METHANOL Production from Biomass

Green Pilot
Kickoff Seminar

Gothenburg
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LTU
Swedish Methanol tests in the 1980-ies

- During 1980-82 a large M15 fuel testing project was done with 1000 vehicles at 19 fuel stations and 11 car makes with 20 million km of driving. As neat fuel M100 was tested 1984-86 by SAAB-Scania and Volvo with 20 vehicles.

- Main results were same or better than for petrol in terms of engine performance, fuel handling and distribution. However, when oil prices fell 1986, investment in required infrastructure became less attractive.
Nynäshamnskombinatet 1984, 1500 MWth plant

- Project developed during 1982-84 by a Swedish team and with involvement of international contractors and process licensors.
- Engineering efforts of this and following NEX projects totaled €30 million.
- Acquired technology knowledge have contributed to today’s status in development.
- No methanol plant built but two IGCC plants in Italy and spinoff into black liquor methanol in Piteå by the team.

Project size: 700 000 t/y of MeOH
Vision for a Methanol based Energy System

- Natural gas
- Fossil MeOH
- Methanol plants

- Wastes

- Liquefact.
- Gasification
- MeOH

- Pyrolysis

- Biomass
- Gasification of biomass
- MeOH
- Renewable MeOH

- SOEC*
- CO₂, H₂O, electr.

- Ports
- 1 2 n nn
- DME

- Distribution

- Marine sector
- Heavy transports

- Chemical industry

- Cars & buses
Different Biomass Conversion Alternatives

• Chemrec black liquor gasification (BLG)
• Biomass gasification
• Addition of pyrolysis oil to BLG
• Renewable power to boost syngas production
Today’s commercial Forrest Industry has two main legs:

1. **New Value Streams from Residuals & Spent Pulping Liquors**
2. **Saw-mill**

Diagram:
- **Forest**
  - Logs
  - Pulp Wood
- **Saw-mill**
  - Wood Products
- **Pulp Mill**
  - Recovery Boiler
  - Pulp

New Value Streams from Residuals & Spent Pulping Liquors
The Vision: Tomorrow’s Biomass flow to the Forrest Industry

TOMORROW

Forest

Logs

Saw-mill

Wood Products

Pulp Wood

Forest Residual

Chemrec Technology

Combined Recovery and Fuel Generation

Pulp Mill

Fuel

New Value Streams from Residuals & Spent Pulping Liquors
MeOH / DME Process - Block Flow Diagram

- **Air Separation**
- **Gasification**
- **Gas Cooling**
- **Smelt Dissolver**
- **CO Shift**
- **Acid Gas Removal**
- **Methanol Synthesis**
- **DME Synthesis**
- **Product Distillation**

**Products:**
- DME
- or
- MeOH

**Overview:**
- "Simple" once-through system.
- Market-ready products.
- Product flexibility.

**Key Processes:**
- Black liquor recovery
- Syngas generation
- H₂S to CO₂ recovery
- Steam generation and use
- Green liquor to pulp mill
Major Biomass Flow from the Forrest including Direct Biomass Gasification

- Logs
- Pulp
- Wood Residual
- Sawmill
- Wood Products
- Pulp Mill
- Combined Recovery and Fuel Generation
- Chemrec Technology
- Direct Biomass Conversion
- Fuel
MeOH / DME Process - Block Flow Diagram

**Chemrec**

- Black Liquor Gasification (BLG) from BL to good quality raw syngas
  - Performed at approx. 30 bar

**CFB, BFB, indirect**

- Biomass drying
- Biomass feeding
- Biomass gasification
- Gas Cooling
- Particle removal
- Tar removal
- Methane conversion
- Carrier gas, CO2

Order of processes indicative only

- The Pulping Process
- Pressurizing pump

*Different processes depending on gasification technology*

**Methanol Synthesis**

**DME Synthesis**

**Product Distillation**

- Products: DME or MeOH

**OK!**

*Gas cleaning*

- *Different processes depending on gasification technology*
BioDME Production Overview

Over 4 ton DME/d was reached in Sep -12

The plant incl. gasification is operated by 2 operators per shift

Key operation data:
- Gasification at 30bar/1050°C
- Methanol synthesis at 130 bar
- DME synthesis at 15 bar
More than 1000 tons of BioDME has been produced since start in Nov 2011 to May 2016.
Fuel Distribution

- Available technology modified for DME
- Safety regulations based on LPG
- ~200 k€ per filling station (+33% vs diesel)
- Easy to achieve

Four filling stations

200 m³ storage tank in Piteå

34 m³ trailer

Four filling stations
Goals achieved for the Volvo field tests
8 trucks, 2013-01-01 to 2014-06-30

<table>
<thead>
<tr>
<th>Km / Mile</th>
<th>Status 2014-08-31</th>
<th>Target June 2014</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total mileage</td>
<td>1 485 000 / 933 000</td>
<td>1 400 000 / 870 000</td>
</tr>
<tr>
<td>1 truck</td>
<td>296 000 / 184 000</td>
<td>250 000 / 155 000</td>
</tr>
</tbody>
</table>

