Status of the Bio-refinery Development in Scandinavia

Presented by: Dr Peter Axegård, STFI
Outline

- Why a pulp mill biorefinery?
- Energy export from modern mills
- Birch bark
- Softwood knots
- Xylan from black liquor
- Glucomannan from TMP white water
- Lignin from black liquor
- Black liquor gasification
- New process for soap removal
- Conclusions
Pulp and Paper Under Pressure

- Increased wood costs
- Increased energy costs
- Decreasing trend prices on pulp
Steady Drop in Market Pulp Prices…

BMSWKP 1975-2003, SEK/tonne

Deflator: PPI for Sweden
Average1999=100

The Pulp Mill Biorefinery

- Wood/Fibre
- Pulp Mills
- Paper Mills
- Conversion
- User
- Reuse
- Energy
- Chemicals
The Pulp Mill Biorefinery

- Chips
  - Bark & forest residues
  - Extractives
  - Glucose
  - Hemicelluloses
  - Lignin

- Pulp mill
  - Spent liquor
  - Phenols
  - Carbon fibre
  - Porous carbon
  - Binders

- Specialty Cellulose
- Pulp
- Paper
- Solid fuel from bark and forest residues
- Solid fuel
### Industrial Wood Based Chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Production Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood tar</td>
<td>1500’s</td>
</tr>
<tr>
<td>Potash</td>
<td>1672 - 1800’s</td>
</tr>
<tr>
<td>Turpentine</td>
<td>1910’s</td>
</tr>
<tr>
<td>Tall Oil</td>
<td>1913</td>
</tr>
<tr>
<td>Ethanol, sulfite</td>
<td>1921</td>
</tr>
<tr>
<td>CMC</td>
<td>1944</td>
</tr>
<tr>
<td>Lignosulfonates</td>
<td>1940-ies</td>
</tr>
<tr>
<td>Sulfite lignin</td>
<td>1965</td>
</tr>
<tr>
<td>Furfural</td>
<td>1968</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>1968</td>
</tr>
<tr>
<td>Xylitol</td>
<td>1974</td>
</tr>
<tr>
<td>Protein</td>
<td>1974- 1991</td>
</tr>
<tr>
<td>Sitosterol, sitostanol</td>
<td>1980</td>
</tr>
<tr>
<td>Lignans</td>
<td>1998</td>
</tr>
</tbody>
</table>
The Pulp Mill Biorefinery

Example 1
Energy efficient modern kraft pulp mills
Södra Cell -
Pulp Producer and Supplier of Energy

- Power: 0.4 TWh
- District heating: 0.4 TWh
- Biofuel: 1.8 TWh
Modern Kraft Pulp Mills are Very Energy Efficient

<table>
<thead>
<tr>
<th>Model Mill Case</th>
<th>Sold Fuel GJ/ADt</th>
<th>Sold power kWh/ADt</th>
<th>”Fossil CO₂ kg/ADt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Mill ECF-bleaching</td>
<td>3.1</td>
<td>540</td>
<td>-260</td>
</tr>
<tr>
<td>Swedish average year 2000</td>
<td>-0.6</td>
<td>-140</td>
<td>+320</td>
</tr>
</tbody>
</table>
The Pulp Mill Biorefinery

Example 2
Fatty acids from birch bark

STFI, VTT
Bark Suberin

SUBERIN
Major Monomers

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_m\text{COOH} \\
\text{CH}_3(\text{CH}_2)_m\text{CH}_2\text{OH} \\
\text{CH}_2(\text{CH}_2)_n\text{COOH} \\
\text{HOOC}(\text{CH}_2)_n\text{COOH} \\
\text{OH} \\
\text{Phenolics} \\
(m = 18 - 30; n = 14 - 20)
\end{align*}
\]

[Rowe J W (Ed.), Natural Products of Woody Plants I, Heidelberg, Germany 1989]
## Fatty Acids in Birch Bark

