

CHEMREC'S ATMOSPHERIC & PRESSURIZED BLG (BLACK LIQUOR GASIFICATION) TECHNOLOGY – STATUS AND FUTURE PLANS

Mats Lindblom and Ingvar Landälv

Chemrec AB

Floragatan 10B

SE-11431 Stockholm, Sweden

ABSTRACT

Chemrec's atmospheric Booster at Weyerhaeuser's New Bern, NC, USA mill started up December 1996. After initial periods of difficulties especially with the ceramic containment material of the reactor vessel the plant has been in commercial operation for many years and tracked the mills chemical recovery needs. The new pressurized, oxygen-blown, development plant (DP1) in Piteå, Sweden has during the first eighteen months since start up in September 2005 had continuous operation periods up to two weeks and produced excellent green liquor at near commercial pressure. A BLG research program has been carried out for the last six years and a further three year program has been initiated for 2007-2009. Plans for scale-up of the pressurized technology to a commercial demonstration for the production of motor fuels or alternatively power and steam at a Swedish pulp mill is under way.

INTRODUCTION

The new era of pressurized, high temperature gasification of black liquor began in September 2005 as the new development plant (DP1) in Piteå for the first time was started up on black liquor. The DP1 is one of two parts of a program for the development of black liquor gasification supported by the Swedish government and industry. The other part is a research program with five sub-projects within the areas of modeling high-temperature inorganic chemistry, fluid-dynamics modeling of critical process units as well as modeling of a full-scale black liquor gasification system integrated to a modern pulp mill.

In the US, Chemrec's atmospheric Booster at Weyerhaeuser's New Bern mill, NC has been in commercial operation for several years. Since the first start-up in December 1996 the atmospheric black liquor gasifier has been in operation about 40,000 hours and has enabled an additional production of more than 170,000 ADt of pulp to the New Bern pulp mill [14] by the additional chemical recovery capacity of the gasifier. In June 2003 the booster was started up with a new design on the reactor vessel and the refractory and since then the gasification plant has operated with good availability. Improvement activities are under way to make further improvements both with respect to energy efficiency, maintenance requirement and availability.

In the autumn 2004 most of the refractory lining was replaced with a new type which then lasted until autumn 2006. The new material which now is used in the entire reactor has

shown better resistance to the corrosive chemical environment inside the gasifier reactor and the lining is expected to last more than two years. During February 2007 an engineering revision was initiated with the objective to establish a cost effective, updated design of the air-blown black liquor gasification concept. The second generation Booster design will be ready in the autumn of this year.

DESCRIPTION OF THE DEVELOPMENT PLANT

The DP1 plant consists of the core parts of a pressurized, entrained-flow oxygen-blown gasification based system which need to be carefully tested. The DP1 also includes units that secure stable operation of the plant but with a simplified function which today would not be chosen while building in commercial scale. The supply of oxygen is from a cryogenic tank and LOX is brought in via truck. Also nitrogen is brought in and in a commercial scale plant producing chemicals or automotive fuels, use of nitrogen will be entirely avoided. A simplified gas cleaning system for H₂S absorption based on short time contactors is used and tested in DP1, however the chosen type of gas cleaning is not a cornerstone for development of black liquor gasification. A drawing of the DP1 plant is shown in Figure 1.

The core units are the entrained flow reactor with the quench cooler, the counter current gas cooler, and heat exchangers for cooling hot green liquor. Black liquor and oxygen is fed in the top of the reactor. The residence time in the reactor is about 5 seconds. The temperature in the reactor is normally kept steadily slightly above 1000°C. The reactor temperature is measured by four thermocouples at different heights.

The product mixture of melted inorganic salts and gas is quenched by water spray at the reactor outlet and gas and salts are separated by gravity. The regenerated salts fall in the quench bottom and form green liquor. The raw syngas is cooled in a counter current gas cooler. The raw gas entering the counter current condenser cooler contains about 70% water vapor which is condensed and falls down and thereby scrubs off fine particulate material and other condensable material from the raw gas.

The cooled raw gas leaving the gas cooler contains 1.4-2.5%vol of H₂S which is to be removed in the H₂S absorption unit. A commercial gas cleaning system comprising conventional units for absorption of acid gas and for recovery of sulphur would be expensive. The short time contactor system was chosen as a promising low-cost solution but is still fairly unproven. The cleaned raw gas is then finally combusted in a flare.

