INTRODUCTION

The pulp and paper industry has made significant advances in pulping operations over the last decade. In particular, the industry has an impressive track record for improvements in energy and environmental performance. Effluent discharge and emissions of sulfur compounds and odorous gases have been reduced considerably and there has been a significant decrease in use of support fossil fuels. In spite of progress in these areas, improvements in energy and capital efficiency is needed to further enhance the industry’s financial performance.

Emerging technologies for gasification of black liquor, a major renewable by-product stream, have the potential to significantly improve overall pulping economy, and energy and environmental performance of a pulp mill [1]. Pressurized black liquor gasification combined cycle (BLGCC) has matured into a demonstration phase and full scale projects are planned for in Scandinavia and North America [2]. The American Forest & Paper Association has through Agenda 2020 recognized BLGCC as one of the key technologies in a sustainable forest industry perspective and the interest in North America for black liquor gasification has increased considerably the last few years [3-5].

Integrated Gasification Combined Cycle technology (IGCC) has advanced rapidly towards broad commercialization in other industries and several full-sized projects have been launched and achieved financial closure in the last five years [6].

While efficient and environmentally friendly generation of power are the primary benefits of IGCC in other industries, gasification of black liquor has the potential to split the sulfur and sodium present in the recovered pulping chemicals into separate process streams. This opens up the opportunity for tailoring the delignification process towards higher yield and/or improved pulp physical properties, a key feature of a versatile kraft chemicals recovery system.

The Tomlinson Recovery Boiler

Present kraft chemical recovery is a mature and well standardized technology. Over 500 recovery boilers are operating in the industry with capacities ranging from a few hundred tons as solids per day up to 4000 ton/day. In spite of maturity and considerable improvements over the years, the Tomlinson recovery boiler with Rankine steam cycle has some significant drawbacks:

- Low thermal efficiency
- Low power-to-heat ratio
- High capital cost
- Complicated maintenance under corrosive conditions
- Risk of smelt/water explosions.

Furthermore, the recovery boiler cannot accommodate any significant sodium/sulfur split, which would be a desirable feature for preparation of high sulfidity or poly sulfide cooking liquors. This deficiency and the incapability to provide sodium-free sulfur streams for mill balance control in bleach plant effluent recycle mill configurations are recognized as other shortcomings of the recovery boiler.

Gasification-based recovery of pulping chemicals is addressing the majority of these concerns and would facilitate recovery and preparation of pulping chemicals for use in advanced sodium/sulfur split delignification schemes.

Chemrec BLGCC Technology

The process layout of Chemrec BLGCC technology has been presented elsewhere [1,7] and the present paper is focused on Chemrec BLGCC fiberline integration, sulfur management and power generation in black liquor gasification compared to traditional recovery technology. A representation of a Chemrec BLGCC island is given in Figure 1.

CHEMREC FIBERLINE INTEGRATION

The principal objective of a kraft chemicals recovery system is to recover the chemicals in a form suitable for conversion to cooking liquors and subsequent use in the delignification process. The Chemrec BLGCC system has an inherent capability for splitting of sodium and sulfur chemicals into separate process
streams, which facilitates the preparation of designed cooking chemicals. In particular, cooking concepts such as high sulfidity black/green liquor impregnation, split sulfidity and polysulfide pulping would become practical in conjunction with chemicals recovery through gasification. The block diagram in Figure 2 shows a typical integration of a polysulfide chemicals recovery system with Chemrec BLGCC.

Maximizing the pulp yield in kraft pulping is presently an area of much activity as the industry seeks to achieve better utilization of the wood resources. This trend has renewed the interest in the use of polysulfide chemicals to improve pulping yield. Polysulfide chemicals have been proven to stabilize the carbohydrates and improve selectivity in kraft pulping. Several comprehensive studies on polysulfide pulping in simulated modern digester systems have been published [8].

Polysulfide pulping has gained a renewed interest recently due to the finding that, besides the carbohydrate stabilizing effect, polysulfide also strongly increases the dissolution of lignin in the first part of the cook [9]. Presently, at least two new polysulfide recovery processes based on partial oxidation of white liquor are on their way to the market [10].

