

# Mass and Energy Balances for Black Liquor Gasification with Borate Autocausticization

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## **Preface**

The research program called the “Black Liquor Gasification (BLG) Program” started in 2004 with the aim to facilitate commercialization of the high temperature black liquor gasification technology in the pulp and paper industry. This 3 year long program has been funded by the Swedish Energy Agency, MISTRA, Vattenfall AB, Smurfit-Kappa Kraftliner AB, SCA Packaging AB, Södra’s Research Foundation, Sveaskog AB, Chemrec AB and County Administrative Board of Norrbotten and ends by the end of 2006. The tasks included construction of and large-scale tests in a gasifier developed by Chemrec AB, dimensioned for 20 ton DS/day, as well as fundamental and applied research on the black liquor gasification process. This thesis was carried out in 2006 at the Energy Technology Center (ETC) in Piteå, Sweden under supervision of Dr. Ingrid Nohlgren, ETC, and prof. Jonas Hedlund, Luleå University of Technology, as a part of the research in the BLG Program and also constituted the final part of the M.Sc. Program in Chemical Engineering at the University of Technology in Luleå, Sweden.



## **Abstract**

Gasification of black liquor is considered to be a promising alternative technique for recovery of black liquor in kraft pulping. Compared to the conventional recovery process, i.e. combustion of black liquor in a recovery boiler, the primary advantage of gasification is the potential to produce biofuels and chemicals. The causticizing demand is though higher for the gasification technology. If the existing lime kiln can not handle the extra load, partial borate autocausticizing may be an alternative.

In this work, the energy balance for a kraft pulp mill using black liquor gasification and partial borate autocausticization is compared with a mill using gasification and extended lime causticizing and also with a mill having a conventional recovery cycle. Additionally, the chemical costs for the partial borate autocausticizing is compared to the investment cost of the larger lime kiln. Mass and energy balances are based on the updated reference mill in the MISTRA Research Program, “The Eco-Cyclic Pulp Mill”, producing 2000 ADt of pulp per day.

The results show that less energy is released to steam production in a gasifier than in a recovery boiler and instead energy is released in chemical form in the produced syn gas. Using partial borate autocausticizing, the demand of external energy is lowered in the lime kiln compared to extended lime causticization. The borate autocausticization, taking place in the gasifier with black liquor as energy source, only demands a third of the energy saved in the lime kiln. On the other hand the chemical costs for the borate autocausticization exceeds the investment cost for a larger lime kiln after five years.



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Finally huge thanks to Joakim for all your love and support. I will make it up to you some day!

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# 1. Introduction

Paper is made of wood fibers. Different pulping technologies are used to liberate the fibers from the wood. The dominating process worldwide is the chemical kraft pulping and it is expected to remain so for many years to come (KAM Final Report, 2000). A byproduct in kraft pulping is black liquor, which contains cooking chemicals, lignin and hemicelluloses. The black liquor is used in the energy and chemical recovery cycle of the kraft process. For more than 30 years, research and development work has been carried out to find gasification-based alternatives to the conventional black liquor recovery process. The aim has been to find a more efficient process where the ratio between electricity and steam produced is higher and the white liquor produced is of higher quality than in the conventional process.

The conventional causticizing with lime is an integral part of the kraft process. However, it has drawbacks as high capital cost and poor energy economy and efficiency. It is also the main consumer of external fuel in the kraft mills. This has led to an interest of alternative causticization technologies, which started in Finland in the 1970's (Kiiskilä and Virkola 1978; Kiiskilä 1979a, b, c; Kiiskilä and Valkonen 1979; Jansson 1977, 1979a, b). Lately, the alternative causticization processes have been brought to life again. One reason is the possibility to combine them with the introduction of black liquor gasification technologies to be able to eliminate the subsequently increase in causticization demand. The non-conventional causticization would then only be partial, i.e. a complement to the conventional causticization.

The non-conventional causticization technologies are based on the concept to add an amphoteric metal oxide ( $\text{Me}_x\text{O}_y$ ) to the furnace, which will convert molten sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) directly to a sodium metal oxide ( $\text{Na}_2\text{Me}_x\text{O}_{y+1}$ ) and  $\text{CO}_2$  at high temperature. The technologies are divided in two groups based on the solubility of the reaction product: (1) autocausticization, where the reaction product is water-soluble and (2) direct causticization, where the reaction product is insoluble. The most promising oxides for autocausticization for kraft pulping are borates (Nohlgren 2004).