The history of DP-1 in brief: Time-critical equipment was ordered in late spring 2004. The reactor vessel had been ordered earlier and was delivered in Sept 2004. Installation began in late October 2004 and was completed in May 2005 and was followed by check-out and commissioning. The first ignition on black liquor took place on September 30, 2005.

During the first seven months after the first start-up was dedicated to both intense testing of different burner types and trouble-shooting efforts such as minor plant modifications, pump replacements, and sorting out problems with measuring equipment that did not function well in this new application.

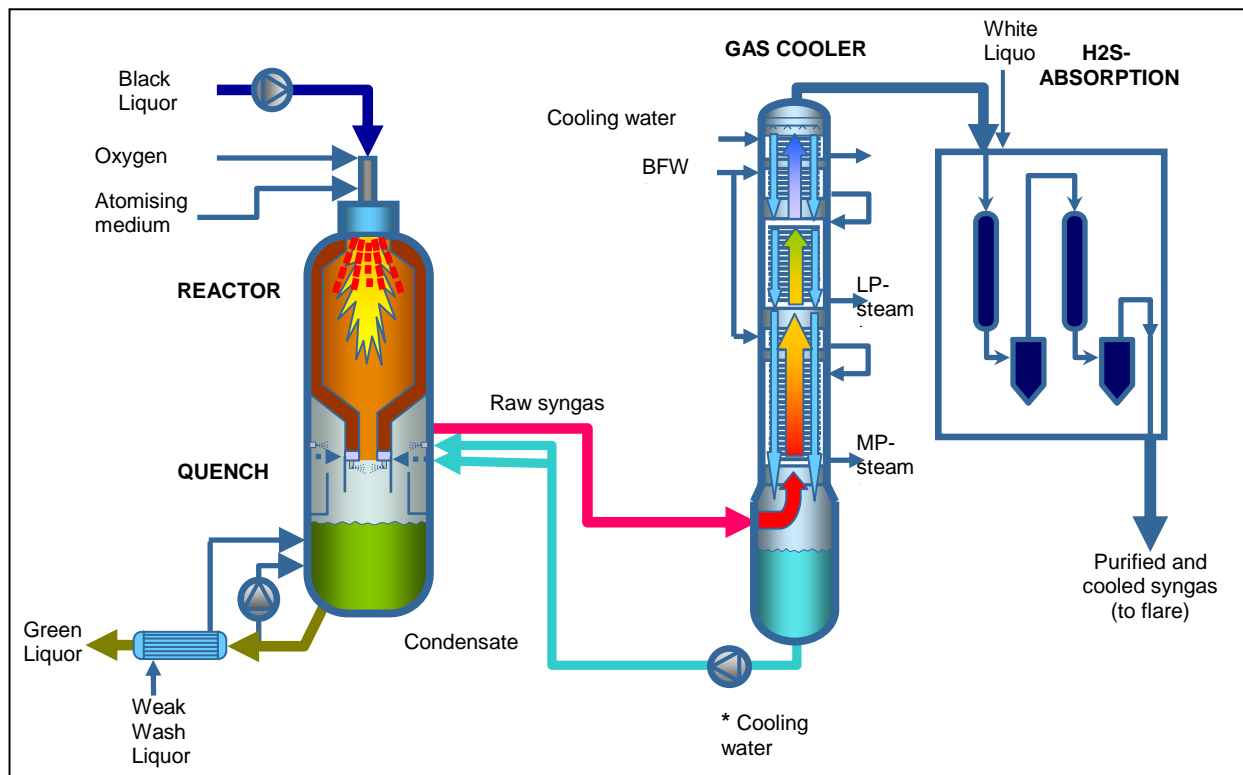


Figure 1: The principal units of the oxygen-blown, pressurized black liquor gasification development plant 1 (DP1) in Piteå, Sweden

A number of modifications both in the process as well as auxiliary systems have accompanied the plant operation and also debugging the control system has continued. A new oil fired start-up burner has replaced the former LPG burner which was difficult to operate. During the *last 12 months* of DP1 activity the following trouble-shooting efforts have been noted:

The Black Liquor Feed System. Blockage of the piston feed pump and the black liquor pre-heater have occurred when there occasionally have been high amounts of fibrous material in the black liquor. A new mass-flow meter made in a candidate material will be tested in parallel to the existing volumetric flow meters. A mass-flow meter could have significant advantages compared to the flow meters currently used.

