



SES6-CT-2003-502705

RENEW

Renewable fuels for advanced powertrains

Integrated Project

Sustainable energy systems

D3.1.1 Report with evaluation of the Skoghall plant performance

Due date of deliverable: 31-12-04

Actual transmission date: 04-02-05

Start date of project: 01-01-04

Duration: 48 months

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Revision

Final
2005-02-04

Project co-funded by the European Commission within the Sixth Framework Programme (2002-2006)		
Dissemination Level		
PU	Public	PU
PP	Restricted to other programme participants (including Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
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Evaluation of the Chemrec Skoghall Pilot Plant

Introduction

The evaluation has been accomplished by a review of Chemrec internal memos and reports, and a more comprehensive article. These are based on data files from the time when the Skoghall plant was in operation on oxygen (1997-2000). Results have been reviewed but original data have not been in detail evaluated since the pilot plant operation stopped almost five years ago and key persons who operated the pilot plant has left the Chemrec organisation.

The Chemrec pressurized pilot plant for gasification of black liquor was in operation between 1994 and 2000. It was located at StoraEnso's Skoghall mill near Karlstad, Sweden. It was started as air-blown and was rebuilt to become oxygen-blown during 1997. The plant was built to test the technical feasibility of black liquor gasification under pressurized conditions, specially focusing the ability to achieve high carbon conversion.

In 1994 the original plant had a capacity of 6 tpd of black liquor, operated at 1.5 MPa pressure and 975°C and comprised an entrained-flow gasification reactor, gas quenching and green liquor production system, gas cooler, green or white liquor scrubbing-based sulfur removal system and flare. The development efforts at that time focused on improving operability and reliability through design modifications. Operation of the plant revealed no problems with carbon conversion, and sulfate reduction was good.

When the pilot plant was modified to be oxygen-blown, it resulted in a capacity increase to 10 tds/day. The calorific value of the fuel gas also increased correspondingly, as a result of removing the dead load of nitrogen in the syngas.

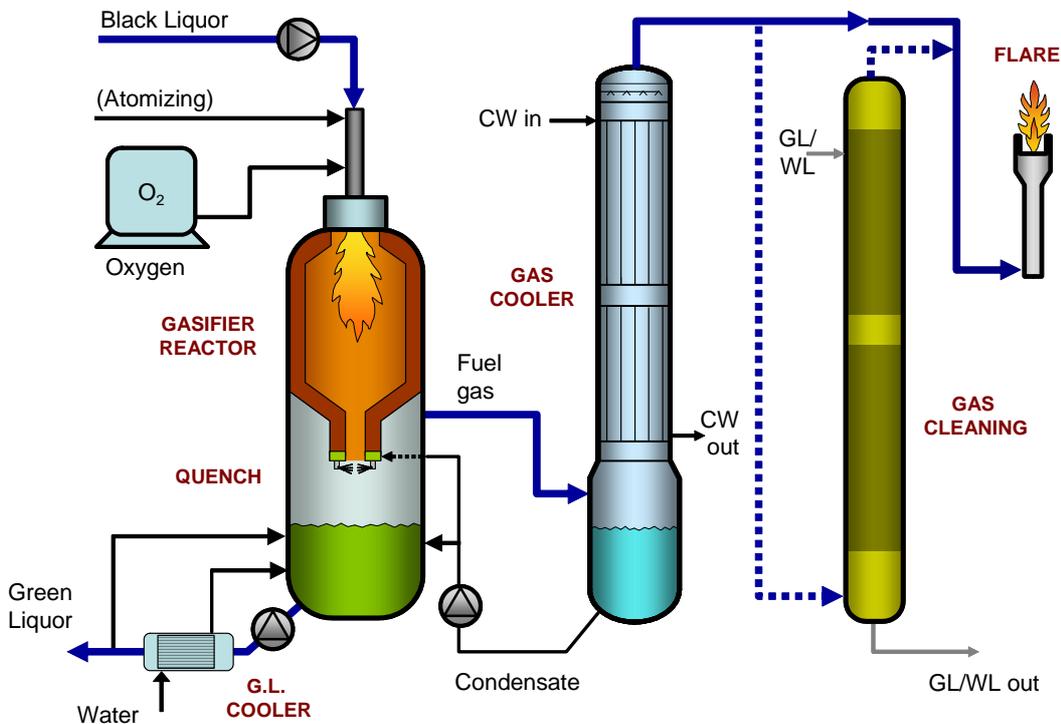


Figure 1. The Chemrec Skoghall pilot plant for pressurized gasification of black liquor.