In this M.Sc. Thesis, the energy balance for a pulp mill with black liquor gasification and partial borate autocausticizing has been evaluated. It was compared to the energy balances for a conventional mill and a mill with black liquor gasification using only conventional causticization.

## 2. Recovery of Kraft Black Liquor

### 2.1 The Conventional Kraft Pulping and Chemical Recovery Process

When producing paper from wood, the fibers have to be liberated from the wood matrix. This process is called pulping, and can be done mechanically or chemically. In chemical pulping the fibers are released by chemically reacting and dissolving the lignin, which holds the fibers together.

The major chemical pulping process is the kraft pulping process. In this process, the pulping liquor is called white liquor and contains sodium hydroxide and sodium sulfide. The active ions during the cook are  $HS^-$ , which is the primary delignifying agent, and  $OH^-$ , keeping the fragments of lignin in solution. The wood chips are treated with the white liquor at elevated temperature and pressure and forms the pulp, which is further processed to paper, and a solution called black liquor.

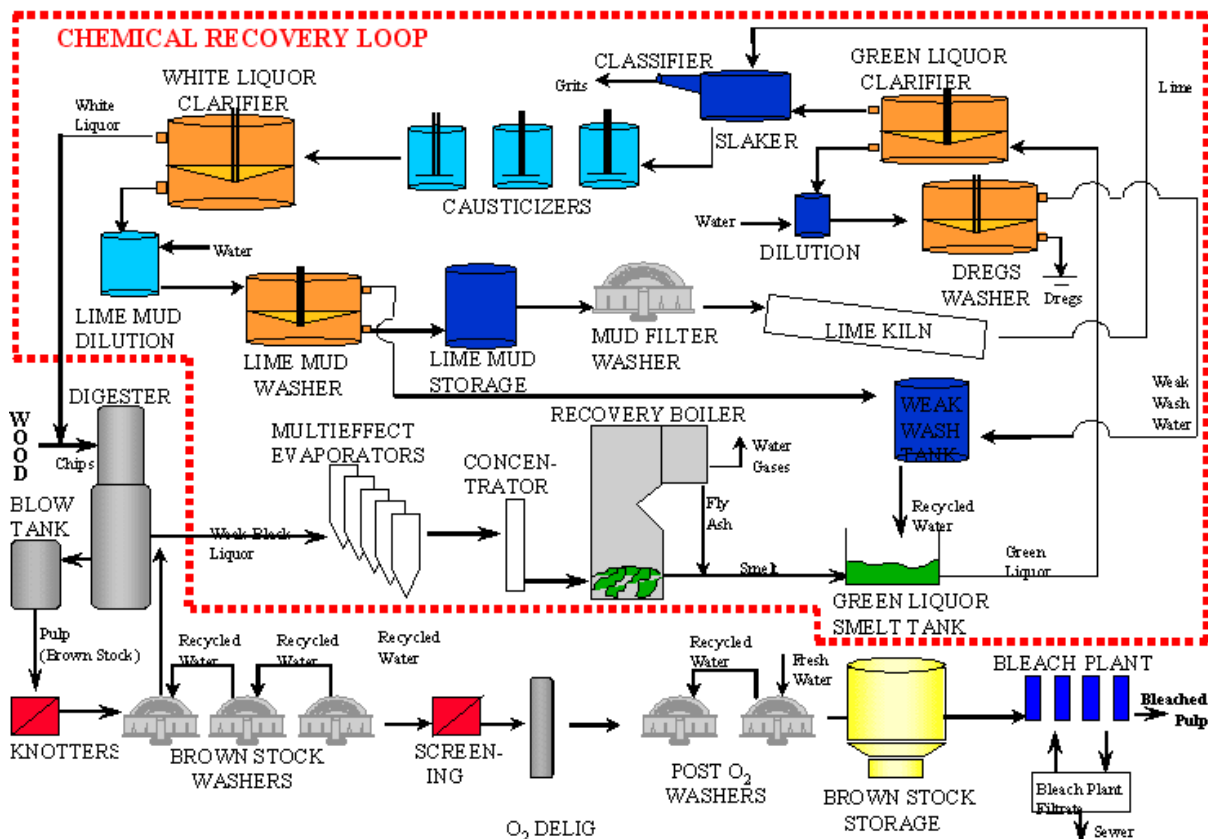


Figure 2.1. The kraft pulping process (Sundar et al. 2003)

