Production of Biomass-Based DME and Methanol via Black Liquor Gasification

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Chemrec AB
www.chemrec.se
Content

1. Forrest biomass handling today and tomorrow
2. The pulp mill becomes a biorefinery
3. Technology
4. Availability comparison / goal
5. At what price?
6. Development and commercialization
7. Why DME and why methanol? The drivers
8. Conclusions
1. Forrest biomass handling today and tomorrow
Major Biomass Flow Today and Tomorrow

TODAY

- Logs
- Forest
- Pulp Wood
- Saw-mill
- Wood Products
- Recovery Boiler
- Pulp Mill
- Pulp

New Value Streams from Residuals & Spent Pulping Liquors
Major Biomass Flow Today and Tomorrow

New Value Streams from Residuals & Spent Pulping Liquors

TOMORROW

Forest

- Logs
- Pulp Wood
- Forest Residual

Saw-mill

- Wood Products

Pulp Mill

- Combined Recovery and Fuel Generation

Pulp

Fuel

New Value Streams from Residuals & Spent Pulping Liquors
2. From Pulp Mill to Biorefinery
The Pulp Mill Biorefinery

TOMORROW
STEP 1

Forest

Logs

Saw-mill

Wood Products

Pulp Wood

Forest Residual

Combined Recovery and Fuel Generation

Pulp Mill

Pulp

Fuel

New Value Streams from Residuals & Spent Pulping Liquors

The Pulp Mill Biorefinery
3. Technology
The Pulp Mill

Wood yard

Cooking

MC-O₂

Bleaching

Evaporation

Bleaching chemical preparation

Effluent treatment

Power generation

Power boiler

Biomass

Power & steam

Typical 5-600 MW

Black liq. energy

Recovery boiler

Pulp dryer

Pulp

Oxygen plant
## Composition of Wood and Black Liquor

### Black Liquor: A Biomass Feedstock in Liquid State

### Black Liquor Composition

<table>
<thead>
<tr>
<th>Component</th>
<th>% Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>34.55</td>
</tr>
<tr>
<td>H</td>
<td>3.59</td>
</tr>
<tr>
<td>S</td>
<td>4.35</td>
</tr>
<tr>
<td>O</td>
<td>34.70</td>
</tr>
<tr>
<td>Na</td>
<td>18.45</td>
</tr>
<tr>
<td>K</td>
<td>2.96</td>
</tr>
<tr>
<td>Cl</td>
<td>1.40</td>
</tr>
<tr>
<td>N</td>
<td>-</td>
</tr>
</tbody>
</table>

Total (%): 100.0

### Combustible Characteristics

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>% Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>BL, Dry Solids</td>
<td>80%</td>
</tr>
<tr>
<td>HHV</td>
<td>MJ/kg, DS 14.2</td>
</tr>
<tr>
<td>NHV</td>
<td>MJ/kg, DS 12.0</td>
</tr>
</tbody>
</table>

### Wood Type Composition

<table>
<thead>
<tr>
<th>Wood Type</th>
<th>Cellulose</th>
<th>Hemi-cellulose</th>
<th>Lignine</th>
<th>Extractives + others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spruce</td>
<td>42%</td>
<td>28%</td>
<td>27%</td>
<td>3%</td>
</tr>
<tr>
<td>Fir</td>
<td>41%</td>
<td>28%</td>
<td>27%</td>
<td>4%</td>
</tr>
<tr>
<td>Birch</td>
<td>41%</td>
<td>34%</td>
<td>21%</td>
<td>4%</td>
</tr>
</tbody>
</table>
The Recovery Boiler is changed to a Gasification Plant for Production of Motor Fuels

Typical 5-600 MW

Biomass

BLGMF Plant

DME/MeOH
The Biomass Intake to the Mill must be Increased to compensate for the withdrawal of Motor Fuel
The Biomass Intake to the Mill must be Increased to compensate for the withdrawal of Motor Fuel.

Typical 5-600 MW

Biomass Plant

DME/MeOH
Black Liquor Gasification to Motor Fuels Process

ASU

Oxygen

Gasification w quench 150MW / train 3x50% 1000°C 30 bar

Steam

Gasification

Raw gas

Gas cleaning and conditioning

Sulphur handling

PS** liquor

White liq.

Syngas

Synthesis- and distillation units

DME/Metanol

* Low Sulphidity
**Poly Sulphide

EL

Black liq.