![Graph showing total field test mileage](image)

**Extended field test**
Chemrec Status as per January 2013

- **Dec 31, 2012**: Chemrec Piteå companies including pilot plants sold by Chemrec AB to LTU Holding AB,
- **Jan 1, 2013**: 17 pilot plant staff employed by LTU.
- **Dec 31, 2012**: License agreement between licensor Chemrec AB & Haldor Topsøe with LTU and LTU Holding. Technology rights stay with licensors.
- **Jan 30, 2013**: Consortium Agreement between parties involved in continued R&D.
- Chemrec has reduced staff awaiting long term stable regulations for advanced biofuels. Two Chemrec Stockholm staff temporarily on leave assigned to LTU
- Continued operation of the plants as part of LTU Biosyngas Program
Biomass flow from the forest can be increased by adding pyrolysis oil to the black liquor flow.
Material and energy balances

PO: 0 MW, 122 MW, 365 MW

- Biomass: 96 MW, 92 MW, 86 MW
- Fuel drying Boiler Turbine: 32 MW, 45 MW, 70 MW
- Electricity: 15 MW, 14 MW, 13 MW
- Bark: 29 MW
- Pulpwood: 420 MW
- Lime kiln fuel: 16 MW, 11 MW, 0 MW
- MeOH: 97 MW, 183 MW, 353 MW
- BFP
- Off-gases: 7 MW, 12 MW, 23 MW
- Pulp: 157 MW
- Electricity to BFP: 20 MW, 31 MW, 55 MW
- Electricity to Pulp mill: 28 MW

PO percentages:
- 0% PO
- 25% PO
- 50% PO
Spot Price Power in Nord Pool

Source: Nord Pool Spot, Nasdaq/OMX Commodities, Svensk Energi

NOTE THE PREDICTION
Power-to-liquids in a biorefinery

In a conventional process 60% of the carbon is vented to the atmosphere as CO2.

The process yield increases 150% if all CO2 is converted to CO with RWGS.

The process yield in the demonstration increases by 76% (once-through RWGS that shifts about 50% of the CO2 to CO).

The concept works with all gasification based BtX processes, e.g. BioDME, Bioliq and Gobigas.
Main Process Blocks (base case biorefinery)

<table>
<thead>
<tr>
<th>Komponent</th>
<th>(1) Rågas, Nm3/h</th>
<th>(2) Oxygen Gas MW</th>
<th>(3) Shifted Gas MW</th>
<th>(4) Removed CO₂ Nm3/h</th>
<th>(5) MeOH, MW / Ton/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>22351 (67MW)</td>
<td>128,1 MW</td>
<td>CO₂ 16819</td>
<td>102.5 / 18.6</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>19416 (67,9 MW)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>12874</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Main Process Blocks (Power to Liquid Case)

Gasification

AGR

Electrolyzer

MeOH Synthesis

Electricity

1.4 MW

Electricity

100.7 MW

<table>
<thead>
<tr>
<th>Komponent</th>
<th>(1) Rågas, Nm³/h</th>
<th>(2) Oxygen Gas MW</th>
<th>(3) Shifted Gas CO₂ Nm³/h</th>
<th>(4) Removed CO₂ MW / Ton/h</th>
<th>(5) MeOH, MW / Ton/h</th>
<th>(6) Gas after H₂ injektion, Nm³/h</th>
<th>(7) Added H₂, Nm³/h</th>
<th>(8) Added O₂, Nm³/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>22351 (67MW)</td>
<td>----</td>
<td>CO₂ 11412</td>
<td>159.3 / 28.9</td>
<td>43775 (131,2 MW)</td>
<td>21424 (64,2 MW)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>19416 (67,9 MW)</td>
<td></td>
<td></td>
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<td>12874</td>
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<td></td>
<td></td>
<td>10712</td>
</tr>
</tbody>
</table>
Some key conclusions - 1

- Methanol from raw gas via shift:
  \[
  (67 + 67.9) \times 0.95 \times 0.8 = 102.5 \text{ MW}
  \]

- Methanol from raw gas with H\textsubscript{2} addition:
  \[
  (67 + 67.9 + 64.2) \times 0.8 = 159.3 \text{ MW}
  \]

- Increased production from a given amount of feedstock:
  \[
  159.3 / 102.5 \times 100 = 55\%
  \]

- Conversion efficiency of hydrogen energy to methanol energy:
  \[
  100 \times (159.3 - 102.5) / 64.2 = 88\%
  \]
Some key conclusions - 2

**Power price 60 €/MWh**

- If Power price is 60€ / MWh then the cost of power in the hydrogen production cost is 60 / 0.64 = 94€ / MWh.
- Savings on power needs for oxygen production corresponds to 7 MW. If this is credited the power consumption for hydrogen the conversion efficiency becomes 64.2 / (100.7-7) = 68.5%
- *Cost of power in the hydrogen production* cost then becomes 60 / 0.685 = 88€ / MWh.