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**Figure 1.** Chemrec BLGCC recovery island.

**Figure 2.** Routes for production of pulping chemicals in the Chemrec BLGCC system.
Polysulfide Pulping

Mechanisms

Most of the yield loss in the kraft process results from alkaline peeling or unzippering reactions of the carbohydrates. Cellulose value is also lost through alkaline extraction and splitting of glycosidic linkages reopening sites for secondary peeling.

The unzippering reaction occurs in a stepwise manner by peeling mono-saccharide units from the end of the cellulose chains one at the time. This degradation starts at 80-100°C and is favored at high alkalinity. The direct cleavage of glycosidic bonds in the cellulose chain by alkaline hydrolysis is most pronounced in the temperature range where delignification becomes of importance, i.e. at approximately 140°C and higher. A low overall pulping temperature is obviously beneficial for carbohydrate preservation.

The peeling reaction is automatically stopped during bulk delignification for still unknown reasons, and the cellulose chain is stabilized towards further degradation by alkali.

The terminal reducing aldehyde group of the cellulose responsible for the initiation of peeling reactions can be eliminated by means of either reducing or oxidation reactions. A very powerful reducing agent, such as sodium borohydride, is required to convert the aldehyde group to a stable primary alcohol. Polysulfides have been shown to oxidize selectively the aldehyde group in preference to a stable carboxyl group.

The reduction in polysaccharide degradation results in a higher yield for a given kappa number compared to conventional kraft cooking or conversely in a lower kappa number for a fixed pulp yield.

In the early stages of pulping, at predetermined temperature and alkalinity, the carbohydrate stabilization reaction takes place:

\[ 2RCHO + 2Na_2S_2 + 6NaOH \rightarrow 2RCOONa + 4Na_2S + 4H_2O \]  \hspace{1cm} (1)

Only a minor fraction of the polysulfide is consumed in this key reaction, and as the temperature is raised, the disproportionation reaction becomes significant:

\[ 4Na_2S_2 + 6NaOH \rightarrow 6Na_2S + Na_2S_2O_3 + 3H_2O \]  \hspace{1cm} (2)

In a real sense, one could consider that sodium sulfide is 'borrowed' when polysulfide is formed in the preparation stage and then recovered again in the digester as delignification is initiated.

Benefits

According to conventional wisdom, an increase in yield of 1% on wood per 1% polysulfide sulfur charged on wood could be expected. The increased yield is mainly a result of glucomannan stabilization in softwoods and xylan stabilization in hardwoods.

Anthraquinone (AQ) addition to polysulfide pulping systems has been shown to be at least additive in its effect of increasing yield and a number of mills are presently using both additives. Most mills operating with polysulfide liquors are in Japan (Table 1).

The tensile strength, bursting strength and folding endurance of polysulfide pulps are at least equivalent to conventional kraft pulps. Tear strength, normally 5-10% lower in polysulfide pulps, may be increased by practicing high-sulfidity black liquor impregnation in conjunction with alkali profile control.

It has been documented that addition of sulfur to the white liquor in a sulfur and alkali profiled modern kraft cook increases the rate of delignification and the H-factor to reach a target kappa can be lowered substantially [11,12]. Figure 3 shows the remaining

![Figure 3. Results from lab cooks (softwood) [11]. Polysulfide addition reduces the H-factor required to reach a given level of delignification.](image-url)
lignin as a function of the H-factor in softwood cooks with and without polysulfide addition.

It was recently demonstrated that there is a significant difference in the yield development and rate of delignification in a polysulfide cook depending on the method of preparation of polysulfide liquor. It is conjectured that longer chain polysulfides have a higher reactivity towards lignin and the method of recovery and consequently the method of preparation of polysulfide chemicals in mill scale could have a great impact on overall pulping economics [13].

**Polysulfide Chemicals Recovery**

**White liquor partial oxidation**

All mills practicing polysulfide pulping at present are preparing the chemicals by catalytic partial oxidation of white liquor. However, polysulfide pulping was practiced in a few mills already in the 1960s by simply adding purchased elemental sulfur to the white liquor:

\[ n \, S^0 + n \, HS^- + OH^- \rightarrow S_n S^{2-} + H_2O \]  

(3)

Polysulfide liquors contain a mixture of polysulfide ions where the integer \( n \) is between 1 and 5. It has been suggested that the most effective species for carbohydrate stabilization is the \( S_4 S^{2-} \) ion [14].