Weak wash

LS* Green liq.
Chemrec Development Plant (DP-1), Piteå, Sweden

- **Black Liquor**
- **Oxygen**
- **Atomizing medium**

**REACTOR**

- **Green Liquor**
- **Weak Wash Liquor**

**QUENCH**

- **Raw syngas**
- **Condensate**

**GAS COOLER**

- **Cooling water**
- **BFW**

**H2S-ABSORPTION**

- **White Liquor**

* Cooling water in DP1

Purified and cooled syngas (to flare)
May 12: Low Content of Char, No Soot and Excellent Settling of Dregs in Green Liquor
BLGMF Block Flow Diagram

The Pulp Mill

- Wood chips
- Fibre line 1 (SCMBB)
  - Cold alkali impregnation
  - Warm BL treatment
  - Hot BL treatment
  - Cooking
- Fibre line 2
  - Thin liquor
  - Evaporation
  - Bleaching
  - Screening & washing
  - Drying
  - Thick liquor
  - Digest

The BLGMF Plant

- Black liquor
- Air Separation
- BL Feeding & Preparation
- BL Gasification Unit
- Raw gas cooling & washing
- Gas Cleaning unit
- Gas Cleaning unit
- CO-Shift conversion
- Final Product
- DME/MeOH synthesis
- Product storage DME/MeOH
- DME/MeOH Distillation
- Purge gas

- Offsites and utilities
  - O2 supply and N2 system
  - O2 supply and N2 system
  - Sulphur recovery unit
  - Syngas
  - MeOH absorbent
  - Fusel oil
  - Final Product
- CO2 to air
  - (Option: CO2 to tall oil production unit)

- Drying
  - PS liquor
  - Claus off-gas
  - Chlorinated liquor

- Thick liquor
  - Screening & washing
  - White liquor
  - Drying
  - Digester
  - Thick liquor

- Thin liquor
  - Evaporation
  - Bleaching
  - Screening & washing
  - Drying
  - Thick liquor
  - Digest

- Pulp
  - To recovery and/or power boiler

Chemrec
4. Availability comparison / goal
## Technology comparison

<table>
<thead>
<tr>
<th></th>
<th>PerstorpOXO (Sweden)</th>
<th>BASF (Germany)</th>
<th>Eastman Chemicals (USA)</th>
<th>Ube Ammonia (Japan)</th>
<th>Chemrec BLGMF</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feedstock</strong></td>
<td>Oil</td>
<td>HVR</td>
<td>HS Coal</td>
<td>HS Coal / Petcock</td>
<td>Black Liquor</td>
</tr>
<tr>
<td><strong>Gasifier size / # of trains</strong></td>
<td>95 MW / 1x100%</td>
<td>150 MW? / 4x33%</td>
<td>300 MW / 2x100%</td>
<td>150 MW / 4x33%</td>
<td>150 MW / 3x50%</td>
</tr>
<tr>
<td><strong>Pressure, bar</strong></td>
<td>30</td>
<td>30</td>
<td>65</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td><strong>Temperature, deg C</strong></td>
<td>1300</td>
<td>1300</td>
<td>~1400</td>
<td>1450</td>
<td>~1000</td>
</tr>
<tr>
<td><strong>Products</strong></td>
<td>Oxo chemicals</td>
<td>Petro-chemicals</td>
<td>Petro-chemicals</td>
<td>Ammonia/ Urea</td>
<td>Fuels/ chemicals</td>
</tr>
</tbody>
</table>
Availability of Gasification Plants

Examples shown are well established technologies with plants in operation more than 20 years.

Planned annual shut-downs normally 7-10 days.

Availability during planned on stream time is on the same level as in the pulp industry, 98-99%. Plants often have one gasifier train as stand-by.

Gasification temperature 1300-1500°C. Chemrec 1000°C.

Gasification pressure 30-65 bar. Chemrec 30 bar.

Thermal input per gasifier 20-600MW. Chemrec 100-150MW in full scale.

Handle soot and slag in the gasification unit. Chemrec handles green liquor.
5. At what price?
Swedish Fuel Consumer Price - average 2005 (Net back calculation)  1USD / 1EUR = 0.78

2.3 USD/gal

10/4/2006
## Base for Economic Calculation

<table>
<thead>
<tr>
<th>Concept</th>
<th>2000 tDS/d BLGMF Plants (Recovery Boiler replacement)</th>
</tr>
</thead>
</table>
| Concept base | Incremental investment  
Replace recovery boiler (RB) investment  
Incremental O&M |
| Plant utilization, h/year | 8400 |
| Time for calculation | 4Q, 2005 |
| Power price | 51 EUR/MWh |
| Biomass price, dry basis | 67 EUR / t |
| Additional Pulp Capacity | No. Recovery boiler replacement |
| Extra pulp | Yes. Due to increased yield (wood to pulp) |
Investment in new Recovery Technology
Capacity: 2000 tDS/d black liquor
Pay Back Calculation; Large BLGMF plants
MeOH: 245 000 t/y or DME: 172 000 t/y