Oxygen and Nitrogen Supply. The original oxygen flow meters were suspected to have caused a number of system trips that have been difficult to track down since the DP-1 does not possess a so-called first out system. A number of trips have occurred in the reactor feed control loop which is connected to the oxygen flow measurement. As the old oxygen flow meters were found to be easily disturbed by vibrations from pumps, these flow meters have recently been replaced with less sensitive equipment.

Green Liquor System. The adaptation of flushing sequences and purging of certain measuring pipes in the quench system has been introduced and the level of the green liquor system in the quench bottom is now monitored and controlled reliably.

The Test Loop for Exposure of Construction Materials to Hot Green Liquor As the test loop is a fully closed circulation loop at elevated temperature and pressure it makes pumping a challenge. As for other pumps, the pump bearing had to be redesigned to become externally flushed with warm sealing water which also has to be of closed loop design. The stand-alone test loop still remains to be taken in service. Meanwhile, there are steel test coupons placed in the DP1 quench and the warmer part of the raw gas cooler.

Development of Black Liquor Burners. A development program for the burner nozzle was a part former BLG program and the burner development has been going on since the first start-up. The burner development is the key activity for reaching full pressure as well as for reaching 100% of the design load. The DP-1 burner has proven to operate steadily and without neither erosive wear inside the feeding canals nor has plugging occurred.

Seven months after the initial start-up, acceptable carbon conversion was obtained. It should here be noted that acceptable carbon conversion means $\geq 99.8\%$ for obtaining good quality green liquor. Continued development work of the burner has resulted in an increase of the operating pressure to 29.6 bar(a) and steady operation on 80% of the design load. Thus, the final step to reach full throughput of 20 ton BLS/d still remains. The reactor temperature has so far been slightly elevated and one goal is to operate the reactor slightly below 1000°C. A lower reactor temperature will reduce the chemical and thermal stress of the refractory and will improve thermal efficiency and also lower oxygen consumption.

It has been noted that good performance of the burner with high carbon conversion also means low methane content and a high purity of the syngas and no tars are then found in the gas cooler or elsewhere. However, the contrary is also true. Lower carbon conversion means slightly elevated methane content, green liquor with poorer settling characteristics, and reduced gas cooler function, probably caused by fouling. A rapid fingerprint analysis showed that the major tar constituent is naphthalene.

Short time Contactors for Selective Absorption of H₂S. H₂S absorption in short time contactors have been studied earlier [1,2] but only in laboratory/bench scale. No reports have been found about testing short time contactors on real syngas. In the short time contactors, white liquor or green liquor is brought into contact with the H₂S laden raw gas. The contact time is to be kept short for a high selectivity. The short time contactor unit has been operated in short test runs for testing efficiency and selectivity. Between 30% and 55% absorption efficiency per contactor step has been measured with high selectivity. Formation of solid sodium bicarbonate salt has been found to occur, which means a risk of plugging. Different process routes of how to avoid formation of solid NaHCO₃ are under evaluation. Continuous testing of the short time contactors is planned during April-June 2007.

Figure 2 shows the accumulated runtime and progress since the first start in September 2005. In end of March 2007 DP1 has been in operation more than 1350 hours. The target to operate the plant 2500 hours before the end of March 2007 has been delayed; the major cause for the delay is shortage of staff. Since December 2006 the run length has been limited to max. 60 hours in length. Four more plant operators were employed in January 2007 and are now in training. According to the plan, the plant will be operated in up to 3-week long continuous operation from mid-April.

In order to get an overview of the development efforts made so far and to optimize the manning needs for the future work, a method for categorization of the root cause of all unplanned stops has been developed. The resulting graph shown in Figure 3 reveals that the control system and the standard equipment cause almost 2/3 of all stops. Since the end of December-2006 five stops have been planned and only three stops have been unplanned.

