CHEMREC Pressurized BLG
(Black Liquor Gasification)
-Status and Future Plans

The 7th International Colloquium on Black Liquor Combustion and Gasification
Jyväskylä, Finland August 2, 2006

www.chemrec.se
Chemrec in Cooperation with and/or in Support by…

Feedstock Supplier

End Users

Authorities

The Pulp Industry
1. DP-1 Experiences from Commissioning and First 9 Months of Operation
DP-1 Project, 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
Excellent green liquor & syngas during 5 day run | May 16-21

DP-1 Plant
Chemrec DP-1 Major Process Units

Black Liquor
Oxygen
Atomising medium

REACTOR

Green Liquor
Weak Wash Liquor

QUENCH

Raw syngas
Condensate

GAS COOLER

Cooling water
BFW*

H2S-ABSORPTION

White Liquor
LP-steam*
MP-steam*

Purified and cooled syngas (to flare)

* Cooling water in DP1

7/26/2006
Short Record of DP-1 Operation

Accumulated Operation (days=24hrs)

First Start!

27 hr test run at 15 bar, 50%

Malfunction of BL Flow Meters

53 hr test run at 50% load, <20 bar

27 hr, 15 bar, Excellent C-conversion
May 12: Low Content of Char, No Soot and Excellent Settling of Dregs in Green Liquor
(..cont´d) Short Record of DP-1 Operation

Accumulated Operation (days=24hrs)

- First Start!
- 27 hr test run at 15 bar, 50%
- Malfunction of BL Flow Meters
- 53 hr test run at 50% load, <20 bar
- 5 days, 20 bar, Excellent C-conversion
- 27 hr, 15 bar, Excellent C-conversion
- 40 hr, 25 bar, Good C-conv.
- Continued burner development!
DP-1 Root Cause Analysis of Planned & Unplanned Stops Sept-05 to June -06

![Bar chart showing number of stops by category]

- Operator: 3 stops
- Standard equipment: 9 stops
- Control system: 10 stops
- Core process: 0 stops
- Non core process: 6 stops
Root Cause Definitions of Un-planned Plant Shut-Downs (...cont’d)

Operator
- Operator error
- Incorrect Operations instructions or policy/procedure
- Unavailability of Operator

Standard equipment specification
- Failure of equipment that is not built for Chemrec. Equipment bought “on-catalogue” or already in general use in industry.
- Standard equipment did not perform according to given specifications.
- Standard equipment specification was wrong or insufficient

Control system design
Operation tripped because of suboptimal or incorrect:
- thresholds for triggers
- programming or error in software
- systems design
- Error in control system hardware
(cont’d…) Root Cause Definitions of Un-planned Plant Shut-Downs

Core Process
• Process or equipment that is key to developing and/or verifying Chemrec core technology
• Burner system, reactor assembly, quench system, counter current condenser, green liquor handling system

Non-core Process
• Process or equipment that is not key to developing and/or verifying Chemrec core technology but is not strictly standard equipment.
• Can be an important process, e.g. the short time contactors, but which is not at the heart of the Chemrec process either by nature or by explicit design choice
• Supply and feed systems for liquids and condensible media such as black liquor, white liquor, steam, condensate, mill water, cooling water, LPG
• Supply and feed systems for gases and non-condensible media such as oxygen, nitrogen, instrument air, plant air.
Preliminary 60% Part load Performance of DP-1

Black Liquor throughput: ~12 tDS/d or ~1.8 MW(lhv)
Gasification agent >99.9% oxygen
Operating temperature: ~1000 °C
Pressure: 21 bar(a)
Carbon conversion: >99.5% (No soot/char)

Raw gas flow: ~530 Nm³/h or ~1.2 MW (as S-free, lhv)

Raw gas Composition:

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<table>
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<tr>
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<tbody>
<tr>
<td>H₂</td>
<td>41</td>
<td>% vol</td>
</tr>
<tr>
<td>CO</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>as N₂ free</td>
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Green Liquor