Plant Description

A schematic drawing of the oxygen-blown pilot plant is presented in Figure 1. The plant comprised four major units: the gasifier reactor, the quench system, the counter-current gas cooler condenser and the gas cleaning system.

The gasifier was an entrained flow, refractory-lined reactor that operated at 1.5 MPa and 975°C. The burner, located in the top of the reactor introduced black liquor, oxygen and an optional atomizing agent into the reactor. The black liquor was partially oxidized to form a combustible fuel gas and a smelt similar to that from a recovery boiler. The smelt and gas exited through a small outlet at the bottom.

The quench system was situated directly underneath the gasifier and was responsible for rapid cooling the products as well as separation of the smelt from the fuel gas. The quench comprised several stages. In the first stage, water or condensate was sprayed into the stream of products leaving the gasifier to cool it so it would not damage the system. The majority of the smelt was then separated from the gas and the smelt fell into the quench sump, which was well mixed and fed with water or weak wash (a diluted form of green liquor), to form green liquor. In the final quenching stage, the gas bubbled through a condensate bath to provide additional cooling and to capture any smelt particles entrained in the gas flow. The condensate in this bath ultimately was fed to the quench sump.

The gas leaving the quench, was approx. 180°C and saturated with water vapour. The raw syngas then passed through a counter current condenser in order to remove the water vapour and for the recovery of the latent heat. The condenser design used in the pilot was essentially a two-stage shell-and-tube heat exchanger with the gas on the tube side. As the water vapour condensed it fell downwards in the tubes against the upward flow of the gas. The intense contact between gas and liquid well removed particles remaining in the gas stream.

In the beginning back in 1994, the plant also comprised a gas cleaning system for removal of sulfur species from the fuel gas by absorption into green liquor, white liquor or weak wash. The process did function as designed, but the process was not enough selective and had a significant co-absorption of CO₂. The test program for the gas cleaning system was concluded in 1996 and the gas cleaning equipment was then taken off-line. The oxygen blown plant then had no gas cleaning system for removal of sulphur species, and the raw syngas leaving the counter-current condenser was sent to the flare after a pressure let-down valve.

The plant was mostly used for day-time test runs generally lasting between 6-12 hrs and was difficult to operate in longer test runs. When not running on black liquor, the unit was kept on hot standby with a propane burner to keep the refractory hot. After start-up with black liquor, the reactor would reach steady state after 60 to 90 minutes. As a result of the start-up procedure, the green liquor was initially out of spec.

The fuel gas composition was monitored for CO₂, CO, H₂, H₂S, CH₄, C₂H₆ and C₂H₄. Green liquor samples were taken approximately once every hour and analyzed for composition as well as settling behaviour. In addition to these standard analyses, sampling ports allowed special analyses, such as measurement of trace species, to be conducted.

Pilot operations since 1997 have mainly been focused on minimizing carbon dioxide absorption into the green liquor. Developing a gasification and quench system with minimal CO₂ absorption is essential for commercialization of the technology since this reaction increases the causticizing

demand of the green liquor. The Skoghall pilot research program significantly advanced the understanding of gasification and quench chemistry, and has resulted in a modern design that promises quality green liquor with an acceptable increase in causticizing load.

Performances and results

System operability

The pilot plant was built primarily for proof of concept and not for the purpose of detailed research in black liquor gasification. Initial efforts in the pilot plant focused on establishing an operating procedure and improving the reliability of the system. Maintaining stable operation proved to be a challenge, where many of the difficulties were related to the burner. The small scale of the nozzle (black liquor passages in early designs were 0.5 mm) made it susceptible to plugging. Several changes were made to the burner design and operating conditions during the life of the plant, and during the later years of operation the reactor had few problems in terms of stability and reliability during day runs.

Hours of operation

The pilot system was in operation on black liquor totally almost 2400 hours until the shut-down in febr 2000. The on-stream time as oxygen-blown was totally more than 600 hours. On two occasions, multi-day operation was attempted and the longest run lasted almost 72 hours. However, the pilot system was not fully capable of such sustained operation. The problems encountered were primarily related to problems with the burner. In the design used in the pilot the black liquor passages in the burner are quite narrow. Such plugging problems are expected to go away for larger systems.