The definitions of the root causes are:

Operator

- Operator error
- Incorrect operations instructions or policy/procedure
- Unavailability of operator

Standard equipment specification

- Failure of equipment that is not built for the DPI. Equipment bought “off-the-shelf” 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 trip due to suboptimal or incorrect:

- Thresholds for triggers
- Programming or error in software
- Systems design
- Error in control system hardware

Core Process

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

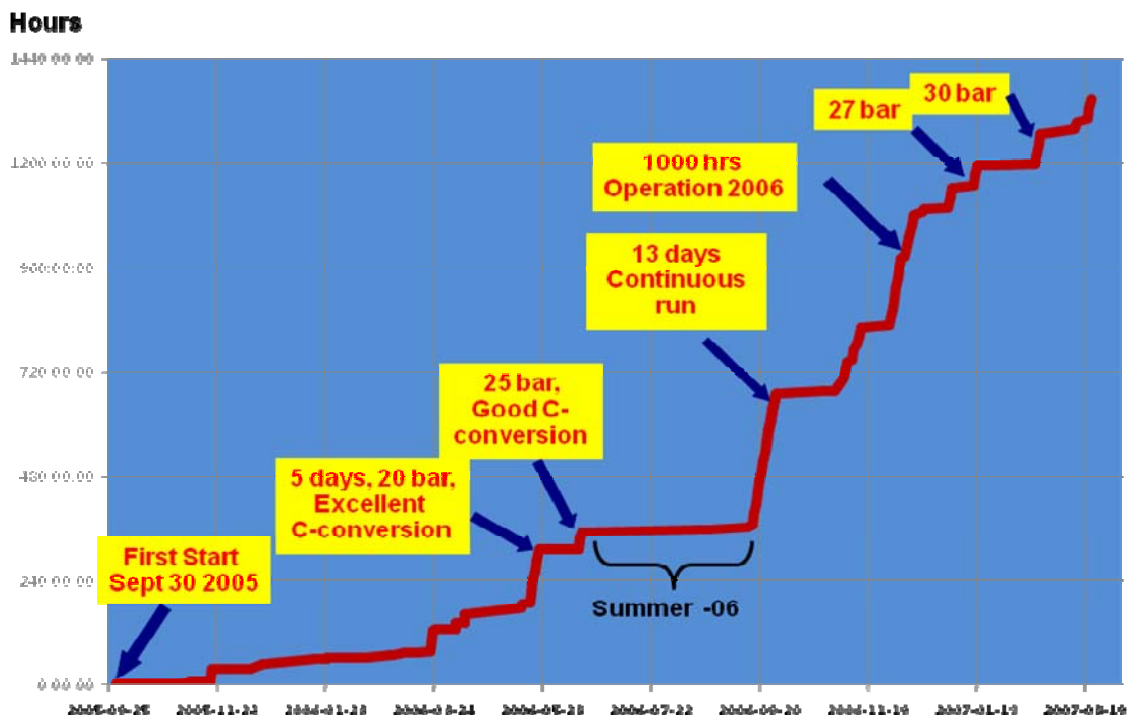


Figure 2. The accumulated run-time during the first 18 months of operation.

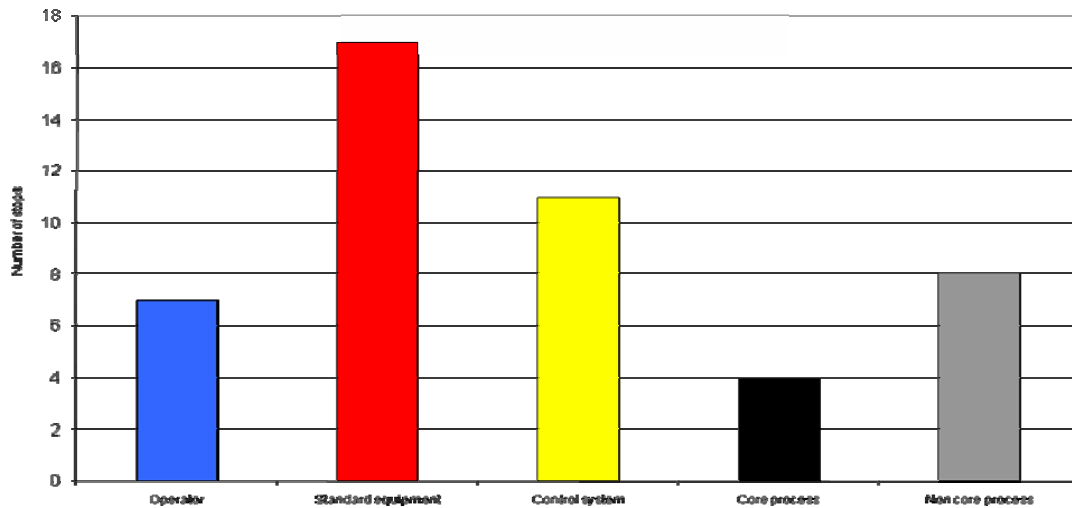


Figure 3. Bar chart diagram of the root causes for unplanned shut-downs between September 2005 and March 2007.