Although successful in terms of yield gain, external sulfur addition to the mill resulted in an intolerable imbalance of sodium and sulfur in the recovery area or excessive sulfur and sodium losses.

Chemicals recovery technology with an inherent capability of separating sodium and sulfur in separate process streams with subsequent conversion of reduced sulfur in a Claus plant to elemental sulfur may reopen this route for polysulfide chemicals recovery [5].

The use of polysulfides in kraft cooking has grown in recent years due to the development of processes for preparation of polysulfides through catalyzed partial oxidation of white liquor. Today at least four processes are available on the market for polysulfide preparation directly in the white liquor [9].

All four processes are based on the same basic chemistry:

\[ (n + 1) \, HS^- + \frac{n}{2} \, O_2 \rightarrow (n - 1) \, OH^- + S_n S^{2-} + H_2O \]  

(4)

The elemental sulfur then reacts with sodium sulfide to form polysulfide in the white liquor in accordance with reaction 3. A competing side reaction forms inert sodium thiosulfate:

\[ 2HS^- + 2O_2 \rightarrow S_2O_3^{2-} + H_2O \]  

(5)

and the efficiency of oxidation processes to produce polysulfides rather than thiosulfate is generally expressed in terms of polysulfide yield (\( Y \)) and polysulfide selectivity (\( S \)), defined as:

\[ Y = \frac{\text{Polysulfide formed}}{\text{Initial sulfide}} \]  

(6)

\[ S = \frac{\text{Polysulfide formed}}{\text{Converted sulfide}} \]  

(7)

Operating data on the processes indicates selectivities in the 70 % range when the catalyst is fresh. A typical polysulfide cooking liquor prepared through white liquor partial oxidation contains 6-10 g/l of sulfur (as S).

The cooking liquor has a substantially lower sulfidity relative to standard kraft white liquor as a large portion of the sulfides has been oxidized. Partial oxidation reactions will form significant quantities of thiosulfate which reduces the amount of effective sulfide available for pulping and increases dead load and corrosion in the liquor cycle. In carbon bed catalyzed processes, the white liquor needs to be very clean, not to contaminate the catalysts.

The rather short chain polysulfides \( S_2 \) and \( S_3 \) are presumably the dominating species in the partially oxidized white liquor. It is believed that polysulfide liquor prepared this way does not give the full yield and H-factor advantage compared to polysulfide liquors prepared using elemental sulfur.

**Chemrec sulfur management**

The fuel gas stream from the Chemrec black liquor gasifier contains a considerable quantity of the sulfur in the black liquor in the form of hydrogen sulfide and carbonyl sulfide. The actual ratio between sulfur in the fuel gas and in the green liquor withdrawn from the gasifier quench can be controlled by selecting operational parameters such as gasifier pressure, gasification temperature, water vapor pressure and addition of certain additives.

By far the most common method for purification of fuel and synthesis gases containing hydrogen sulfide are the solvent-based regenerative processes. These
processes use either physical solvents, chemical solvents or a combination of both to absorb hydrogen sulfide, forming a rich solvent stream. The rich solvent is then regenerated using steam, vacuum, or other means to liberate the acid gas for downstream processing in a Claus unit [15].

When the hydrogen sulfide content of the fuel or synthesis gas makes up an appreciable fraction of the total gas stream and the operating pressure is high, as in a Chemrec BLGCC scheme, a physical solvent gas clean-up system should be considered. Examples of commercial physical solvent processes include Purisol (Lurgi), Rectisol (Lurgi), Polar (Linde), Selexol (UOP) and Sepasolv MPE (BASF).

The purified fuel gas exiting the gas clean-up plant is optionally conditioned in a last stage before it is discharged for final oxidation in a gas turbine combustor. The acid gas withdrawn from the gas clean-up plant is directed to a Claus plant for conversion of the hydrogen sulfide to elemental sulfur.