Gasification Efficiency

Conversion of the black liquor was acceptable during normal operation. Carbon conversions were generally above 98%, with 99% being more typical of steady-state operation. During particularly stable runs, carbon conversions higher than 99.5% were achieved.

The sulfate reduction was good. Of the sulfur entering the system, roughly 2% exited as sulfate and 45% exited as sulfide in the green liquor, with the remainder of the sulfur being present as H₂S in the gas.

Green Liquor Quality

Concentrations of un-dissolved material in the green liquor from the pilot plant generally ranged from 2700-3700 mg/liter, which is about twice that of recovery boiler green liquor. Of this, inorganic constituents corresponded to 500-900 mg/liter, about half that of recovery boiler green liquor.

Concentrations of undissolved organics were in the range 2000-3000 mg/liter, which was several times higher than recovery boiler green liquor. Analysis of the organic material indicated the presence of dissolved lignin, suggesting incomplete conversion of the black liquor. In addition, there was a mix of polyaromatic hydrocarbons (“tars”) ranging from naphthalene to pyrene.

Production of such “tars” during biomass gasification is common, and occurs because there is not enough oxygen available to break the aromatic rings in the fuel by thermal oxidation.

During some particularly stable runs, the concentration of undissolved material measured below 1000 mg/liter, and was made up of approximately half organic and half inorganic components.

Settling rates for the pilot green liquor were longer than for green liquor from a recovery boiler system. Filterability was never measured, but experience from atmospheric Chemrec units indicates that filterability of green liquor from a gasifier is better than that of recovery boiler green liquor. The solids in gasifier green liquor are presumably less dense than those in recovery boiler green liquor. A “popcorn” structure would explain the poorer settling and better filterability.

Fuel Gas Quality

The approximate composition of the fuel gas generated in the gasifier (as O₂-blown) is presented in Table 1. The combustible species (H₂, CO, CH₄ and H₂S) account for roughly half the gas volume. With a heating value on the order of 6.4 MJ/Nm³ the gas is classified as a “medium Btu gas” and can be fired in a modern gas turbine. It should be noticed that the presence of nitrogen is due to needs of blanketing gas and alike in a pilot plant set-up. In commercial application nitrogen gas addition will be at or close to zero. Nitrogen in the black liquor is very low. If the gas is used as fuel gas in a combined cycle the presence of nitrogen is to no disadvantage but when the gas is purified to syngas quality then inert molecules such as methane, nitrogen and argon lower the efficiency of the fuel production.

Table 1. Dry Fuel Gas Composition.

Component	Concentration, (vol%)
CO	21 - 24
H ₂	27 - 32
CO ₂	29 - 36
CH ₄	0.7 - 1.3
H ₂ S	1.5 - 2.8
N ₂	9 - 14

Variation in fuel gas composition with temperature corresponds well with Chemrec’s model for the process, as seen in Figure 2. One significant exception is the methane content where the dry raw gas contains about ten times more CH₄ than expected by calculated for equilibrium. It is well-known within biomass gasification that the CH₄ content can be higher than calculated. A possible explanation is that more CH₄ is formed by tar cracking than what is decomposed by equilibrium reactions.

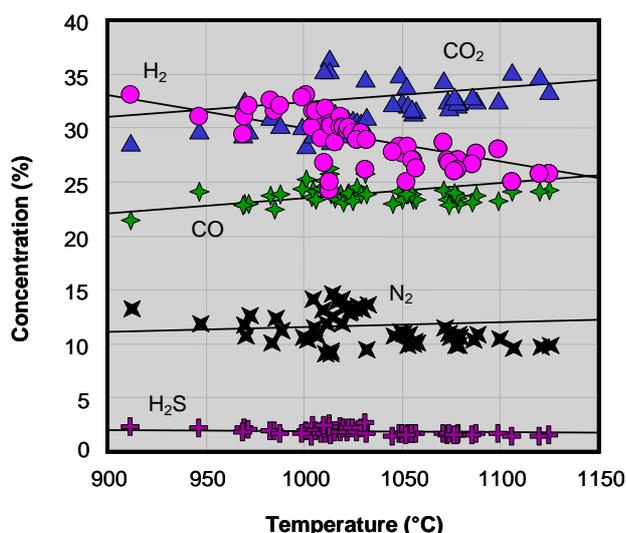


Figure 2. Measured dry gas composition vs. reactor temperature compared to Chemrec's simulator model. Points = measured data, Lines = model prediction.