Non-core Process

- Process or equipment that is not key to developing and/or verifying 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 process either by nature or by explicit design choice.
- Supply and feed systems for liquids and condensable, non-condensable media.

RESULTS

The syngas composition as shown in Figure 4 (as nitrogen free) was recorded while operating on 80% load and 29 bar(a) pressure. The gas composition is measured by NDIR instrument for CO, CO₂, CH₄ and a TCD for H₂. The H₂S and COS contents are measured in a GC. The measured gas composition is normally very stable, but deviates from what

can be predicted by equilibrium calculations. By volume, the composition is generally 43% H₂, 30% CO, 27% CO₂, 1% CH₄, 1.4% H₂S and 25-40 ppm COS.

The content of nitrogen has been deducted from the raw gas composition provided, but constitutes normally around 10-30% of the dry syngas. The major portion of the nitrogen is introduced in the quench. Nitrogen is also used to assist black liquor atomization and for purging various instruments and measuring canals in the reactor and quench parts.

The green liquor produced in DP1 is sampled and tested and the density and the settling characteristics are measured every four hours. Samples for chemical analysis are taken out normally every twelve hours or before altering any operating parameter. The diagram in Figure 5 is shown to illustrate the variations in the green liquor during a test trial for quench optimization. The TTA (total titratable alkali) should normally be around 160 g/l (as NaOH) but variations can occur as a

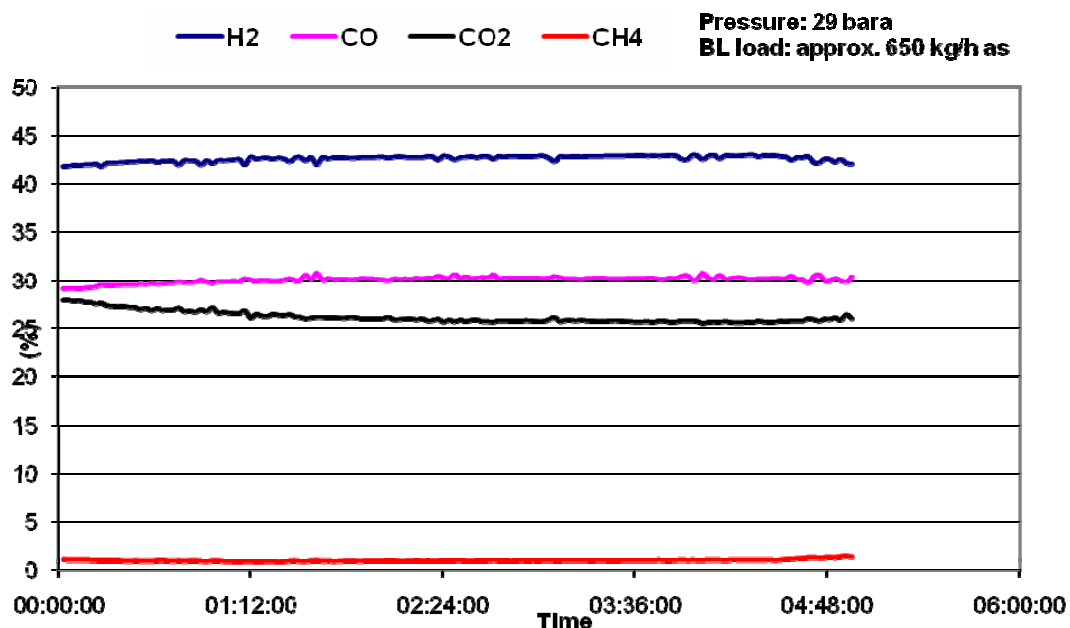


Figure 4. Measured raw gas composition during five hours operation. Measured gas flow 720 Nm³/h (as dry, N₂ free).

result of changes in condensate or water. For certain testing purposes the green liquor is currently optimized *not* to contain any sodium hydroxide.

THE BLG DEVELOPMENT PROGRAM

A program for research and development within the area of pressurized black liquor gasification started in 2001 with 4 sub-projects and was expanded in 2004 with four more sub-projects. The first part of the BLG program ended in December 2006. The first phase of the BLG has been described earlier [13]. A second phase of the BLG development program, named BLG2 program, will continue the research in a reduced number of work-packages (WP:s). The objective of the research within the BLG2 program is to work with the technology developer to bring pressurized oxygen blown black liquor gasification technology to a successful commercial breakthrough.