An important process in most oil and natural gas refining and processing facilities, the Claus process converts hydrogen sulfide to hot liquid elemental sulfur by the following reactions:

\[
\begin{align*}
\text{H}_2\text{S} + \frac{3}{2} \text{O}_2 & \rightarrow \text{SO}_2 + \text{H}_2\text{O} \\
2\text{H}_2\text{S} + \text{SO}_2 & \rightarrow 3\text{S}^0 + 2\text{H}_2\text{O} \\
\text{H}_2\text{S} + \frac{1}{2} \text{O}_2 & \rightarrow \text{S}^0 + \text{H}_2\text{O}
\end{align*}
\]

(8)  (9)  (10)

The elemental sulfur can subsequently be used for preparation of strong polysulfide cooking liquor by mixing the liquid elemental sulfur in white, green or black liquor in accordance with reaction 3. If desired, a major portion of the polysulfide chemicals can be charged in the beginning of the cook independent on the charge of effective alkali. The polysulfide chain length, the integer \( n \) in reaction 3, can be selected as desired with potential benefits in stabilization efficiency and H-factor needs.

The Claus process typically recovers 97% of the sulfur in the acid gas and the sulfur recovery unit must be followed by some tail gas treatment. Most modern mills have a non-condensable and odorous gases treatment facility in which the tail gas from a Claus plant could be discharged. Another option would be to use the Claus plant tail gas for in situ preparation of sulfuric acid. This route would be particularly advantageous in mills practicing peroxymonosulfuric acid delignification.

Sulfuric acid is currently purchased for use in a number of operations in the mill. Sulfur chemicals are normally purged from the mill through the discharge of saltcake which results in a loss of sodium units. The lost sodium units are made-up through the purchase of caustic. By generating sulfuric acid on-site with internally available sulfur, discharge of saltcake and purchase of caustic can be significantly reduced.

**Peroxymonosulfuric acid delignification**

Peroacids, such as Caro’s acid or peroxymonosulfuric acid (Px) and its inorganic salts (caroates) have been proposed as a replacement for chlorine compounds in delignifying and bleaching of wood pulps. It is well known that pulp treatment with small quantities of peroxymonosulfuric acid or caroates between or before oxygen delignification stages improves the overall selectivity. The nonchlorine sequence OPxO can selectively achieve greater than 80 % delignification. The combination of ozone and Px or caroate provides a superior delignification to that provided by either alone. The addition of ozone to caroate increases oxidizing power of caroate without increasing effluent, and the addition of caroate to ozone decreases the degradation of cellulose without decreasing the degradation of lignin. Industrial scale application of peroxymonosulfuric acid in pulp mills has recently been reported [16].

Peroxyacids are used commercially for chemical syntheses, but the scale of consumption in a pulp bleaching application requires safe and economical generation of peroxyacids at the pulp mill site.

Caro’s acid can be prepared by the reaction of concentrated sulfuric acid and hydrogen peroxide. The acid has to be prepared from sulfur chemicals recovered from the mill liquor system to avoid upsetting the sulfur inventory in the mill. Hydrogen peroxide can be purchased from external sources. However, on site preparation from available oxygen and hydrogen extracted from the reducing gases in a Chemrec scheme should be considered [17].

It has recently been proposed to use peroxymonosulfuric acid for pretreatment of the wood chips prior to delignification [18]. This oxidative pretreatment will introduce more carbonyl and carboxyl groups into the lignin, which will enhance breakdown and increase its hydrophilicity and solubility in the subsequent alkaline cooking stages.

Besides a yield increase, very strong TCF kraft pulps can be prepared by peracids-enhanced delignification, in particular when pretreatment is combined with peracid post treatment of the brownstock.
In situ sulfur management will become mandatory in mills practicing peroxy-sulfuric acid delignification. Gasification of sulfur-loaded bleach and spent pulping liquors would be the most economical choice for in situ sulfurous chemicals recovery.

**ENERGY INTEGRATION**

A significant driving force for introduction of black liquor gasification is its potential to substantially increase the efficiency of combined heat and power generation in the pulp mill. A Chemrec BLGCC system will produce on the order of twice as much electricity per ton of black liquor solids as a modern recovery boiler system. With a well-designed heat recovery system the increase in power generation can be achieved with little or no extra fuel consumption. The efficiency improvements are mainly due to (1) the use of black liquor fuel gas as the fuel for a gas turbine, and (2) the high pressure of the heat recovery system.