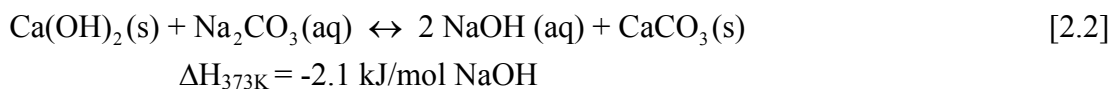
The black liquor contains the spent pulping chemicals and dissolved organic material, which corresponds to about half of the wood material used for pulping. An efficient recovery of both the pulping chemicals and the energy latent in the organic material is a requirement for the pulping process to be economically feasible. The energy is recovered by combustion in a so called recovery boiler of Tomlinson type, developed around 1930 and the pulping chemicals are recovered by step wise chemical reactions described below. Before the black liquor from the pulping unit can be burned in the recovery boiler its heating value has to be increased. This is done by evaporation, increasing the dry content from 15-20% to 70-80%. The

evaporated liquid contains mostly water (>95%) but also some organic compounds. The strong black liquor is sprayed as droplets into the recovery boiler, where air is added at different heights of the boiler, creating a reducing atmosphere in the bottom of the recovery boiler and an oxidizing atmosphere in the upper part. The chemicals are recovered as a salt smelt containing mainly  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{S}$  from the bottom of the recovery boiler and the energy is recovered by heat exchangers in the form of steam. Low energy efficiency is a drawback together with a rather high capital cost.

The salt smelt from the recovery boiler is dissolved in weak wash from the lime mud washer and forms a solution called green liquor, and a solid residue, called green liquor sludge, which is separated from the green liquor by filtration or sedimentation. Reburned lime,  $\text{CaO}$  is then mixed into the green liquor in the slaker and the slaking reaction takes place:



The formed slaked lime,  $\text{Ca(OH)}_2$  reacts further with the carbonate ions in the green liquor forming hydroxide ions and solid calcium carbonate (i.e. lime mud). The produced solution is called white liquor, i.e. the desired pulping solution. This reaction is called the causticizing reaction:



The completeness of this reaction is called the causticizing efficiency. This should be as high as possible to minimize the load of inert  $\text{Na}_2\text{CO}_3$  in the liquor. The efficiency is typically around 80-90% and depends on parameters such as alkali concentration, sulfidity level and excess lime.

The produced white liquor and lime mud,  $\text{CaCO}_3$  are separated by filtration or sedimentation. The white liquor is recycled to the digester and the lime mud is washed with water, dried and then calcined in the lime kiln forming lime ( $\text{CaO}$ ) which is recycled to the slaking and causticization units:



Approximate values of heat of reaction for Reactions 2.1-2.3 are taken from Nohlgren (2002).

The conventional chemical recovery process is a routine commercial operation but has several drawbacks:

- High capital cost
- Low energy efficiency
- Low calcination efficiency, which results in high dead load of  $\text{Na}_2\text{CO}_3$  and consequently increased energy demand in e.g. the digester, evaporator and recovery boiler
- Risk of smelt explosion when dissolving the salt smelt
- The lime kiln is the main consumer of external fuel in a kraft pulp mill

## **2.2 Alternative Black Liquor Recovery Technologies**

Over the years several different alternative black liquor recovery processes have been developed. They can roughly be divided into new processes for the chemical recovery (i.e. alternative causticization processes) and for the energy recovery of black liquor (i.e. gasification processes). In addition, the alternative causticization processes and gasification processes may also be combined. The drawbacks of the conventional recovery process listed above have been the drivers for development of these new concepts.

### **2.2.1 Gasification Processes**

Gasification of black liquor is considered to be a promising alternative technique for recovery of black liquor in kraft pulping (Nohlgren 2002). Compared to the conventional recovery process, i.e. combustion in the recovery boiler, the primary advantage of the gasifier is the potential to significantly increase electrical power production and overall thermal efficiency of the mill. It has the potential to double the power output, reduce operational costs and improve safety (Whitty and Baxter 2001). Today, however, the most important potential is considered to be to convert the produced gas into speciality chemicals or “green” fuels such as DME (dimethylether), methanol or synthetic diesel (Gebart et al. 2005). The reason for this change of interests is the possible lack of fossil fuels in the future as well as the greenhouse gas emission problems.

