Tomorrow's biorefineries in Europe

Paper-mills options for partial conversion: Example of an integrated Biorefinery

Kyriakos Panopoulos
CERTH – Greece

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Gasification based biorefinery

Willow / Poland

Giant Reed / Greece

Wood / Sweden

Pulp industry

Black Liquor
Gasification based biorefinery

Willow / Poland

Giant Reed / Greece

Wood / Sweden

Pulp industry

Black Liquor
Mapping Production / Consumption

Recovery Boilers in Europe

- Cluster of mills
- Important single mill

Chemrec
Brief description

- The primary technology for a Syngas Biorefinery is biomass gasification.

- For a fast track to materialization of the Syngas Biorefinery, the Chemrec process is selected. This process gasifies black liquor deriving from the Kraft pulping process.

- A typical mid-size European mill, with a capacity of 1300 ton pulp per day, produces 2000 ton black liquor dry solids per day (2000 tDS/d) corresponding to about 270 MW thermal energy.

The novel products identified from this biorefinery are:

- Production of Hydrogen peroxide ($\text{H}_2\text{O}_2$)
- Production of Dimethyl disulphide (DMDS)
- Production of higher alcohols (HA)
- Energy production
High Pressure SynGas / H2O2 BIOREFINERY: Combined production in a Paper Mill. **Specifics: High Pressure Syngas**

- **WOOD** → **Syngas** → **Gas Cleaning** → **H2S** → **DMDS**
- **Black Liquor Gasification** → **Syngas** → **Gas Cleaning** → **H2S** → **DMDS**
- **Higher Alcohols** → **Syngas** → **Gas Cleaning** → **H2S** → **DMDS**
- **Paper Mill** → **Paper Pulp**

**Cu – based cat**
**Mo – based cat**

- **H2** → **H2O2**
  - Well established « AQ » process was selected
  - Direct and indirect methods through MeOH
Production yields overview

2500 ton /d
Biomass → 2000 tons/d
Black Liquor → 1057 ton/d
syngas → W tons of
product D

### Ultimate Analysis (Dry basis %)

<table>
<thead>
<tr>
<th></th>
<th>wood</th>
<th>black liquor</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>48.75</td>
<td>31.3</td>
</tr>
<tr>
<td>H</td>
<td>6.54</td>
<td>3.4</td>
</tr>
<tr>
<td>O</td>
<td>44.10</td>
<td>37.3</td>
</tr>
<tr>
<td>S</td>
<td>0.24</td>
<td>5.6</td>
</tr>
<tr>
<td>N</td>
<td>0.05</td>
<td>0.1</td>
</tr>
<tr>
<td>Na</td>
<td>-</td>
<td>22.4</td>
</tr>
</tbody>
</table>

### Moisture

<table>
<thead>
<tr>
<th></th>
<th>wood</th>
<th>black liquor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.1</td>
<td>24.8</td>
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</tbody>
</table>

### Proximate analysis (%)

<table>
<thead>
<tr>
<th></th>
<th>wood</th>
<th>black liquor</th>
</tr>
</thead>
<tbody>
<tr>
<td>moisture</td>
<td>9.88</td>
<td>21.6</td>
</tr>
<tr>
<td>fixed carbon</td>
<td>89.8</td>
<td>21.6</td>
</tr>
<tr>
<td>volatiles</td>
<td>0.32</td>
<td>41.2</td>
</tr>
</tbody>
</table>

### HHV (MJ/kg)

|       | 18.88 | 12.57 |

#### Ton/d

- **MeOH**: 399.6
- **EtOH**: 22.9
- **PrOH**: 69.3
- **BuOH**: 8.6
- **PeOH**: 1.9
- **H2O2**: 45.7
- **DMDS**: 30.4

#### H2O2

- **Used**: -11.0
- **Cu- cat**: 399.6
- **Mo cat**: 11

#### Paper Industry

- Bleaching
- Tradable Commodity
- Upgrading
- Side Product

Confidential
Map of commercial and pilot units for higher alcohols production form syngas
## SWOT analysis