**Power Generation**

Today, most of the electricity generated in pulp mills is produced in back-pressure steam turbines. Modern recovery boilers with new and efficient steam turbines are capable of producing on the order of 450-500 kWh/ADt of pulp (depending on the pulp quality and the degree of closure). Thermodynamics severely limits the efficiency of a back-pressure steam cycle because the ‘condenser’ temperature must be high to provide heat for the mill, typically 150°C and higher. Compared to a steam cycle designed purely for power generation, where the condenser pressure is set by the available cooling water temperature, the back-pressure cycle is therefore only about half as efficient. The power-to-heat ratio is accordingly low, at best approximately 0.25 kWh/kWh\textsubscript{hp}, but most mills generate substantially less electricity per unit of heat used. In markets where the electricity-to-fuel price ratio is high, improving the power-to-heat ratio may have a significant impact on pulping economics.

**Gas Turbine Technology**

Gas turbines are the key to designing an efficient combined heat and power system with a high power-to-heat ratio. Modern aeroderivative gas turbines show electric efficiencies close to, and in some cases, above 40%. Industrial gas turbines have lower pressure ratios and slightly lower electric efficiencies, but are more efficient in combined cycle and combined heat and power operation because of the higher exhaust temperature and smaller stack losses. Both types of gas turbines are considered for BLGCC.

A typical mill producing 500,000 ADt/a of bleached kraft pulp will generate on the order of 250 MW of black liquor fuel gas, enough to fill one large industrial gas turbine or two medium-sized aeroderivatives. Natural-gas-fired machines in these sizes are already found in several installations in the pulp and paper industry, mostly in non-integrated paper mills [19,20], but also in some integrated pulp and paper mills [21].

Because of the relatively low heating value of black liquor fuel gas, a greater mass flow will pass through the gas turbine expander and the output will be considerably higher than on natural gas. A machine rated on natural gas can thus generate up to 20% more power on a synthesis gas like that from BLG. The maximum increase in power output is limited by required margins, e.g. in the compressor or on the shaft. Black liquor fuel gas has a lower heating value of approximately 8-9 MJ/m\textsuperscript{3} (about one fourth that of natural gas) and is classified as a medium heating value gas.

Gas turbine development has accelerated in the last decade as combined cycle technology has gained acceptance as the most thermodynamically efficient and cost-effective way of generating power when natural gas is available. Increasing the turbine rotor inlet temperature (TRIT) is the most important objective of this development, as it leads both to higher efficiency and higher output per unit of air compressed. The 1980s ‘E’ generation of gas turbines achieved TRITs of about 1100°C; the 1990s ‘F’ generation of turbines reached close to 1300°C; and, early next decade, ‘G’ and ‘H’ generation gas turbines will use TRITs in excess of 1400°C, giving greater than 60% efficiency (on natural gas) in combined cycle condensing power plants.

Key issues for the use of gas turbines in the BLGCC concept are (1) the availability of suitable burners, (2) adequate compressor margins, and (3) the removal of alkali compounds from the black liquor fuel gas.

Burners must be modified for low and medium heating value gases to ensure flame stability under lean combustion conditions and to accommodate the high flame propagation speed of hydrogen in the gas. Neither of these issues present great technical challenges but development and testing of a new burner adds significantly to the engineering costs of a project. Fortunately, BLGCC can draw on burner development for other gasification applications (coal, residual oil and biomass). To date, at least five manufacturers (General Electric, ABB, Siemens, 

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Nuovo Pignone and EGT) have developed burners for low and medium heating value gases.

Experience from other IGCC applications shows that a significant increase in power output can be achieved within existing compressor margins. For example, in two installations, General Electric gas turbines rated at 159 MW on natural gas are running at 192 MW output using coal gas [22,23].

The high temperatures experienced by the first turbine stages make them very susceptible to alkali-induced corrosion, and manufacturers specify lower than ppm levels of Na and K in the fuel gas as a requirement [24]. Given that black liquor solids contain up to 25% Na and K it is essential that the gas clean-up system is designed with alkali removal in mind.