In a gasifier, part of the sulfur in the black liquor will be released to the gas phase mainly as  $H_2S$ . The sodium left by the sulfur ions then reacts with carbonate to form  $Na_2CO_3$ . In this way, more  $Na_2CO_3$  is formed than in the conventional process, which leads to a higher causticization demand (Nohlgren 2004). However, the separation of sulfur and sodium also gives the possibility to produce white liquors with different sulfidity, which could be used for advanced pulping methods to increase pulp yield (Gebart et al. 2005).

The different gasification processes for kraft black liquor recovery can roughly be categorized into low and high temperature processes. Low temperature processes work below  $715^\circ C$  and the inorganic salts are removed as dry solids. High temperature processes operate above  $900^\circ C$  and an inorganic salt smelt is obtained. Trials to develop a commercially feasible process for black liquor gasification have been performed by a dozen companies and the history of black liquor gasification development is well described by Whitty and Baxter (2001) and Whitty and Verrill (2004). However, only two technologies are currently being commercially pursued; the MTCI (low temperature) and Chemrec (high temperature) technologies. They are therefore, described in more detail below.

#### **The MTCI Technology**

MTCI uses low temperature gasification with a bubbling fluidized bed steam reformer (Durai-Swamy et al. 1991; Mansour et al. 1992; Mansour et al. 1993; Mansour et al. 1997; Rockvam 2001; Whitty and Verrill 2004) operating at  $580-620^\circ C$ . The bed is indirectly heated by several bundles of pulsed combustion tubes, which burn some of the produced gas. Black liquor is sprayed into the fluidized bed and coats the solids, where it is quickly dried and pyrolyzed. The remaining char reacts with steam to produce a hydrogen-rich fuel gas (Rockvam 2001).

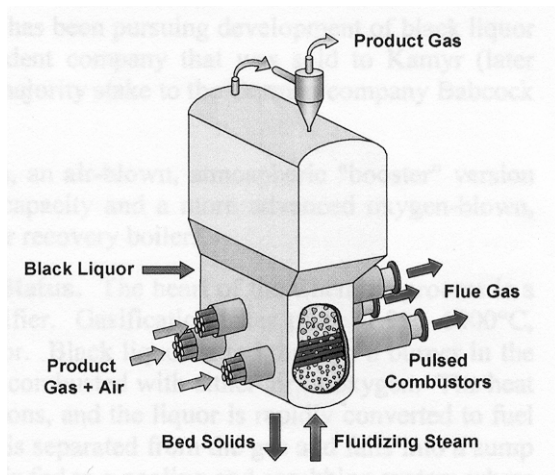


Figure 2.2. MTCI steam reformer (Whitty and Baxter 2001)

Part of the bed material is continuously removed, dissolved in water and cleaned from unburned carbon to obtain green liquor. The produced gas is passed through a cyclone to separate solids and then to a heat recovery steam generator. Part of the generated steam is used in the gasifier as both reactant and fluidizing medium. The gas continues through a Venturi, a gas cooler and is finally cleaned from  $H_2S$  in a scrubber with some of the green liquor. The cleaned gas contains about 73%  $H_2$ , 14%  $CO_2$ , 5%  $CH_4$  and 5%  $CO$  (Rockvam 2001). The heating value of the gas is high ( $\sim 13 \text{ MJ/Nm}^3$ ). It can be burned in an auxiliary boiler, used in a fuel cell to generate electricity and pressurized it can be fired in a gas turbine.

MTCI has two projects running today, both in mills with a  $Na_2CO_3$  semi-chemical cooking process. The first project is for Georgia Pacific Corporation's Big Island mill in Virginia. This system is a full-scale gasifier, designed to process 200 ton dry solids per day (Georgia-Pacific 2006, personal communication) and is fully integrated with the mill (DeCarrera 2006). The second project is for the Norampac Trenton mill, which had no chemical recovery before the steam reformer commission began 2003 (Middleton 2006). This gasifier has a processing rate of 115 ton DS/day.

### The Chemrec Technology

Chemrec is working on both an atmospheric version and a pressurized version of a high temperature downflow entrained flow reactor (Brown and Landälv 2001; Kignell 1989; Stigsson 1998; Whitty and Nilsson 2001; Whitty and Verrill 2004). The atmospheric version is mainly considered as a booster to give additional black liquor processing capacity. The pressurized version is more advanced and would replace a recovery boiler or function as a booster.