**Power price 45 €/MWh**

- *If average power price is 45€ / MWh the corresponding cost element is 66 €/MWh*
Some key conclusions - 3

• If Power price average is 45€ / MWh then the cost of power in the methanol production cost is $45 / 0.685 / 0.8 = 82€ / MWh.$

• This concept is economically at least as good as adding capacity via pyrolysis oil addition to black liquor
Raw syngas from natural gas and biomass respectively utilizing black liquor in pulp mills (energy balances)

Partial oxidation of N.G. \( \eta = 0.8 \)

\[ \text{Natural gas} \quad 100\text{MW} \quad \rightarrow \quad \text{Raw syngas} \quad 80\text{MW} \]

\( \Rightarrow \) WGS => H\(_2\)/CO adjustment \( \eta = 0.95 \)

\[ \text{Black Liquor} \quad \rightarrow \quad \text{Gasification of Black Liquor} \]

\( \Rightarrow \) Methanol synthesis & distillation \( \eta = 0.8 \)

\[ \text{Methanol} \quad \rightarrow \quad \text{MeOH} \quad 70\text{MW} \]

Biomass to MeOH: \( \eta = \text{ca} \ 0.7^* \)

\[ \text{Biomass} \quad 100\text{MW} \quad \rightarrow \quad \text{Biomass H&P boiler} \]

\[ \rightarrow \quad \text{Heat & power} \]

\[ \text{Pulp wood} \quad \rightarrow \quad \text{Pulp Mill} \]

\[ \rightarrow \quad \text{Pulp} \]

\[ \rightarrow \quad \text{Biomass} \]

\[ \Rightarrow \text{The Chemrec Concept} \]

\[ \Rightarrow \text{Raw syntgas} \quad 91\text{MW} \quad \rightarrow \quad 87.5\text{MW} \]

\[ \Rightarrow \text{MeOH} \quad 70\text{MW} \]

\[ \Rightarrow \text{http://www.princeton.edu/pei/energy/publications/texts/Princeton-Biorefinery-Study-Final-Report-Vol._1.pdf p. 56} \]

European Union Natural Gas Import Price
(USD/MMBtu)

1 MWh = 3,4095 MMBTU
1 USD = 8,5 SEK

Source: https://ycharts.com/indicators/europe_natural_gas_price
Raw syngas from natural gas and biomass respectively utilizing black liquor in pulp mills (Cost of feedstock vs cost of raw syngas)

- Natural gas:
  - Partial oxidation of N.G. $\eta = 0.8$
  - $12-23$ (4,2-8 USD/MMBtu)

- Biomass:
  - $10-20$

- Black Liquor:
  - Gasification of Black Liquor
  - $\eta = 0.95$

- WGS $\rightarrow$ H$_2$/CO adjustment

- Methanol synthesis & distillation $\eta = 0.8$

- $\eta$=energy conversion efficiency (chemically bounded energy OUT/IN)

- Biomass to MeOH: $\eta = ca 0.7^*$

- The Chemrec Concept
  - 87.5MW
  - 70MW

- $\text{öre/kWh} = 0.105$ €cent/kWh

Recovery boilers in Sweden

Methanol production potential from EU Black liquor (BL) capacity combined with addition of Pyrolysis Liquid (PL) and electricity

NOTE: Approximate calculation only

<table>
<thead>
<tr>
<th></th>
<th>TWh/y</th>
<th>Toe/y</th>
<th>% of EU estimate* of transport fuel in 2030 (350 Mtoe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BL in Europe</td>
<td>140</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>MeOH fr BL in Europe</td>
<td>77</td>
<td>6,7</td>
<td>1.9</td>
</tr>
<tr>
<td>PL part 25% BL + PL:</td>
<td>155</td>
<td>13,4</td>
<td>3.8</td>
</tr>
<tr>
<td>Production x 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PL part 50% in BL+PL:</td>
<td>230</td>
<td>20</td>
<td>5.7</td>
</tr>
<tr>
<td>Production x 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Add H2 instead of shift</td>
<td>370</td>
<td>32</td>
<td>9.1</td>
</tr>
<tr>
<td>Add Reversed shift</td>
<td>580</td>
<td>50</td>
<td>14.3</td>
</tr>
</tbody>
</table>

BL Energy is a substantial energy source in some states in the US e.g. Georgia.

More than 100 suitable pulp mills in North America with 200-400 MW of Black Liquor per plant.

In the World: approx. 80,000 MW Black Liquor or 250 – 300 large plants.
Cost of Crude Oil vs. production cost of 2\textsuperscript{nd} generation biofuels

Today’s cost for biofuels in Europe (approx.): 45 USD/bbl crude oil, 0.40 EUR/lit.

Long term stable legislation is required to cope with the difference.

Research partners and sponsors from 2001 until today