As in a recovery boiler, most alkali from the gasifier will be effectively captured as sulfide and carbonate in the smelt, but the vapor pressures of, for example, Na(g), K(g), NaCl(g), KCl(g), NaOH(g), and KOH(g) are not entirely negligible at the gasifier exit temperature. Fortunately, alkali vaporization is approximately inversely proportional to pressure, and is therefore considerably suppressed at the high operating pressure in a Chemrec BLGCC system — more than an order of magnitude compared to atmospheric operation [25,26].

At present, the most reliable way of removing alkali in the gas is water quenching followed by low temperature gas clean-up. Measurements performed in the Chemrec pressurized pilot plant have shown that alkali levels in gas from the syngas condensing cooler are within the range required by gas turbine manufacturers. In the full-scale BLGCC, the gas will be further cleaned after the syngas cooler by extensive gas-liquid contact in the acid gas removal system.

**Chemrec BLGCC power generation capability**

The cold gas efficiency across the gasifier in the Chemrec BLGCC is approximately 70%, i.e. this is the fraction of the black liquor heating value (NHV, dry basis) that is recovered as heating value in the gas [24]. Black liquor has a net heating value of about 12 GJ/tDS, which means that after gasification about 8.5 GJ/tDS is available as a gaseous fuel.

Combined cycle efficiencies are in the 42-47 percent range with existing gas turbines and taking the high back pressure into account for the steam cycle. The potential for power generation is therefore 3.5-4 GJ/tDS or up to about 1.1 MWh/tDS. This is the gross power generated; when parasitic power consumption — primarily in the ASU — is accounted for, the net power available for the mill amounts to 0.9-1 MWh/tDS [27].

Cold gas efficiency is primarily a function of gasifier temperature and black liquor dry solids content. It is thus beneficial to keep the temperature as low as possible while still achieving acceptable carbon conversion and sulfate reduction rates.

The steam cycle in a Chemrec BLGCC is quite small, contributing 15-20% of the power. The reasons for this are that the gas turbine is an efficient power generator and that a large share of the mill’s needs for low and medium pressure steam is raised in the syngas cooler. The consequence is that in some applications the system may be simplified by eliminating the steam cycle. In a retrofit situation the mill’s existing steam turbine can be used, but in a new mill or when the existing steam turbine is old, the simple cycle could be an attractive alternative. The Chemrec BLG/GT would generate 15-20% less power than the BLGCC but a corresponding amount of extra heat.

An alternative configuration to the simple and combined cycles is to use steam injection in the gas turbine (referred to as ‘STIG’ cycle) to augment power output. The STIG cycle generates more power than the simple cycle, but at a lower capital cost than the combined cycle because gas and steam both expand in the same turbine. Natural-gas-fired STIG cycles have been implemented in a number of projects over the last ten years. One of the first large installations was at a paper mill [28]. An additional advantage of the STIG is that it can be used to absorb swings in steam production and consumption, which is of particular interest for mills with a steam surplus during part of the year.

**Heat Recovery**

The increase in power-to-heat ratio would shift the energy balance towards more power and less steam, if the total efficiency remained constant. In the Chemrec BLGCC, however, the total efficiency also increases compared to a recovery boiler.

A high operating pressure makes it possible to recover heat from cooling of the gas and smelt at temperatures suitable for steam generation. Latent heat from condensation of water in the gas is also recovered and the total efficiency is therefore almost independent of the black liquor solids content, as opposed to the situation in a recovery boiler. Figure 4 shows how heat recovery benefits from an increased operating pressure in the gasifier and the associated heat recovery systems [26].
Figure 4 also shows that there is useful heat available in the temperature interval from 160 to 120°C. This heat may be used to replace low-pressure steam in the mill, primarily by preheating boiler feedwater. Also heat below 100°C may be used to preheat make-up boiler feedwater. In mills with relatively open bleach plants, there is also a need to heat wash water. As mills move towards greater closure, including improved condensate recovery, low-temperature heat may be used in more innovative ways, e.g. in the bleach plant or to preheat white and black liquor [29].