<table>
<thead>
<tr>
<th>Product</th>
<th>MeOH</th>
<th>DME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant size, tDS/d of Black Liquor</td>
<td>2000</td>
<td>2000</td>
</tr>
<tr>
<td>Incremental Revenues and costs, MEUR/y</td>
<td>+49 / +82</td>
<td>+56 / +94</td>
</tr>
<tr>
<td>MeOH/DME product excl. / incl. Swedish CO₂ tax (Not including VAT, energy tax and distribution)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extra pulp yield (at 550 USD/t)</td>
<td>+ 7</td>
<td>+ 7</td>
</tr>
<tr>
<td>Additional biomass, 67 EUR/t (dry)</td>
<td>- 8</td>
<td>- 8</td>
</tr>
<tr>
<td>Operation &amp; Maintenance</td>
<td>- 5</td>
<td>- 5</td>
</tr>
<tr>
<td>Electricity purchase, 51 EUR/MWh</td>
<td>- 14</td>
<td>- 14</td>
</tr>
<tr>
<td>Net Operating benefit</td>
<td>29 / 62</td>
<td>36 / 74</td>
</tr>
<tr>
<td>Investment, MEUR</td>
<td>280</td>
<td>280</td>
</tr>
<tr>
<td>Investment incl. integration with mill</td>
<td>- 130</td>
<td>- 130</td>
</tr>
<tr>
<td>Recovery Boiler Investment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Incremental investment</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Pay-back time, years</td>
<td>5.2 / 2.4</td>
<td>4.2 / 2.0</td>
</tr>
</tbody>
</table>
6. Development and Commercialization
# Chemrec Development Timeline

<table>
<thead>
<tr>
<th>P*</th>
<th>Oxidant</th>
<th>Capacity**</th>
<th>Location</th>
<th>85-89</th>
<th>90-94</th>
<th>95-99</th>
<th>00-05</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Air</td>
<td>3 (0.5)</td>
<td>SKF, Hofors, Sweden</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Air</td>
<td>75 (11)</td>
<td>AssiDomän, Frövi, Sweden</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>A</td>
<td>Air</td>
<td>330 (50)</td>
<td>Weyerhaeuser, New Bern, USA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Air / O₂</td>
<td>6 / 10 (1 / 1.5)</td>
<td>Stora Enso, Karlstad, Sweden</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>O₂</td>
<td>20 (3)</td>
<td>Kappa, Piteå, Sweden</td>
<td></td>
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</tbody>
</table>

*) Pressure in bar, or A for atmospheric pressure

**) Capacity given as tonnes of dry substance black liquor/24 hours and in MW (LHV) of black liquor flow
Chemrec’s Booster in New Bern, NC - USA

Operates as a booster unit to the recovery boiler in the Weyerhaeuser pulp mill in New Bern, North Carolina

Corresponds to ~15% of the mill’s production

Start up: Dec 1996
Capacity: 330 tDS/day
50 MW
Oxidant: Air
Pressure: Atmospheric
Chemrec’s Development Plant, Piteå, Sweden, Milestones

2004
Ordering critical Components: June
Financing completed: Sept
Start of mechanical erection: Oct

2005
Mechanical completion: May
Commissioning: May-Sep
Start of operation: Sep 30
Test runs & debugging: Oct-Dec

2006
Test runs & debugging: Jan-Mar
Burner optimization: Apr-May
Longest run 13 days (excellent syngas and green liquor quality): Sept

DP-1 Plant
Chemrec’s Development Plant, Piteå, Sweden
## Time Schedule Pressurized BLG Development

### Activity: DP-1, Piteå, Sweden (3 MW)
- EPC
- Operation
- DME-demo at DP-1, Pitea

<table>
<thead>
<tr>
<th>Year</th>
<th>Quarter</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>1 2 3 4</td>
<td>1 2 3 4</td>
<td>1 2 3 4</td>
<td>1 2 3 4</td>
<td>1 2 3 4</td>
</tr>
<tr>
<td>DP-1</td>
<td>EPC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Operation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DME-demo</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Activity: Demos in Sweden
- DP-2 BLGMF (45 MW)
- DP-3 BLGMF (65 MW)

### Activity: Commercialisation
7. Why DME and why methanol?

The drivers
Chemrec gave a presentation to the Swedish Prime Minister’s “Commission against Oil Dependence” Hearing on January 20, 2006

We emphasized the following:
Watch the whole chain: From use of land to useful energy e.g. on an engine shaft