<p>| | |</p>
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<tr>
<td>Flow, kg/h</td>
<td>1150</td>
</tr>
<tr>
<td>Temp, °C</td>
<td>80</td>
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<tr>
<td>TTA (g NaOH/l)</td>
<td>143</td>
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<tr>
<td>NaOH</td>
<td>0.7</td>
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<tr>
<td>NaHCO₃</td>
<td>0.0</td>
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<tr>
<td>NaHS (g/l)</td>
<td>12</td>
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<tr>
<td>Na₂CO₃ (g/l)</td>
<td>130</td>
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<tr>
<td>SO₄²⁻</td>
<td>0.3</td>
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<tr>
<td>Baumé</td>
<td>20</td>
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<tr>
<td>Density</td>
<td>1.16</td>
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<tr>
<td>S-reduction</td>
<td>97.6%</td>
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</tbody>
</table>

Na & Sulphur Separation: ~60% of incoming S found in Green Liquor
Key Operational Issues in DP-1 first 9 months

A. Black liquor Circulation pump
Was not equipped with external flushing. N2 blanket on tank. New pump installed in February.

B. Black liquor Flow Meters
Failure due to corrosion. New flow meters were taken in operation in March.

C. Oxygen and Nitrogen Supply
The AGA Gas supply system has been manually controlled and did not have any automatic restarting system. This will be fixed within short.

D. Level control in Green Liquor System
Flushing/purging of measuring pipes & instruments has been introduced.

E. Material test loop for hot Green liquor
(Not a directly operational issue). Rebuilt after safety review. The pump seals designed wrong way. The pump will soon be changed/modified.

F. Continued Development of Black Liquor Burner
New development started in March. Testing of new burners began in May.
Planned DP-1 Operation until 2007-03-31

Operation days (=24hrs)

2500 hrs

According to plan

Completed
2. The BLG Program 2004-2006
BLG Program - Previous & Current Phase ending Dec-06

Phase 0

0. Co-ordination\n1. Reactor/nozzle CFD modeling (ETC/LuTH)
2. Quench/Cooler CFD modeling (LuTH)
3. Inorganic Chemistry (UmU)
4. Reaction kinetics (CTH)

Phase 1

5. Direct Causticization with borates (ETC)
6. Alternate cooking cycles (STFI)
7. Non process elements (STFI)
8. Construction materials for green liquor (KI)

MUSD / phase
- Phase 0: 2.4
- Phase 1: 5.7

2001 - 2003
2004 - 2006
BLG Program – Phase 1 ending Dec-06

WP1. Modelling, simulation and optimisation of a black liquor gasification Reactor (ETC-Piteå /Luleå Tech. Univ.)
Development and validation of a computer model for the hot parts of the gasifier. The model shall be validated by comparison to the DP1 reactor and then be used for studies of scale-up effects.

WP2. Validation of models for the quench and the counter current condensor in a black liquor gasifier (Luleå Tech. Univ.)
Development and validation of a computer model for the quench cooler and counter current condenser. The model shall be validated by comparison to the DP1 reactor and then be used for studies of scale-up effects.

WP3. Gas phase reactions, smelt formation and green liquor quality in pressurized black liquor gasification (Umeå Univ.)
Detailed studies of reaction kinetics for the inorganic reactions between smelt, water spray and syngas. Determination of fundamental thermo-chemical data that are needed as input to computer models.

WP4. The kinetics of the gasification of black liquor (Chalmers Tech. Univ.)
Detailed studies of reaction kinetics for the gasification reactions (drying, pyrolysis and char gasification). Theoretical and experimental studies of swelling of black liquor droplets during gasification. Determination of fundamental data and reduced models that can be implemented in computer models.
WP5. Borate autocausticizing and chemical recovery of sulphur-free pulping processes (ETC-Piteå)
Evaluate possibilities for borate autocausticization during black liquor gasification conditions. The objective is to eliminate the need for increased causticization capacity, and thereby the demand for redesigning the existing lime kilns when introducing black liquor gasification in the pulping process.

WP6. Pulps produced with liquors from new recovery systems (STFI-Packforsk)
The increased control of process chemistry, which is made possible by introduction of black liquor gasification, opens the possibility to implement modified pulping processes. This project is focused on investigation of the yield increase with so called ZAP pulping when combined with black liquor gasification.

WP7. Kidneys in a kraft pulp mill with a pressurized black liquor gasification system (STFI-Packforsk)
In the recovery boiler process there is a natural purging mechanism for non-process elements through the electrostatic precipitator dust. No natural purging mechanism exists in the black liquor gasifier. Alternative methods for control of accumulation of non-process elements will be studied in this project.