The BLG2 program consists of two major parts, a process optimization and development program carried out by the technology developer and a research program of five WP:s. Researchers from different institutions will work together to accomplish the goal specified in the WP. The new program is expected to be more efficient as the researchers have learnt to know each other and have a more clear understanding of the task of each WP. The WP:s have been defined as follows:

WP1 Experiments in the DP1 gasifier. Utilize the DP1 plant for experimental studies of gas composition, green liquor quality, smelt behavior etc. under real process conditions. A sampling probe for the extraction of samples from the reactor has been developed and is currently under engineering. Hazard and operability analysis (HAZOP) will soon be completed. The sample probe has not yet been tested due to the risk analysis work.

WP2 Applied process chemistry. Existing knowledge and results from the DP1 will be combined to develop a sufficiently good understanding of the process to be able to predict potential problem areas and to explain possible unexpected results from experiments.

WP3 Mill integration. The objective is to find ways of integrating black liquor gasification in the pulping process to optimize productivity and costs.

WP4 Process modeling. Scale-up from the DP1 scale to commercial scale is a significant size increment (15-20 times scale-up) which can lead to unexpected results. The goal in this work package is to calibrate and refine process models that were developed in the old BLG program so that they can reliably predict the performance of larger plants.

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.

The DP1 plant staff will follow and participate in WP1 to 5 activities as spelled out in the BLG2 Program 2007 – 2009. From the DP1 plant perspective the key activities from 2007 to 2009 will continue to optimize and advance the technology of high temperature gasification of black liquor in entrained flow reactors with the following goals:

Overall process optimization

- Produce good green liquor at minimum reactor temperature - maximize efficiency
- Secure a high green liquor quality and settling/filterability characteristics.
- Identify the best means of handling of trace components.
- Consider constructional changes with the aspect of both gaining efficiency and avoiding complexity.

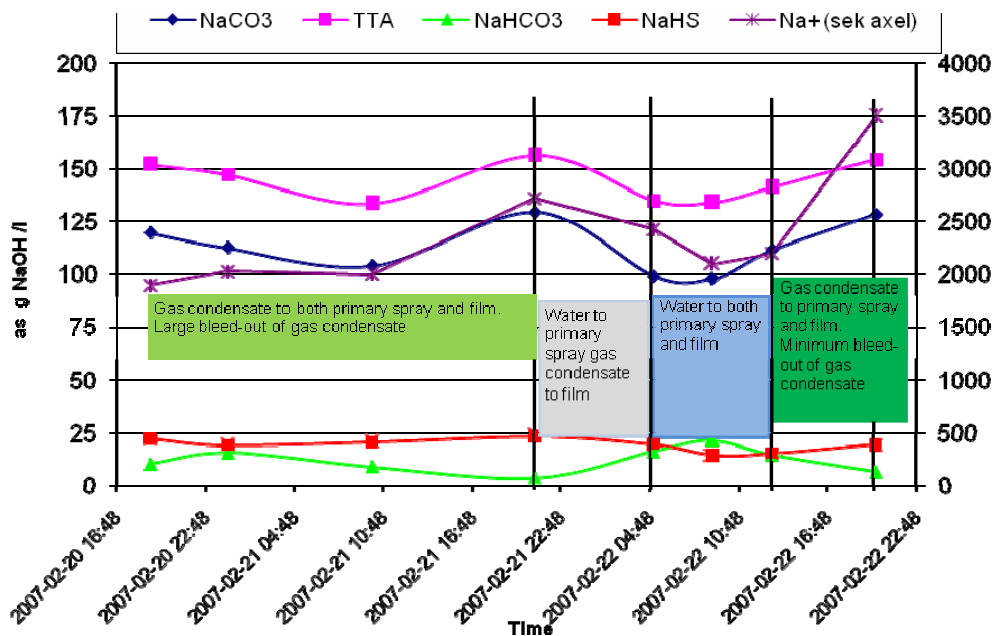


Figure 5. Composition of green liquor samples analyzed by a modified TTA analysis of the green liquor during 30 hours during a quench optimization test where gas condensate is temporarily replaced with water.

Demonstrate durable operation during long-term testing:

- Testing of the plant major equipment.
- Long-term exposure of construction materials to hot green liquor.