Use of land
  - wheat
  - raps
  - biomass

Conversion to fuel
  - fermentation
  - gasification
  - etc

Example:
  - ethanol
  - RME
  - DME/methanol

Conversion to useful energy in the vehicle
  - Diesel cycle
  - Otto cycle

Finally utilized energy
“Well to wheel” analysis (Volvo study)

Energy efficiency, %  CO2-equivalents, g/kWh

Fossil

Renewable

Diesel (crude oil) hybrid
Diesel (crude oil)
DME (natural gas)
MeOH (natural gas)
CNG (natural gas)
Synthetic diesel (natural gas)
Hydrogen (electr. EU mix) hybrid
DME (wood, black liquor) hybrid
Hydrogen (electr. wind) hybrid
MeOH (wood, black liquor)
Biogas (sewage)
DME (wood)
MeOH (wood)
Ethanol (wood)
RME (rape seed)
Ethanol (wheat)

0%  10%  20%  30%  40%  50%  60%  70%  80%  90%  100%  110%  120%  130%  140%  150%

0  300  600  900  1200  1500

Energy efficiency, %  CO2-equivalents, g/kWh
The use of land

Example:
- wheat
- raps
- biomass

Use of land
Base long term policy decisions on WtW type base data

Distance per hectare and year
(Heavy duty vehicle)

Source: AB Volvo

Diesel engine efficiency assumed for all fuels
The Fuel Generation Process

Conversion to fuel
- fermentation
- gasification
- etc

Example:
- ethanol
- RME
- DME/methanol

Example:
- wheat
- raps
- biomass

Use of land
The Route via Gasification and Syngas to Automotive Fuels

Coal → CO₂ → Syngas (CO+H₂) → Syntetic Diesel (FTD)

Heavy oils
Natural Gas
Biomass
Black liquor

Methanol
DME (DiMethylEter)
Hydrogen
The engine cycle

Conversion to useful energy in the vehicle
- Diesel cycle
- Otto cycle

Conversion to fuel
- fermentation
- gasification
- etc

Example:
- ethanol
- RME
- DME/methanol

Conversion to
useful energy
in the vehicle

Use of land

Example:
- wheat
- raps
- biomass

Finally utilized energy
VOLVO's DME-powered Truck
Honored Best New Achievement by “Best of What's New” Science Magazine, Nov 2005

- + 20% on power when optimized for ethanol
- + 16% on torque when optimized for ethanol
- Will be even higher figures when optimized for methanol
- SAAB (GM Europe) is now testing M100 in parallel with E100
Methanol & DME are “Relatives”
DME is dehydrated methanol
# Introduction Strategy

<table>
<thead>
<tr>
<th>Automotive Fuel</th>
<th>Low blends</th>
<th>As pure fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>DME</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol (E)</td>
<td>E5 (E10)</td>
<td></td>
</tr>
<tr>
<td>Alcohols (A)</td>
<td></td>
<td>A100</td>
</tr>
<tr>
<td>Methanol (M)</td>
<td>M3</td>
<td></td>
</tr>
</tbody>
</table>

**SHORT TERM ----> LONGER TERMIN**
8. Conclusions
Conclusions

• The pulp industry is by far the greatest commercial user of forest biomass material
• More than 600 TWh / 2200PJ of black liquor energy is used within the pulp mills world wide. This can be converted to:
  - 30 milj tons gasoline equiv. (World)
  - 6 milj tons gasoline equiv. (Europe)
• The pulp mill can become an efficient user of the third fraction of the forest material, wood residues not suited for logging or pulp wood
• DME and methanol can with the proposed system be generated at prices close to energy price of diesel and gasoline at crude prices of 30 USD/bbl
• Fuel generation at pulp mills becomes a second main product generating a cash flow on the level of 1/3 of the cash flow of the pulp
Conclusion con’d

• Potential to generate near 30% of Sweden’s current consumption of automotive fuels through black liquor gasification at the Swedish pulp mills.
  - In Finland ~50%
  - In Canada ~7%

• Volvo and Eucar/Concawe LCA analysis show that black liquor based production:
  - is among the most effective renewable production routes
  - has one of the highest CO2 reduction efficiencies

For more information see:

www.chemrec.se
www.aboutdme.org
Chemrec in Cooperation with and in Support by…

Feedstock Supplier

VOLVO

VATTENFALL

End Users

Authorities

SVEASKOG

Kappa Packaging

The Pulp Industry

MISTRA

EU Flag

Energimyndigheten

SCA

SÖDRA

LÄNSSTYRELSEN I NORRBOTTENS LÄN