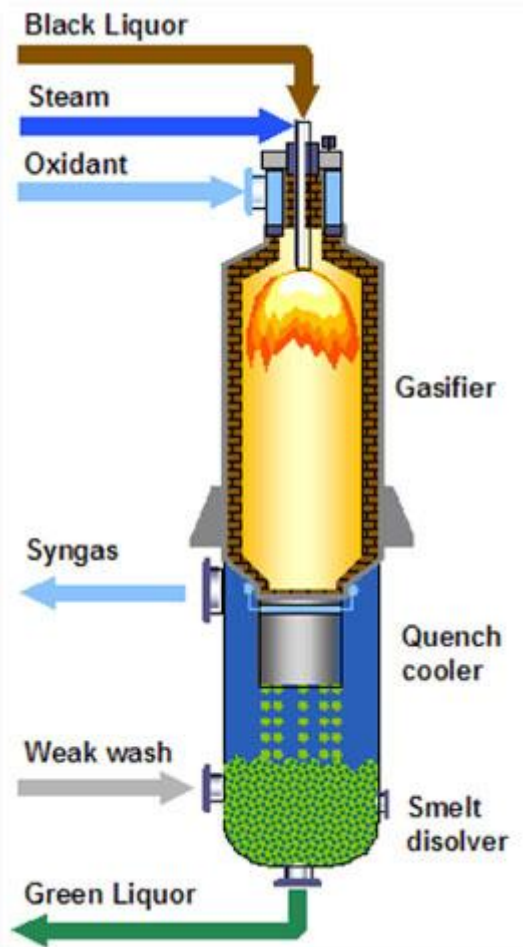


Figure 2.3. Chemrec gasifier (Chemrec AB)

In the atmospheric system, black liquor is fed as droplets through a burner at the top of the reactor. The droplets are partially combusted with air or oxygen at 950-1000°C and atmospheric pressure. The heat generated sustains the gasification reactions. The salt smelt is separated from the gas, falls into a sump and dissolves to form green liquor. The produced gas passes a cooling and scrubbing system to condense water vapor and remove H<sub>2</sub>S. The gas has low heating value (~2.8 MJ/Nm<sup>3</sup>) and is suitable for firing in an auxiliary boiler. It consists of 15-17% CO<sub>2</sub>, 10-15% H<sub>2</sub>, 8-12% CO, 0.2-1% CH<sub>4</sub> and 55-65% N<sub>2</sub> (Lindblom 2003). The thermal efficiency is quite low.

An atmospheric Chemrec Booster system with a firing rate of 270 ton DS/day is in use at Weyerhaeuser's New Bern mill since 1997. However, it was shut down in 2001 due to extensive cracking in the reactor shell and it was started again in 2003. The gasifier had then been rebuilt with a new reactor vessel as well as a modified refractory lining design and it has operated well since then. (Brown et al. 2004)

The pressurized system is similar but operates at a pressure of 30 atm. The salt smelt is separated from the gas in a quench device. The gas cleanup system is more advanced, cleaning the gas of fine particles and condensed hydrocarbons. The sulfur-rich gas stream separated in an absorber/stripper system can be used to prepare advanced pulping solutions. The gas produced has a higher heating value (~7.5 MJ/Nm<sup>3</sup>) and can be e.g. fired in a gas turbine to produce electricity or used to produce biofuels such as methanol or dimethyl ether (DME). The exhaust from the turbine is passed through a heat recovery steam generator. The thermal efficiency is above 80%.

A pressurized system has been built within the Swedish national BLG program (2004-2006) in Piteå, Sweden. It is a development plant built for 20 ton DS/day. The system includes the processes of gasification and quenching, gas cooling and gas cleaning. The produced gas has been determined to contain about 41% H<sub>2</sub>, 31% CO<sub>2</sub>, 25% CO, 2% CH<sub>4</sub> and 1.4% H<sub>2</sub>S (Lindblom 2006). The aim of the program is a verified process that will be ready for scale up (15 times) as well as an optimized integration of the process with the pulping cycle.