Mill Energy Balances

A number of studies have been published on the energy balances of different proposed black liquor gasification cogeneration systems [30-35]. All point towards a significant potential to increase power generation from black liquor.

Figure 5 shows a comparison of design-point performance between a Chemrec BLGCC system and a modern recovery boiler system, according to the input data in Table 2 and 3. The recovery boiler and mill data are those of a reference mill used in the research program "The Ecocyclic Pulp Mill", an effort financed by the Swedish Foundation for Strategic Environmental Research (Mistra). The reference mill is based on current state-of-the-art technology for a market pulp mill [36].

The reference market pulp mill generates a surplus of steam from the black liquor and bark, even after using some of the bark to fuel the lime kiln. The integrated mill uses some purchased fuel (for simplicity, assumed to be bark) to meet its steam demand. When black liquor is gasified, some of the sulfur is converted to $\text{H}_2\text{S}$ instead of $\text{Na}_2\text{S}$, which reduces the amount of effective alkali produced from the hydrolysis of sulfide ions. To compensate for this, more lime must be added to the green liquor, and fuel use in the lime kiln is about 20% higher. There is therefore slightly less bark available for steam production in the gasifier cases.

Table 2. Mill configuration and data.

<table>
<thead>
<tr>
<th>Mill</th>
<th>Market pulp</th>
<th>Integrated</th>
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<tbody>
<tr>
<td>Pulp Production (ADt/d)</td>
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<td>1000</td>
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<tr>
<td>BLS to Recovery (tDS/d)</td>
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<td>1800</td>
</tr>
<tr>
<td>Falling Bark (tDS/d)</td>
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<td>182</td>
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<tr>
<td>Purchased Bark (tDS/d)</td>
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<td>118</td>
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<tr>
<td>Process Steam Demand</td>
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<td>MP, 12 bar(a) (GJ/ADt)</td>
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<td>6.5</td>
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<tr>
<td>LP, 4.5 bar(a) (GJ/ADt)</td>
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<td>7.8</td>
</tr>
<tr>
<td>Steam Turbine Cond./Extr.</td>
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</table>

Table 3. Key inputs for the recovery systems.

<table>
<thead>
<tr>
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<th>Tomlinson Boiler</th>
<th>Chemrec BLGCC</th>
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<tbody>
<tr>
<td>Dry Solids Content (%DS)</td>
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<td>80</td>
</tr>
<tr>
<td>Gas Turbine</td>
<td>--</td>
<td>FA class</td>
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<tr>
<td>HP Steam Data</td>
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<tr>
<td>Pressure (bar(a))</td>
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<td>79</td>
</tr>
<tr>
<td>Temperature (°C)</td>
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<td>485</td>
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<tr>
<td>Sootblowing Steam (%)</td>
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<td>0</td>
</tr>
<tr>
<td>Bark for Lime Kiln (t/d)</td>
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<td>118</td>
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<tr>
<td>Purchased Bark to meet steam demand</td>
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<td></td>
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<tr>
<td>Gas Cleanup</td>
<td>ESP</td>
<td>physical solvent</td>
</tr>
</tbody>
</table>

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To evaluate the maximum amount of power that could be produced from the surplus steam, a condensing/extraction steam turbine is included as part of the market pulp reference mill. It should be noted that condensing turbines are not common in the Scandinavian industry today, as they are hard to justify economically. If a mill has a steam surplus, it tends to be greater in the summer when power prices are low.

The example for the Chemrec BLGCC is based on data for a gas turbine of the current generation of heavy-duty turbines, as exemplified by the General Electric 6FA or Siemens KWU 64.3A. These turbines are found in a number of large cogeneration and combined cycle applications, the 6FA notably at a paper mill in Finland (natural-gas-fired) [20], and in an IGCC project in the US (coal gas) [6].

For the market pulp mill with the condensing extraction steam turbine, the Chemrec BLGCC generates about 2000 kWh/ADt (net), which is 750 kWh/ADt more than the recovery boiler system at the same fuel input. In the integrated mill with back pressure steam turbines, the difference is about 800 kWh/ADt. Net power generation is the power available for the mill or other users after accounting for all internal power consumers, such as compressors, fans, gas clean-up systems and feedwater pumps.