In order to obtain a high quality fuel gas, it is desirable to operate the gasifier at the lowest temperature that still gives good conversion. Experience with the pilot showed that this temperature was around 975°C.

Presence of alkali in raw gas

On two occasions alkali concentrations in the fuel gas were measured. Concentrations after the counter-current condenser averaged 0.20 ppmw for oxygen-blown gasification. During air-blown gasification, alkali concentrations as low as 0.01 ppmw were measured in the gas after the scrubber. Such a measurement was never taken for oxygen-blown gasification, but it can be expected to be about 0.02 ppmw, still well within turbine specifications.

Reactor Durability

The gasifier reactor was lined with a ceramic refractory. The initial refractory material did not stand up well to the corrosiveness of the black liquor gasification environment and showed significant deterioration after relatively little running time. The refractory was replaced with a different type in 1996, and this remained in place until the plant was shut down four years later.

When the plant was decommissioned, the refractory was pulled and analyzed. Crosscuts of the bricks showed that there had been only limited penetration of alkali species into the material. The same type of material has been used in the Chemec atmospheric airblown gasifier in operation in the US. There the lining was in service in the order of 9000 h. In September 2004 that lining was changed out to an improved type which is expected to last for at least two years. This type of material will also be used in the DP-1 plant in Piteå which is planned to start operation the first quarter of 2005. Overall, the refractory in the Skoghall plant held up very well, particularly considering the rough treatment it received over the years.

Sulfur Chemistry

When black liquor is gasified, more of the sulfur ends up in the gas phase than when it is combusted in a recovery boiler. This effect becomes more pronounced when pressure increases or temperature decreases. The sulphurous gas species will have to be removed from the fuel gas in an acid gas removal (AGR) system.

Most of the sulphurous components in the gas occur as H_2S and a small fraction as COS. The AGR systems downstream of the gasification cooling normally much easier absorb H_2S than COS. It is therefore an advantage if COS can be reduced to low numbers upstream the AGR unit. Therefore, a COS hydrolysis system is often installed upstream of the AGR system in plants similar to the Chemrec process to convert the COS to H_2S .

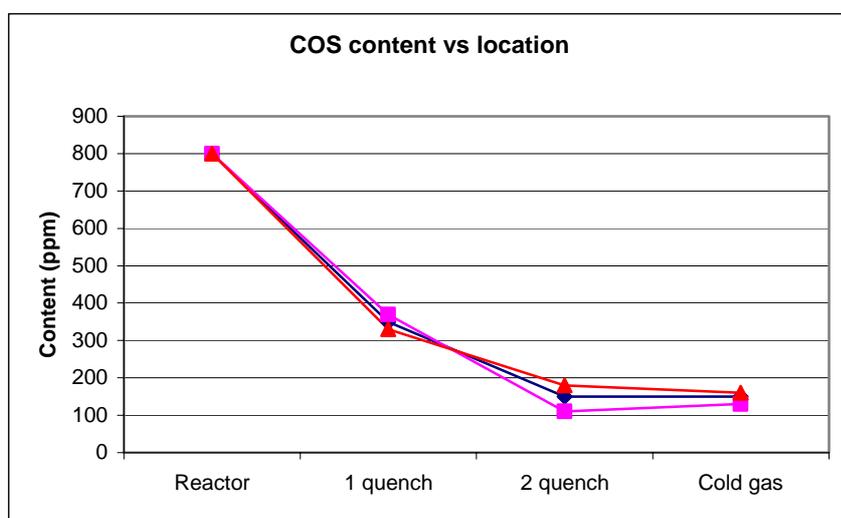


Figure 3. Progression of COS concentration from reactor through condenser/cooler. Reactor concentration estimated by equilibrium and three measurements.