WP8. Material investigation in Hot Green liquor (Swedish Corrosion Institute)
In pressurized black liquor gasification the green liquor temperature can be as high as 220ºC, which will severely increase the corrosion rate of the materials in contact with green liquor. The knowledge of the impact on the materials is limited. In this project, materials suitable for contact with hot green liquor will be identified by experimental studies of stress corrosion.
3. The BLG II Program 2007-2009
BLG II- Program Main Goal

Work with Chemrec to bring the pressurized oxygen blown Black Liquor gasification technology to a successful commercial breakthrough.
Structure of BLG II R&D-programme 2007-2009

1. Experiments in DP-1
2. Applied Process Chemistry
3. Mill integration
4. Process modelling
5. Underpinning process chemistry

Project coordination
BLG II R&D Programme 2007-2009

The new BLG program consists of two major parts, a process optimisation and development program carried out by Chemrec AB and a research program of five subprojects/workpackages:

- **WP1 Experiments in the DP-1 gasifier**
  The goal here is to utilise the world unique gasifier in Piteå for experimental studies of gas composition, green liquor quality, smelt behaviour etc. under real process conditions.

- **WP2 Applied process chemistry**
  Existing knowledge and results from the DP-1 will be combined to develop a sufficiently good understanding of the process to be able to predict potential problem areas and to explain possible surprising results from experiments.

- **WP3 Mill integration**
  Objectives are to find ways of integrating black liquor gasification in the pulping process to optimise productivity and costs.

- **WP4 Process modelling**
  Scale-up from the DP-1 scale to commercial scale is a significant size increment (15-100 times scale-up) which may lead to unpleasant surprises. The goal in this work package is to calibrate and refine process models that were developed in the old program so that they can reliably predict the performance of larger gasifiers.

- **WP5 Underpinning process chemistry**
  The goal for this work package is to determine missing critical data and to further develop theoretical models that are needed in the other work packages.
Key Chemrec Process Activities 2007 to 2009 within the BLG II Program

1. Follow and participate in WP-1 to 5 activities as spelled out in the BLG II Program 2007 - 09 Document

2. Optimize and Advance the Technology
   - Overall process Optimization
   - Run good Green liquor at minimum temperature - maximize efficiency
   - Secure Green Liquor quality and settling/filterability characteristics.
   - Identify best means of handling of trace components.
   - Constructional changes to be considered.

3. Durable Operation long-term testing:
   - Long-term testing of plant equipment.
   - Long-term exposure of construction materials to hot Green Liquor.

4. Feed Flexibility:
   - Testing Black Liquor from different pulp mill also Sulfite Black Liquors.

5. Scale-up of Plant
   - Finalize tool for scale up of key equipment
   - Scale-up Reactor & Burner, Quench and Counter Current Condenser
4. Plans for scale-up to Commercial Demonstration of BLG with motor fuels production
Black Liquor Gasification - General Scheme

- Air separation
- Oxygen
- Power
- Black liquor
- Gasification and Quench
- Rawgas
- Steam
- Gas cooling
- Gas Purification
- Sulphur Management
- Poly Sulph.
- White liquor
- WS Green liq.
- Combined Cycle
- Synthesis- and Distillation
- Power & Steam
- or
- or
- DME/Methanol
# Plant and train sizes

<table>
<thead>
<tr>
<th>Plant</th>
<th>Train</th>
<th>Size when full replacing of recovery boilers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pilot</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Skoghall</td>
<td>Pilot</td>
<td></td>
</tr>
<tr>
<td>In operation 1996-2000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DP-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Piteå</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Start-up</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sept 2005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DP-2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Piteå/Mörrum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(&lt;15% of boiler capacity)</td>
<td></td>
<td></td>
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<tr>
<td>Start-up</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BLGMF plants</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Train size when full replacing of recovery boilers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 tDS/day</td>
<td>20 tDS/day (~3 MW&lt;sub&gt;t&lt;/sub&gt;)</td>
<td>~300 tDS/day (40-45 MW&lt;sub&gt;t&lt;/sub&gt;)</td>
</tr>
<tr>
<td>15 bar</td>
<td>32 bar</td>
<td>~30 bar x 2</td>
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## 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>
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<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>
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<tr>
<td><strong>Products</strong></td>
<td>Oxo chemicals</td>
<td>Petrochemicals</td>
<td>Photo-Chemicals</td>
<td>Ammonia</td>
<td>Fuels/chemicals</td>
</tr>
</tbody>
</table>