Feed flexibility:

- Test black liquor from different pulp mills including sulfite black liquors.

Scale-up of plant

- Finalize the tools for scale-up of key equipment.
- Initiate scale-up of reactor and burner, quench and counter current condenser.

COMMERCIALIZATION AND SCALE-UP OF THE TECHNOLOGY

The next planned step on the way to a commercial technology is development plant 2 (DP2) at a size of approximately 500 tpd of black liquor. The DP2 plant shall be a demonstration of the full BLG concept comprising all units. DP2 can be either a power producing scheme (BLGCC) or a scheme for the production of automotive fuels (BLGMF). The conceptual study named BLGMF [4] was studied for a large-scale plant and produced 275 MWt DME. The BLGMF study was based on a eco-cyclic reference model mill [10] producing 2000 tpd of paper pulp, which served as a well-established basis for any technical and economic comparison.

In March 2006 the preliminary engineering of a 350 ton bls/d demonstration plant for production of DME and methanol from black liquor was completed. The work has been part of the EU funded RENEW project initiated 2004 with the participation of Chemrec AB (the BLG technology provider), Södra Cell, AB VOLVO, STFI and Ecotrafic. In spite of the relatively small scale, the DME production from black liquor in the demonstration scale will maintain a high yield of production.

The RENEW demonstration project was designed to produce 23 MW DME from 45 MWt black liquor. In addition, the demonstration plant was designed to be flexible and can produce everything from 80% methanol and 20% DME all the way to 100% DME in two separate product streams. The DME is planned to be part of the introduction of DME as fuel for heavy duty vehicles. The remaining production capacity will be generated as methanol which can be used for the production of RME or blended directly in gasoline together with ethanol. This is allowed according to today's gasoline specification.

DME PRODUCTION IN DP1

In different Well-to Wheel studies DME from biomass via black liquor gasification ranks the highest regarding energy efficiency and the lowest regarding contribution to the greenhouse effect by minimum net CO₂ emissions [15]. Today, all methanol and DME available on the market are of fossil origin. Both within the EU and United States there are no initiatives towards introducing new types of *fossil* motor fuels on the market.

Methanol production from biomass gasification has been studied already many years ago [5, 7-9]. In Sweden, more than twenty years ago, Thermal Processes in Studsvik

demonstrated pressurized oxygen-blown biomass gasification for the purpose of methanol production but the production itself was never demonstrated. In the late 1980's, Kemira in Oulu, Finland, operated a fluidized bed gasifier on peat for ammonia production based on syngas but the plant was discontinued as the market price of ammonia sloped [12].

The gap which still remains to be closed by a successful demonstration is the production of DME or methanol from a syngas via gasification of a renewable. There is thus a need to demonstrate that renewable DME/ methanol is available in practice and to show that the technology exists and will be proven to function.

Since the first start-up of DP1 there is a growing interest in making use of the 2 MW of syngas which now is just burnt in a flare. A small scale production of DME in DP1 either directly or indirectly via methanol can become reality within a near future and ongoing preparations are scheduling for a start of production in the second quarter of 2009. The demonstration value for the new technology from well-to-wheel, that is, from black liquor in a pulp mill to a clean renewable motor fuel for modern vehicles, is high.

The DP1 plant can theoretically produce 4 t/d of DME and even if the efficiency from black liquor to DME/methanol would be lower, the production will be more than enough to demonstrate the technology and to conduct fleet testing of DME powered trucks and other vehicles. DME production in DP1 has advantages as well as disadvantages. The major advantage is a low investment cost and one disadvantage is the lack of a commercially proven gas cleaning and sulphur removal. The DME fuel production will be depend on a simplified gas cleaning which is currently under testing. The DP1 is rapidly gaining on-stream time and the ongoing tests with the short time contactor system for removal of H₂S are promising.

CONCLUSIONS

Chemrec's atmospheric Black Liquor Gasification (BLG) Booster at Weyerhaeuser's New Bern mill, NC, USA has, since December 1996, been in commercial operation for about 40,000 hours and has enabled an additional production of more than 170,000 ADt of pulp to the mill.

For Chemrec's pressurized BLG development plant DP-1 at Smurfit Kappa Kraftliner's Piteå, Sweden mill the first eighteen months of operation have been successful in spite of several instrument design problems encountered during the early part of this period. The plant has been operated more than 1350 hours, with the longest continuous run achieved so far lasting thirteen days. The operating pressure has reached near 30 bar(a) pressure, the capacity level attained is near 80% of the full design capacity and excellent carbon conversion is achieved.