## 2.2.2 Non-conventional Causticization Processes

The main concept in non-conventional causticization technologies is to add an amphoteric metal oxide ( $\text{Me}_x\text{O}_y$ ) or salt to convert molten  $\text{Na}_2\text{CO}_3$  directly to  $\text{Na}_2\text{Me}_x\text{O}_{y+1}$  and  $\text{CO}_2$  in the furnace. The resulting smelt will yield the caustic directly by dissolving it in water. (Nohlgren 2004)

The non-conventional causticization technologies can be categorized by the solubility of the reaction product. In direct causticizing the reaction product is insoluble in caustic solution and is separated from the liquor. Titanate is considered as the most promising agent for direct causticization in kraft pulping. In autocausticization the reaction product is soluble. Hence the decarbonizing agent follows the entire pulping and recovery cycle and changes the characteristics of the white liquor. Higher ion strength may be a disadvantage in both digestion and washing of pulp. Also the dead load decreases the overall energy efficiency. (Richards et al. 2002) Therefore only partial autocausticization is interesting, which is when an autocausticizing system is added to the conventional process. This could be attractive when the need of causticization exceeds the capacity of the lime furnace, which may happen e.g. when a recovery boiler is replaced by a gasifier (see above). Proposed oxides for autocausticization in the literature are  $\text{P}_2\text{O}_5$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{B}_2\text{O}_3$ . Borates are the most promising ones for kraft pulping (Nohlgren 2004). Therefore, borates are the focus in this work and will be discussed in more detail below.

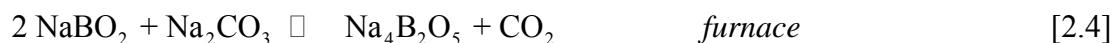
### Partial Borate Autocausticization

Phase diagram of the  $\text{Na}_2\text{O}$ - $\text{B}_2\text{O}_3$  system show that  $\text{Na}_2\text{O}$  and  $\text{B}_2\text{O}_3$  form 12 different sodium compounds with different Na:B ratios (Milman and Bouaziz 1968). This implies a high affinity of borates to sodium compounds. Only sodium borates relevant to autocausticization are listed in Table 2.1.

*Table 2.1. The sodium borates relevant to borate autocausticization (Nohlgren 2004; Tran et al. 1999)*

<b>Compound</b>	<b>Na:B molar ratio</b>
$\text{Na}_2\text{B}_4\text{O}_7$ (or $\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ )	1:2
$\text{NaBO}_2$ (or $\text{Na}_2\text{O}\cdot \text{B}_2\text{O}_3$ )	1:1
$\text{Na}_6\text{B}_4\text{O}_9$ (or $3\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ )	3:2
$\text{Na}_4\text{B}_2\text{O}_5$ (or $2\text{Na}_2\text{O}\cdot \text{B}_2\text{O}_3$ )	2:1
$\text{Na}_{10}\text{B}_4\text{O}_{11}$ (or $5\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ )	5:2
$\text{Na}_3\text{BO}_3$ (or $3\text{Na}_2\text{O}\cdot \text{B}_2\text{O}_3$ )	3:1

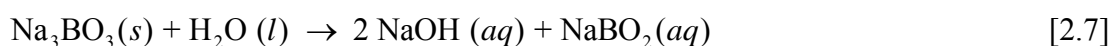
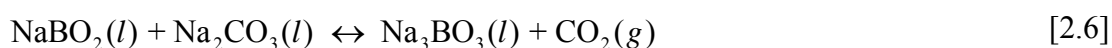
Janson was the first to suggest the use of sodium borates for causticization in the late 1970s (Janson 1977; Janson 1979a; Janson 1979b). Janson proposed that  $\text{NaBO}_2$  (sodium metaborate) reacts with  $\text{Na}_2\text{CO}_3$  in the smelt and forms  $\text{Na}_4\text{B}_2\text{O}_5$  (disodium borate). In a second reaction step the  $\text{Na}_4\text{B}_2\text{O}_5$  can be hydrolyzed in water to regenerate  $\text{NaBO}_2$  and form  $\text{NaOH}$  in water solution.



It can be seen that two moles of NaBO<sub>2</sub> are needed for every sodium carbonate to be causticized. Janson found that Reaction 2.4 is severely hindered if the molar ratio of the reactants is higher than 1.5:1 and will not occur at molar ratios higher than 3:1. Partial auto-causticization is likely to have much higher ratio than that (Tran et al. 1999). Janson stated that Na<sub>2</sub>S did not affect the auto-causticizing reactions and that the presence of borates in molten carbonate reduces loss of sodium from smelt as well as lowers the melting point of the smelt.