**Notes:**
- BLGMF: Black Liquor Gasifier Model
- HVR: Hydrocracking Vessel Reactor
Availability of Gasification Plants

- Comparison with 4 well established gasification based plants. Each of them has been in operation more than 20 years using heavy oil or coal as fuels.
- Planned annual shut-downs normally 7-10 days per year.
- 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.
Large BLGMF Plant

- Black Liquor
- ASU
- O₂
- 1 x 100%
- 4 x 33%
- G1, C1
- G2, C2
- G3, C3
- G4, C4
- Pre-wash
- Abs I
- CO-shift
- Abs II
- Abs. Regen
- Claus unit
- H₂S Abs
- High S Green Liquor
- Methanol Synthesis unit
- Final Distillation
- Final product
- IP-Steam
- 1 x 100%
- 1 x 100%
- 1 x 100%
- Liq. Sulphur

Chemrec
# Time Schedule Pressurized BLG Development

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<tr>
<th>Activity</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
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<tbody>
<tr>
<td>DP-1, Piteå, Sweden (3 MW)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>• EPC</td>
<td></td>
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</tr>
<tr>
<td>• Operation</td>
<td></td>
<td></td>
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<tr>
<td>• DME-demo at DP-1, Pitea</td>
<td></td>
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<tr>
<td>Demos in Sweden</td>
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<td></td>
</tr>
<tr>
<td>• DP-2 BLGMF (45 MW)</td>
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<td></td>
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<td></td>
<td></td>
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<tr>
<td>• DP-3 BLGMF (65 MW)</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Commercialisation</td>
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## Volvo DME Roadmap

**Issue: 2006_2 by 24440**

### External influences
- US02
- EU4
- Tier3
- EU4
- US07
- EU5
- US10

### Engine and vehicle development
- **AFFORHD (2G FM9 truck)**
- **2G Field Test (3 HD trucks)**
- **3G Field Test (30 HD trucks)**
- **3G Buss Demo**

### Fuel production development
- **Piteå (BLG pilot)**
- **RENEW (SP3)**
- **Växjö Värnamo Biomass Gasification Center**

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<thead>
<tr>
<th>Year</th>
<th>Planned</th>
<th>Decided</th>
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<tr>
<td>2010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2011</td>
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</tbody>
</table>

- **Vehicles start**
- **Vehicles start**
- **Vehicle start**
- **Vehicle start**
- **Production project**
- **Vehicle delivery**
- **Test fuel delivery**
- **Fuel delivery**

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7/26/2006
Tentative Flow Scheme DP-1 Fuel Production

DP-1 Syngas fr STC

CO-shift

By-pass (~50%)

Final absorber (WL-based)

Guard-bed

W.L to mill

DME or MeOH
P.D.U
Process Developmt Unit

Raw MeOH or DME

Train /Truck

~6 Ton Methanol / day
or
~4 ton DME / day

HP-steam (DP-1/mill)

White Liquor (DP-1/mill)

C.W

HP-steam (Dp-1/mill)

C.W

Train /Truck

~6 Ton Methanol / day
or
~4 ton DME / day
**DP3 Overall Production and Consumption figures**

Södra Cell’s Pulp mill at Mörrum

- **WOOD FOR PULPING**
- **PULP/PAPER**

**O₂ Plant**
- 45 MW(NHV) Black liquor
- LP steam 18-21 tph
- Sulphur (PS liquor) 0.5 tph
- Purge gas 2.6 MW(LHV)

**Gasification**

**Gas Cleaning + Synthesis**
- 4,200 Nm³/h (100% O₂)

**BLGMF PLANT**
- 18-21 MW(LHV) biomass to compensate for BLGMF automotive fuel generation*)
- 5.2 MWe
- ~ 23 MW(LHV) 4 t/h of MeOH (or corresp. DME)
- 1 MW D.H.

*) May be decreased by energy optimisation within the mill
Black liquor: ~45MW