But the behaviour of COS is different in a Chemrec system compared to similar systems based on residual oil or coal. After about one hour of operation the level of carbonyl sulphide, COS reached a constant level. Measurements in showed that the concentration of COS was quite lower than expected at equilibrium at the actual temperature in the reactor. The COS content was therefore measured in the quench at its different stages. Results from the pilot plant as shown in Figure. 3. These suggest that it may not be necessary to introduce a COS hydrolysis step since such hydrolysis apparently takes place naturally in the quench system.

Small quantities of methyl mercaptan and dimethyl sulfide were also measured in the fuel gas.

Table 2. Sulfur Species in Fuel Gas

Component	Concentration	Unit
H_2S	1.5 -2.8	% vol
COS	100-200	ppm(v)
CH_3SH	50-100	ppm(v)
$(CH_3)_2S$	traces	
CS_2	not detected	
$(CH_3)_2S$	not detected	

Quench Design and Performance

The quench system is one of the more complicated parts of the pressurized gasification system. It needs to cool the products from the gasifier and separate the gas and smelt, and also to suppress undesirable side reactions that destroy the quality of the green liquor and increase causticizing load. One of the most important elements of the pilot research program was the development of a quench system that would cool and separate efficiently while maintaining quality green liquor.

Green Liquor Chemistry in a Gasification System

Roughly 50% of the sulfur in a pressurized gasification system ends up as H₂S (and some other minor sulphurous components) in the fuel gas. Therefore there is less sulfide in the green liquor than for a recovery boiler, and, correspondingly, more carbonate. In order to maintain white liquor quality, the green liquor from a gasification-based system requires more causticizing. Depending on mill chemistry and gasifier configuration, the lime kiln load in a pressurized gasification-based system will be around 25% higher than in a recovery boiler-based system.

The causticizing load can become even higher if there is significant contact between the green liquor and the fuel gas. Green liquor will absorb CO₂, which destroys hydroxide and forms carbonate. Under severe circumstances, if there is no hydroxide remaining, additional CO₂ absorption will form bicarbonate from carbonate. Significant CO₂ absorption by green liquor will result in excessive causticizing load increase.

The intimate contact between gas and liquid in the quench system makes it an ideal environment for CO₂ absorption reactions. The quench design must therefore minimize contact between the fuel gas and potential absorbents, and avoid conditions conducive to CO₂ absorption.

Quench System Performance

The quench system performance is reflected in the green liquor quality, and the results presented here report that quality in terms of the causticizing load increase a mill would see if the recovery boiler was entirely replaced by a pressurized gasification system.

During the pilot plant's early years the quench system was modified a number of times in an effort to boost performance and minimize CO₂ absorption. Initial modifications were quite extensive and involved completely rebuilding much of the quench system. The "double quench" design finally selected was first installed in the pilot system in early 1998, and has proven to perform its multiple functions well. Minor modifications since then have improved the runability of the quench system. The improvement in quench performance with design changes over the lifetime of the pilot can be seen in Table 3.

Table 3. Improvements in quench performance through design changes'

Quench design	Year	Caustic. load increase
Single, standard, bubble quench	1994	80%
Single, standard, non-bubble quench	1995	55%
Two stage quench	1998	45%
Two stage quench - optimised	2000	37%

The final phase of the pilot development program aimed to optimize the operating conditions of the quench system to allow sufficient cooling of the products while minimizing CO₂ absorption. As shown in Figure 4, four zones for possible CO₂ absorption were identified and focused upon to determine how much of a role they play in reducing green liquor quality. Operating conditions for each zone were then optimized. The overall result was an improvement in green liquor quality.

