
- Water insoluble, hardly soluble in any solvent
- Low reactivity - hard to modify chemically at reasonable cost
- Impurity level will be high
  - hard to separate
  - impure products
  - many side streams
Oxidation of lignosulfonate to vanillin and oxylignins

Copper catalyst is recycled due to strict limitations on copper in effluent.

crude softwood lignin
Lignins – the future source of aromatics and phenolics?

- Structure of lignins invites to conversion to aromatic monomers and oligomers
- All processes (catalytic, enzymatic, thermochemical) so far have very low yields, typically 2-3% – Are we just splitting off monomers at the end linked by ether bonds?
- Binding energies indicate that it should be possible to break the C-C bonds without breaking the ring?
- Separation costs high.

**Alternative strategies:**

- Produce oligomers
- Functionalize to improve reactivity by phenol
- Feed lignins directly into oil refineries (Preem) – All conversion systems in place – Improve aromatic content of feedstock – Shale gas contain no aromatics
- Use for energy – we need energy too.
- Produce water soluble lignins that can be modified by traditional chemistry
THANK YOU