**Emissions**

The acid gas removal system is capable of bringing the fuel gas concentration of H₂S and COS down to levels of 5-50 ppm, ensuring that SOₓ emissions from the HRSG will be on par with or lower than those from a recovery boiler. The acid gases removed are converted to sulfur in the Claus plant. As pointed out above, TRS in the Claus plant tail gas needs to be accommodated in the NCG system or it could be used for sulfuric acid production. It could also be recycled to the gas clean-up system.

As in a recovery boiler, NOₓ may be produced via two pathways in a BLGCC system, either as thermal-NOₓ in the hot combustion zone, or from oxidation of nitrogen in the fuel. Combustion temperatures are low in a recovery boiler and thermal-NOₓ formation is therefore of minor significance. Fuel-NOₓ formation via ammonia is considered to be the most important source of NOₓ in the recovery boiler [37].

Gas turbines were earlier troubled by a high production of thermal-NOₓ. The most common methods for NOₓ abatement have been steam or water injection, but in the past ten years gas turbine manufacturers have put much effort into the development of dry low-NOₓ burners, which now guarantee 10-25 ppm NOₓ in flue gas when using natural gas fuel.

A synthesis gas such as that from BLG carries inert gases into the combustor, thus decreasing the flame temperature in the same way as is done in a low-NOₓ burner. Thermal-NOₓ from firing of black liquor fuel gas in modified diffusion-flame burners has been estimated to fall in the same range as from natural gas fired in a low-NOₓ burner [38]. The fuel-NOₓ contribution will be small, since most of the ammonia formed in the gasifier will leave with the green liquor.
Due to the efficient gas clean-up system and the high temperature in the gas turbine combustor, emissions of particulates and combustibles are negligible from the Chemrec BLGCC compared to the recovery boiler.

CHEMREC BLGCC TECHNOLOGY COMMERCIALIZATION

Kvaerner Chemrec have been in the forefront of developing and commercializing black liquor gasification for several years. A Chemrec Booster gasification plant with a capacity of 330 tDS/d has been in operation at the Weyerhaeuser New Bern mill since early 1997. As a new technology, the gasifier has presented many technical challenges. Kvaerner Chemrec and the Weyerhaeuser mill team have worked together to overcome these challenges and a final acceptance test is planned for the first quarter 1999 [39]. The Chemrec Booster technology is targeted to relieve overloaded recovery boilers, and unlike retrofitting a recovery boiler, this system can be installed without mill shutdowns. Pending a successful outcome of the final acceptance test, the Chemrec Booster will be available for commercial offerings in the near future.

Recently, Kvaerner Chemrec and Air Products & Chemicals in USA entered into a long-term technical and commercial arrangement to further develop and commercialize Chemrec BLGCC systems. Air Products is a world class supplier of industrial gases and industrial gases equipment with a strong presence on the important markets for black liquor gasification.

During 1998, Kvaerner Chemrec and Air Products reached an agreement with a US pulp and paper producer to initiate front-end design work on a pressurized Chemrec demonstration plant.

Kvaerner Chemrec has been awarded a substantial grant from FABEL – a Swedish government fund for the promotion of projects for power from biomass – for erection of a Chemrec BLGCC demonstration plant. Negotiations with mills and power utilities are ongoing to establish a BLGCC project in Sweden.

In the European Community Fifth Framework R&D Programme, recently agreed by the Council of Ministers, black liquor gasification has been identified as one of the areas for support in the Pulp and Paper industry segment. In a recent European Community Conference held on Pulp and Paper R&D needs it was noted:

"Maximizing biomass based electricity generation in pulp mills ties in with the improvement of the sustainable development status of the future Pulp & Paper industry. The development of economical gasification of the spent pulping liquor and other forest industry residues could potentially generate as much as 2 MWh electricity per ADt. The introduction of this technology is a research task that requires Europe-wide co-operation between the members of the forest industry cluster" [40].

After over ten years of intense research and development efforts, black liquor gasification is ready for demonstration in full scale. Pending the outcome of demonstration programs, the Chemrec BLGCC is expected to be fully commercial around 2003-2004.

REFERENCES