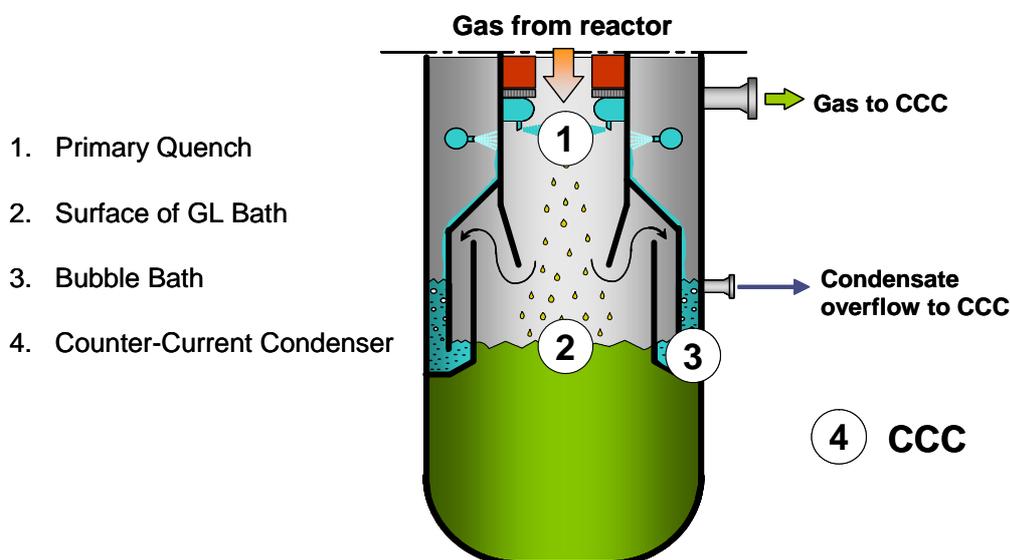


Figure 4. The Skoghall pilot quench system and the zones of possible CO₂ absorption.

Zone 1 was the primary quench, where the products from the reactor are initially cooled by spraying with condensate or fresh water. Figure 5 shows the improvement in green liquor quality that resulted from optimization of the primary quench. The data in the figure is ordered chronologically, and each data point is the average green liquor quality for one day's operation. Clearly, the nozzle configuration is an important factor for the green liquor quality and the amount of CO₂ absorption.

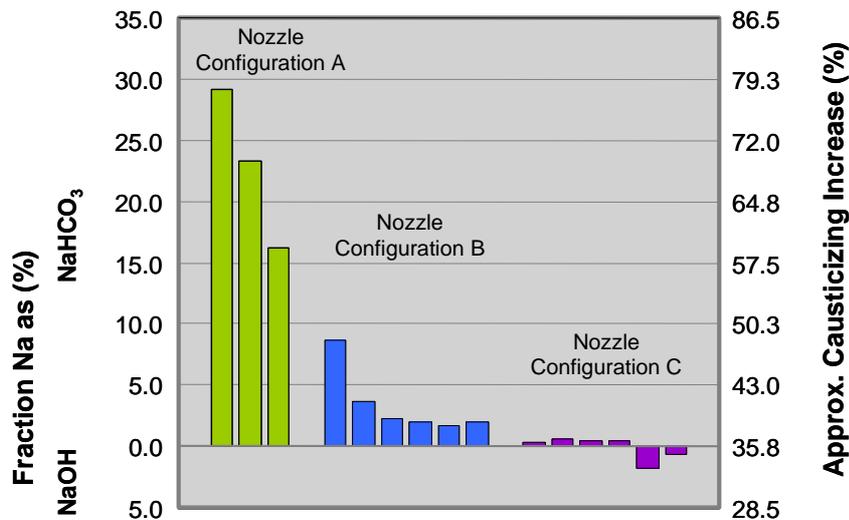


Figure 5. Improvement in green liquor quality as a result of changes in nozzle configuration and operating conditions in the primary quench. Data points are ordered chronologically and cover five months of operation.

For any particular nozzle configuration, the green liquor quality could be improved by optimizing the operating conditions in the primary quench. Of the four quench zones examined, Zone 1 was found to have the most impact on green liquor quality.

Zone 2 was the surface of the quench bath. During operation the quench bath is boiling, and one theory suggests that the upwards-rising steam creates a blanket to that minimizes contact between the CO₂-containing fuel gas and the green liquor. To test this idea, the recirculation loop for the green liquor bath was run through a cooler to keep the bath from boiling. The green liquor quality did not worsen with this configuration, however, so it would seem that the surface of the bath does not contribute significantly to CO₂ absorption.

Zones 3 and 4 were the secondary “bubble bath” quench and the counter-current condenser. Separating the roles of these two zones is not possible since the condensate from both is mixed and sent to the quench bath. To test how much influence these zones had on green liquor quality, the system was modified so that the condensate from the counter-current condenser was sewerred, and fresh water was fed to the quench instead. As shown in Figure. 5, when operated in this manner, the pilot system produced the best green liquor ever. Though disposing of condensate in this manner is maybe not a realistic solution, means of addressing the problem have been developed and will be implemented in the next generation of the system.