<table>
<thead>
<tr>
<th>Strengths</th>
<th>Weaknesses</th>
<th>Opportunities</th>
<th>Threats</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diversity of products both chemicals &amp; fuels</td>
<td>Relatively low selectivity towards HA</td>
<td>Replacing carbon emitting processes</td>
<td>Capital Costs high</td>
</tr>
<tr>
<td>On site H₂O₂ production has increased cost reduction (no need for transportation).</td>
<td>Biofuel market needs to be created in parallel (MeOH and EtOH).</td>
<td>Synergy in revenues</td>
<td>Opex high compared to Natural Gas.</td>
</tr>
<tr>
<td>The target products are high volume</td>
<td>MeSH production from natural gas is currently far less costly.</td>
<td>Drawing incentives from both agriculture and New business for European farmers</td>
<td>Biomass based alternative technologies (FT, NexBTL, Ecofining, Gevo)</td>
</tr>
<tr>
<td>Existing know-how on process steps</td>
<td>MeSH is a toxic material not easily transported. So an additional step to transform it on site to DMDS or other</td>
<td></td>
<td>Papermills lack of financial resources</td>
</tr>
<tr>
<td>Sustainable production (LCA).</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Porter’s Six Forces Analysis- Value Chain 5: Value proposition for Paper Mills
Black Liquor Gazification, and conversion to Higher Alcohols, H$_2$O$_2$, and others

<table>
<thead>
<tr>
<th>Category</th>
<th>Relative Power</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bargaining power of Suppliers (of Biomass)</td>
<td>Medium</td>
<td><strong>Paper Mills</strong> try to find better value secondary products. Additional biomass or organic wastes can be used for energy production. Other options include stand alone gasification plants - in that case feedstock capacity building is difficult (logistics).</td>
</tr>
<tr>
<td>Bargaining Power of Customers (of chemicals &amp; fuels)</td>
<td>Medium</td>
<td><strong>Paper Mills are also H2O2 consumers.</strong> They can see a value of on-site production in reducing the transportation cost and storage. Large array of customer industries for higher alcohols. Customer / producer need to be satisfied with HA mixture composition / efficiency (respectively)</td>
</tr>
<tr>
<td>Threat of New Competitors</td>
<td>Low</td>
<td>Absolute cost (CAPEX + OPEX) remains high for fuels compared to current market. Substituting fossil based chemicals might attract subsidies but this will attract also new competitors.</td>
</tr>
<tr>
<td>Threat of Substitute Products or services</td>
<td>Medium</td>
<td>H2O2 production sites are far from paper mills and this means transporting 50 % water. Nevertheless NG costs are currently very low (alternative route) Biobased higher alcohols can be produced by other processes as well.</td>
</tr>
<tr>
<td>Competitive Rivalry</td>
<td>High</td>
<td>Many Biomass gasification projects close to demo phase, Diverse reactor technologies: low or high pressure; Fluidized bed, entrained flow etc for handling different feedstock (south/north)</td>
</tr>
<tr>
<td>Stakeholders: Government / Public</td>
<td>High</td>
<td>Government can positively favor renewable products (Bio-Preferred) and Biofuels, through subsidies, Existing projects receive positive public reception and news coverage</td>
</tr>
</tbody>
</table>
IP score – Competition benchmark

Diagnostic report on risk and potential factors

- VC5 - Production of Syngas from Natural Gas (Conventional techno)
- VC5 - Production of Higher Alcohols with MeOH and EtOH
- VC5 - On-site H2O2 Production
- VC5 - MeSH synthesis from Syngas
- VC5 - Current MeSH Process from Methanol + H25
LCA

Significant benefit in terms of:
• climate change,
• water withdrawal,
• ecosystem quality and
• human health
with respect to conventional production routes for the specific set of co-products (incl. alcohols, hydrogen peroxide and di-methyl sulphide).