The first five years of the Swedish BLG program has provided an in-depth knowledge theoretical support for the development work of pressurized black liquor gasification. The continuation of the R&D work in the new BLG2 program has begun and will form an important tool to reach commercialization.

Manufacture of renewable motor fuels by using the black liquor derived syngas from the DP-1 plant in Piteå is a

potential fast-track route to demonstrate the entire chain from black liquor energy to DME powered vehicles in fleet tests in Sweden.

Demonstration scale production of DME and methanol from black liquor can be done cost and energy efficiently within a few years. The production potential of a demo scale 500 tpd black liquor gasification plant is 21 000 tons of gasoline equivalents per year produced as DME and methanol.

ACKNOWLEDGMENTS

The authors wish to acknowledge the Swedish National Energy Agency (STEM), the Swedish strategic environmental research foundation (MISTRA), the regional authority in Northern Sweden (Länsstyrelsen Norrbottens län), Sveaskog AB, Vattenfall AB, SmurfitKappa AB, SCA Packaging and Södra Cell AB.

REFERENCES

1. Al-Wohouh, M., H., v. Heiningen, A., R., P., Kubes, G., J., "Selective Absorption of H₂S from a CO₂ Containing Gas in a Solution of Sodium Carbonate" AIChE Symposium Series No 311, Volume 22, 1996.
2. Wallin, M., Olausson, S., Simultaneous Absorption of H₂S and CO₂ into a Solution of Sodium Carbonate, Chem. Eng. Comm. Vol 123, pp 43-59, 1993.
3. Gebart, R., "The BLG2 Program: Black liquor gasification – enabling technology for renewable transportation fuels" Application for financial support to MISTRA, 2006.
4. Ekbohm, T., Lindblom, M., Berglin, N., Ahlvik, P., "Technical and commercial feasibility study of Black Liquor Gasification with methanol/DME production as motor fuels for automotive uses – BLGMF", Final report under EU contract 4.1030/Z/01-087/2001, 2003.
5. Bain, R., L., "Material and Energy Balances for Methanol from Biomass Using Biomass Gasifiers", Report NREL Golden CO, Jan. 14, 1992.
6. Berglin, N., Eriksson, H., Berntsson, T., "Performance evaluation of competing designs for efficient cogeneration from Black Liquor", 2nd Biennial Johan Gullichsen Colloquium, Helsinki, Finland, September 9-10, 1999.
7. Browne, S., H., "The economics of production of methanol from biomass in Hawaii", Hawaii Natural Energy Institute, Univ. of Hawaii Coll. of Business Admin., ISBN 0-910091-65-X, 1996.
8. Elam, N., Ekström, C., Östman, A., Rensfelt, E., "Methanol and Ethanol from Lignocellulosic Wood Fuels", Report Project Bioenergy 1994/1, Vattenfall AB, Sweden ISSN 1100-5130, 1994.
9. Ekström, C., Kopp, F., "Biobränslebaserat metanol-/elkombinat - översiktlig studie", Vattenfall Research (UB) 1992/30 ISSN 1103-2782, Vällingby Sweden, 1992 (in Swedish).
10. Jönsson, T., Axegård, P., Ledung, L., "Reference Mill for the Ecocyclic Pulp Mill Program", KAM Report nr B25,

Swedish Pulp and Paper Research Institute (STFI), Stockholm, November, 1998 (in Swedish).

11. Katofsky, R., E., "The Production of Methanol and Hydrogen from Biomass", PU/CEES Report No. 279, Princeton University, 1993.
12. Koljonen, J., Kurkela, E., Wilén, C., "Peat-Based HTW Plant at Oulu" Bioresource Technology 46 pp. 95-101, 1993.
13. Lindblom, M., Landälv, I., "Status of the Swedish National Black Liquor Gasification (BLG) Development Program" TAPPI Engineering, Pulping & Environmental, Atlanta, Georgia, USA, Nov 5-8, 2006.
14. Brown, C., Personal Communication, March 2007.
15. Ahlvik, P., Brandberg, Å., Hädell, O., Gustafsson, P., "Well-To Wheel Efficiency for alternative fuels from natural gas or biomass" Swedish National Road Administration, Vehicle Standards Division October 2001.