The factors influencing the destruction of green liquor by CO₂ absorption are now well understood. The optimum operating conditions for the system have been identified, allowing much better control of green liquor quality. In commercial systems, it should be possible to keep the associated increase in causticizing load near the theoretical minimum.

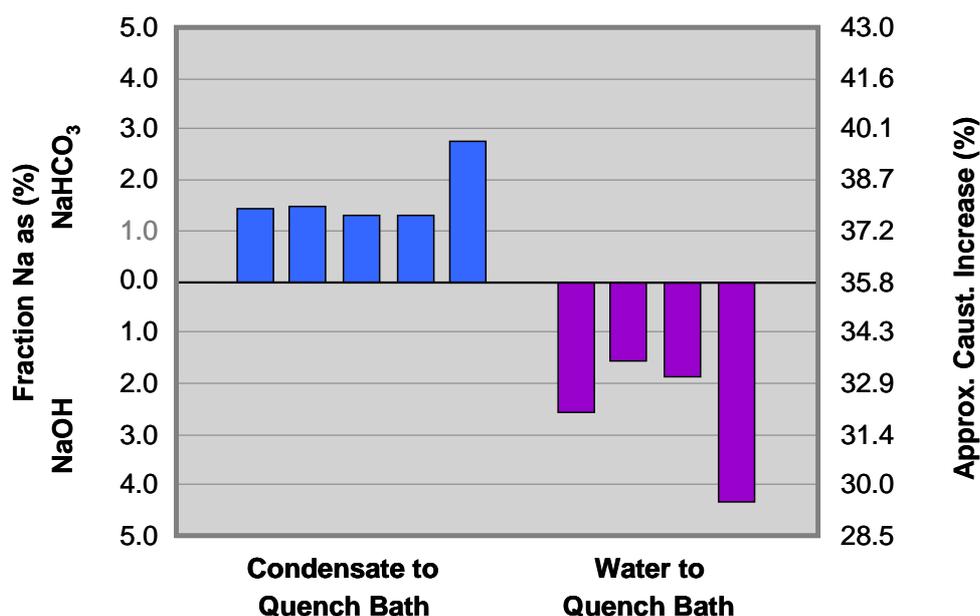


Figure 6. Influence of CO₂ absorption into condensate on green liquor quality.

Conclusions and way forward

A pilot plant for high temperature, pressurized, entrained-flow gasification of black liquor was operated by Chemrec AB from 1994 to 2000 and proved that such a system, either air-blown or oxygen-blown, is a technically feasible means of converting black liquor to green liquor and fuel gas. The carbon conversion in the system is acceptable, and sulfur reduction is good.

In the oxygen-blown gasification tests in Skoghall, approximately half the fuel gas comprised combustible species (hydrogen, carbon monoxide, methane and hydrogen sulfide) with the remainder being primarily carbon dioxide and nitrogen. The fuel gas is classified as a medium-heating value gas (6.4 MJ/Nm³) and upon exiting the system it is of sufficient quality for use in a modern gas turbine. If nitrogen is avoided as blanketing gas in the gasifier and another AGR process is utilized for gas cleaning the raw gas can be upgraded to high quality syngas well suited for synthesis to e.g. methanol and DME.

Depending on the process conditions, approx. 55-60% of the sulfur in the system exits as hydrogen sulfide in the gas stream. This natural split of sulfur from sodium opens up opportunities for advanced cooking methods such as polysulfide cooking. However, the lack of sulfide in the green liquor results in a higher causticizing need for a gasification-based system than for a traditional recovery-boiler based system. A minimum theoretical causticizing load increase with pressurized black liquor gasification can be calculated, and it is generally around 25%. Absorption of CO₂ into the green liquor will make the increase in causticizing load even higher, but advances in design and operation of the system have increased control of CO₂ absorption. Commercial gasification systems should be able to produce green liquor that will keep the causticizing load increase near the theoretical minimum.

The Skoghall pilot plant was decommissioned in early 2000, having served its purpose to prove that pressurized black liquor gasification is technically feasible. Several critical design issues were solved in the pilot plant, and valuable data on gasification behavior was obtained.

The Skoghall pilot did have a number of shortcomings, one being that it operated at only half the pressure designated for the full-scale system. Also, due to its initial designation as a proof-of-concept plant it was not built for detailed research and development, and lacked efficient means for sampling within the process.