Ecosystem quality is favourable to the compared to conventional routes. The main reason for this is that the avoided product in this case is considered to be ethanol from biomass (considered as a mix of 40% corn-based from US, 40% sugarcane-based from Brazil, 15% wheat-based from Europe and 5% lignocellulosic).
Capital Cost impact

What do we get for 400 M€ CAPEX?
Jobs creation

100 M€ Capex => 50-70 direct and 200-280 construction jobs

Prepared by ARKEMA

Direct Jobs Construction
Direct jobs Operation
Public Support M Euro

Capital Cost M€ (assuming plant constructed in France, April 2011)
VC5 cost analysis – Black liquor to $\text{H}_2\text{O}_2$, higher alcohols and DMS

- **Base case**: 47% chance of being profitable
- **Best case**: 100% chance of being profitable but requires
  - very low wood cost
  - 40% of capital cost offset against recovery boiler cost
- Heat integration essential for good economics

Net present value – Value Chain 5 hydrogen peroxide, higher alcohols and DMS
Summary of Value Chain 5: High pressure Syngas / HA & H_2O_2 Biorefinery

Need, Market Opportunity & Impact

Need: H_2O_2 is required on site in pulp & paper industries, directly as fuels, as fuel additives for octane or cetane enhancement, as oxygenate fuel additives for environmental reasons, and as intermediates to form other fuel additives as well as for the production of solvents or other chemical sub-processes in the chemical industry.

Market Opportunity: There is a growing need for fuels and CO_2 neutral products

Impact: Gasification can both cover energy and power demands of the total process as well as provide processes routes for intermediate chemicals production. This important combination is expected to push the gasification technology into diverse application coupled with almost all diverse technology bio-refineries.

Technology

Wood → Pulp → Black Liquor → HA → Fuel additives, Chemicals
H_2O_2 → Paper Industry
DMDS → Sulfur Chemicals

Technology Development Milestone (T.R.L.)

<table>
<thead>
<tr>
<th>Step</th>
<th>TRL</th>
<th>Risk</th>
<th>Measure of Success</th>
</tr>
</thead>
<tbody>
<tr>
<td>Higher alcohols synthesis from Syngas from EuroBioRef technology</td>
<td>4</td>
<td>medium</td>
<td>Stable catalyst performance</td>
</tr>
<tr>
<td>MeSH Synthesis from Methanol</td>
<td>9</td>
<td>low</td>
<td>Already at commercial scale, but not biobased</td>
</tr>
<tr>
<td>MeSH synthesis through direct syngas</td>
<td>4</td>
<td>Medium</td>
<td>Stable catalyst performance</td>
</tr>
<tr>
<td>H_2O_2 synthesis</td>
<td>7</td>
<td>Low</td>
<td>Stable catalyst performance</td>
</tr>
<tr>
<td>Gas cleaning</td>
<td>6</td>
<td>Low</td>
<td>Proper gas cleaning</td>
</tr>
<tr>
<td>Solid Biomass Gasification</td>
<td>6</td>
<td>Low</td>
<td>Robust performance without downtime due to agglomeration/defluidization as well problems.</td>
</tr>
<tr>
<td>Black liquor gasification</td>
<td>7/8</td>
<td>low</td>
<td>In operation in Chemrec at large pilot scale under pressure (level 7 or 8). Would be 9 if at atmospheric pressure and with Air.</td>
</tr>
</tbody>
</table>

Business Model

Pulp & Paper Industry

CHEMREC

Fuel /Refinery Industry
Thanks to Carl-Johan Hjerpe (NYKOMB) Angeliki Lemonidou (CERTH), Raf Roelant & Wei Zhao (PDC), Arnaud Dauriat (Quantis), Raphael Slade (Imperial College) and all the Value Chain contributors.

Thanks for your attention!