<table>
<thead>
<tr>
<th>C&lt;sub&gt;16&lt;/sub&gt;-Family</th>
<th>C&lt;sub&gt;18&lt;/sub&gt;-Family</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;14&lt;/sub&gt;-COOH</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;7&lt;/sub&gt;-CH = CH-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;7&lt;/sub&gt;-COOH</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;14&lt;/sub&gt;-COOH</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;7&lt;/sub&gt;-CH = CH-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;7&lt;/sub&gt;-COOH</td>
</tr>
<tr>
<td>OH</td>
<td>OH</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;x&lt;/sub&gt;-CH-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;y&lt;/sub&gt;-COOH</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;7&lt;/sub&gt;-CH - CH-(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;7&lt;/sub&gt;-COOH</td>
</tr>
<tr>
<td>OH</td>
<td>OH</td>
</tr>
<tr>
<td>OH</td>
<td>OH</td>
</tr>
</tbody>
</table>
The Pulp Mill Biorefinery

Example 3
Lignans from softwood knots

Åbo Akademi
Spruce
Picea abies

As it happened in 1998 - - -

Knot, branch base

10% lignans!
Lignans
Pinoresinol

Stilbenes
Pinosylvin

Flavanoids
Catechin

Tropolones
Thujaaplin (corrosive)

Tannins (garvämmen)
Gallic acid
The Pulp Mill Biorefinery

Example 4
Xylan from black liquor

STFI
Hemicelluloses in Softwood

O-acetyl-galactoglucomannan
(DP ~100)

Arabino-4-O-methylglucuronoxyylan
(DP ~100)
Kraft Pulping - Hemicelluloses

*O*-acetyl-*galactoglucomannan*

~ 130 kg /tonne wood is degraded into sugar acids and to other low molar mass sugars found in the cooking liquor

*O*-acetyl-4-*O*-methylglucuronoxylan

~ 150 kg /tonne wood is dissolved in the cooking liquor, most of it in polymeric form
Degree of Polymerization for SW Xylan

Dissolving pulp
DPw = 24

Sulphite pulp
DPw = 50

Kraft pulp
DPw = 104

Spruce wood
Chlorite delign.
DPw = 136

Molar mass

Xylan From Black Liquor

Chips → Pre-impregnation → Flash steam → to BL evaporation

white liquor

Lignin & Xylan

Black liquor* → Digester → to O2 delignification

Washing

wash liquid

white liquor
Mill Trial With Ceramic Membrane 2005
High Retention of SW Hemicelluloses
- cut-off 4 - 8 kDaltons
Fouling in Mill Pilot – No Problem!!

5 kDalton

145 °C
Xylan Sorbs Onto Fibers

Debranching of xylan in the cooking liquor

Aggregation of xylan polymers

Aggregation and sorption

Sorption of xylan onto fibre surface
The Pulp Mill Biorefinery

Example 5
Glucomannan from TMP white water

STFI, Åbo Akademi
Glucomannan From TMP White Water

Interesting barrier properties!
The Pulp Mill Biorefinery

Example 6
Lignin from black liquor

FRAM2-program

STFI, Chalmers, LTH, Sydkraft, ÅF, Fortum, Södra, StoraEnso, Weyerhaeuser…….
Lignin Removal

Evaporation

Recovery boiler

White liquor preparation

Digester

Pulp bleaching

Wood chips

Pulp
Removal of Lignin – Industrial Value

- Removal of lignin is a low capital-cost alternative to de-bottleneck the recovery boiler
- Lignin can replace mineral oil in the lime kiln or outside the pulp mill or be a chemical feed-stock for “green chemicals
Lignin Removal – Precipitation/washing

Weak Black liquor

Evaporation

Black liquor (30-40 % DS)

Precipitation

Filtering, washing

Lignin

To recovery boiler

Acid

Cooking chemicals, organic substances
Mobile Equipment for Lignin Removal

Precipitation vessel

0.1 m² filter press
New Process for Lignin Removal

Weak liquor tank

Evaporators

To recovery boiler

Recirculation of washing and filtration liquid

Precipitation tank

Filtration

Slurry tank

Washing

Carbon dioxide inlet

Lignin

Black liq. (30% DS)

Filtration

Slurry liquid

Wash liquid
Mill Pilot 2004 – 10 Tonnes Produced
Mill Pilot Trials

Specific filtering resistance, m/kg

Filtration cycle no.