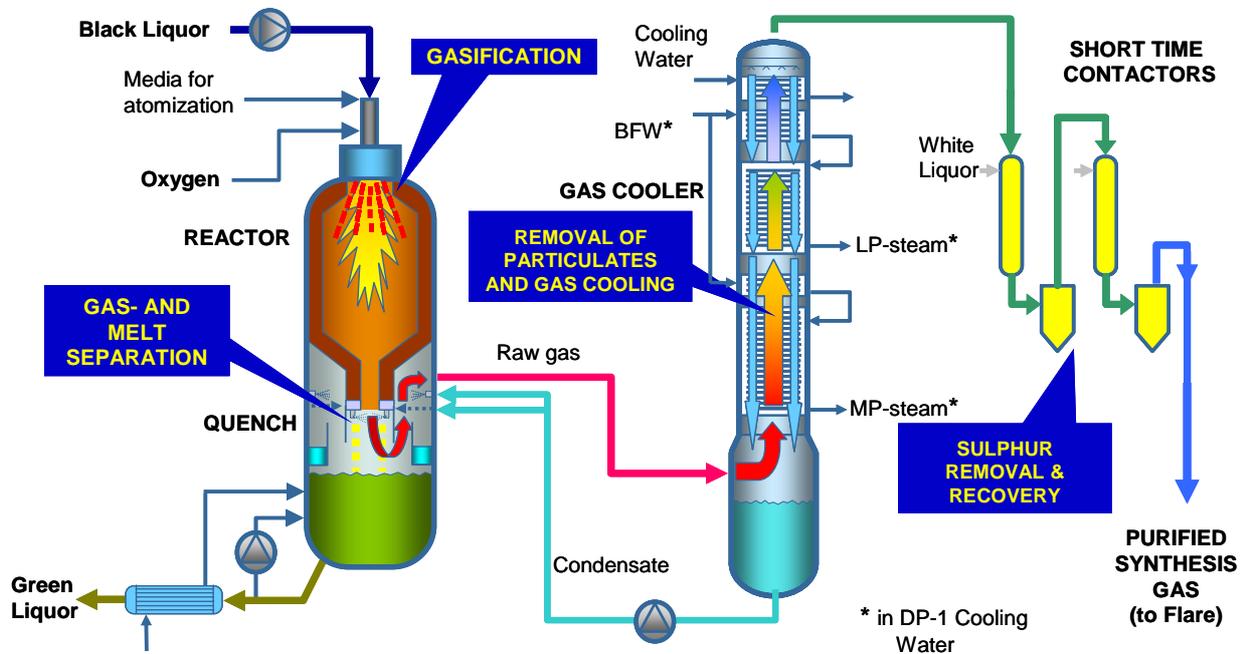


Figure 7. Scheme of the DP-1 plant (Development Plant 1) in Piteå.

The new development plant, DP-1 in Piteå in northern Sweden (Figure 7) which will be mechanically complete within short is being built and equipped to be able to accomplish those tasks that the previous plant was unable to do. The plant is designed at double capacity, 20 tDS/d and at “commercial” pressure, 3.0 MPa, which means that the quench temperature will be approximately 220°C instead of the 180°C in the Skoghall plant due to the higher temperature for the steam saturation point. Raising the quench temperature can mean a remarkable increased stress to the construction materials. Therefore the DP-1 also includes a pump around system for hot pressurised green liquor that will allow long-term continuous testing of construction materials at full temperature even while the the DP-1 plant is not running. The DP-1 plant is very well instrumented to make it possible to narrow in on heat and material balances and includes on-line monitoring on black liquor properties such as viscosity and dry solids content in order to have better control the behaviour of the burner-reactor assembly.

The volume of the quench part of is considerably larger to make control of key parameters more reliable. The DP-1 plant also includes a sulphur absorption unit for capture of H₂S from the syngas using white liquor using a series of so-called short time contactors. The intention is to operate the DP-1 plant continuously in campaigns with a duration of up to three weeks.

The overall plan for DP-1 is that after approximately one year of operation there should be enough available data to make a safe up-scaling to demonstration size which is preliminary put at 300 tDS/d corresponding to about 45 MW_{th}.

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