α

av(m/kg)

Same level as kaolin
Lignin from Mill Pilot

60-70 % Dry solids
0.1 - 0.5 % ash
0.05 – 0.4 % Na
Possible Lignin Applications

- Solid fuel for lime kilns
- Carbon fiber for composites
- Porous carbon structures

- Chemicals
  - Fenols
  - Binder
  - Dispersant
  - Sequestering
Lignin Pellets 700 kg/m$^3$
Lignin Removal - Mill Pre-study

A recovery boiler limited kraft pulp mill
Annual capacity of 250,000 t
Capacity increased 25% to 320,000 tpy
This corresponds to 50,000 tonnes of lignin per year

- The investment is reduced 140 MSEK (18 MUSD)
- If lignin replaces mineral oil the annual revenue is 40 MSEK (5 MUSD).
Example 7
Gasification of black liquor

Swedish BLG Program

STFI, ETC, Chalmers, Umeå Univ., ETC, Luleå Technical Univ., Corrosion Institute
Swedish BLG Program

0. Synthesis and coordination

Gasifier projects
1. CFD modelling of gasification reactor (ETC)
2. CFD modelling of quench cooler and condenser (Luleå Technical Univ.)
3. Smelt formation (Umeå Univ.)
4. Gasification kinetics (Chalmers)

Mill-oriented projects
5. Autocausticising with borates (ETC)
6. Pulping with new liquors (STFI-Packforsk)
7. Kidneys, NPEs (STFI-Packforsk)
8. Construction materials hot green liquor (Corrosion Institute)
Swedish BLG Program

**Funding from**
- **Government:** Swedish Energy Agency, County of Norrbotten
- **Foundation:** MISTRA
- **Forest ind.:** Sveaskog, Södra, SCA, Kappa
- **Utility:** Vattenfall

**45 MSEK** (~ 5 MEUR) to Swedish Research Program

**55 MSEK** (~ 6 MEUR) to Development Plant DP-1
The Thermal Pulp Mill Biorefinery

- Chips
- Pulp mill
  - Spent liquor
  - Biomass and black liquor gasification
- Cellulose
  - Particles
  - Fibres
  - Films
  - Sponges
- Pulp
- Paper
- Electric power
- Methanol/DME
- Higher hydrocarbons
Black Liquor Gasification Combi Cycle

Over 1000 kWh ptp
Black Liquor Gasification Motor Fuel

Methanol or DME

300 – 600 kg methanol/DME ptp
Black Liquor Gasification
Production of Methanol/DME

2200 t/d of Dry Wood

Wood for Pulping

Falling Bark

Biomass Boiler Plant

Biomass

24.3 t/h Bark
66 MW

33.4 MW

Power

Bark

210,000 t/yr
Methanol
141 MW

Methanol/DME

Black Liquor Gasification and Motor Fuel Plant

Black Liquor

Steam

Pulp and Paper Processing Plant

Green Liquor

1000 t/d of ADt (350,000 t/yr)
The Pulp Mill Biorefinery

Example 8
New process for removal of soap from black liquor

Kiram, Aga Linde
New Process for Soap Removal
Kappa Kraftliner Mill, Piteå, Sweden

First step of a wood extractives refinery

- In operation spring 2006
- Capacity 25,000 tons of raw extractives (tall soap) per year
- Decreased use of sulfuric acid
- Final products
  - Resins for binders formulations
  - Fatty acid ester (biodiesel)
  - \( \beta \)-sitosterol
Södra Cell – Future Plans
Pulp producer and energy supplier
EUROPEAN INITIATIVES PROMOTING “THE BIOREFINERY”

Forest-Based Sector Technology Platform

Seventh Framework Programme
Commission proposal for 2007-2013 (Billion €)

Bio-refineries

Wood, Crops, Grasses Forestry or Agricultural Residues Animal or Municipal Waste

Heat, Electricity, Fuels Chemicals Materials Food, Feed, Fibre

will be supported in two FP7 Thematic Priorities:
Food, agriculture and bio-technology and Energy
Is the Future Pulp Mill a Biorefinery?
Wood Biorefinery Vision

Today's limited biorefinery

- **Lignocellulosic feedstocks** (woody biomass, straw, etc.)
  - **Main product** (mainly from cellulose, in part from hemicellulose) - For sale
  - **Residual material** (mainly lignin, also some hemicellulose) - For on-site energy production; often excess energy available

Tomorrow's versatile biorefinery

- **Lignocellulosic feedstocks** (woody biomass, straw, etc.)
  - **Main product** (mainly from cellulose, in part from hemicellulose) - For sale
  - **LIGNIN AND REFINING**
    - **Hemi** - Variety of higher-value products for sale and/or on-site use
The Future Pulp Mill is A Wood Biorefinery