Tran et al. (1999) determined that the smelt reaction could go one step further (T>900°C), Reaction 2.6. The same conclusion was made at the Institute of Paper Chemistry in Appleton, WI, in 1987. Tran et al. also found that the reaction could take place at any Na:B ratio, though it depends on the temperature and the pressure of CO<sub>2</sub>. The contradiction to Janson's conclusions is according to Tran et al. caused by Janson's larger sample size and lack of purge to remove formed CO<sub>2</sub>, which hinders Reaction 2.6. Also Janson adjusted the Na:B molar ratio using an aqueous solution of NaOH, which is not realistic because there is little or no NaOH in smelt.

In water the Na<sub>3</sub>BO<sub>3</sub> hydrolyzes into NaOH and NaBO<sub>2</sub> (T<100°C), Reaction 2.7.



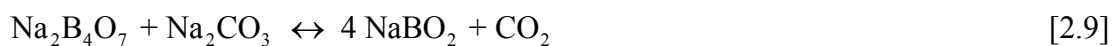
According to the theory of Tran et al., borate auto-causticization is possible since the reaction occurs at the ratio of Na:B in the smelt (much higher than 3). In addition, according to Reaction 2.6 only one mole of NaBO<sub>2</sub> is needed for every Na<sub>2</sub>CO<sub>3</sub> to be converted. Therefore, only half the amount of borate is needed compared to the reaction proposed by Janson (Reaction 2.4). This implies half as much NaBO<sub>2</sub> and a reduction of the dead load effects caused by the borate addition in the cooking liquors.

Multiphase chemical equilibrium calculations of the furnace process done by Hupa et al. (2001) also show that boron addition in the liquor will change the smelt bed composition significantly under equilibrium conditions and result in formation of Na<sub>3</sub>BO<sub>3</sub>, which will be completely dissolved in the molten bed at furnace temperatures.

The effect of the presence of CO<sub>2</sub> on Reaction 2.6 is not a problem in a recovery boiler since the CO<sub>2</sub> pressure is very low in the smelt. Solid carbon is present in the smelt at high temperatures and it consumes the carbon dioxide, forming carbon monoxide (Reaction 2.8, 1000°C).



Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (Borax) can be added to the system instead of NaBO<sub>2</sub>. The Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> reacts with Na<sub>2</sub>CO<sub>3</sub> to form NaBO<sub>2</sub> according to Reaction 2.9, which then can react further to Na<sub>3</sub>BO<sub>3</sub> as described above (Reaction 2.6) (Tran et al. 2001). Borax is cheaper than Na<sub>2</sub>BO<sub>3</sub> and therefore it is the most likely make-up chemical used in a commercial system (Tran et al. 1999).



$\text{Na}_3\text{BO}_3$  can then be hydrolyzed in water to  $\text{NaBO}_2$  (Reaction 2.7), which is still the main sodium borate compound in the solution (Tran et al. 1999).

The black liquor evaporator efficiency is affected by the boiling point rise of added  $\text{NaBO}_2$ (aq). Therefore, Bujanovic and Cameron (2001) have studied the effect of  $\text{NaBO}_2$  on the boiling point rise of black liquor. They found the effect to be low. At 120 % autocausticizing to a 60% solids liquor the boiling point rise was measured to about 5 K and at lower degrees of autocausticizing the boiling point rise would also be lower. At 30% autocausticization the boiling point rise was about 0.7 K.

Sodium borates can retard cellulose peeling reactions (Timell 1965) and results from laboratory studies suggest that there can be an increase in pulp yield by 1-2% when  $\text{NaBO}_2$  is added to the cooking liquor (Genco et al. 2002; Bujanovic et al. 2003). Furthermore, work by Econotech Services suggests that the use of borate may give better pulp quality and less shrinking during bleaching (Tran et al. 1999).

Several mill trials with partial borate autocausticization have been carried out in North America (Hoddenbagh et al. 2001; Kochesfahni and Bair 2002). Six mill trials are described by Kochesfahni and Bair (2002). They carried out short-term trials to evaluate the effect of the technology on specific parts of the mill and long-term trials to demonstrate the overall effects of the technology on the mill operations. At autocausticizing levels up to 25% no undesired effects could be observed on digesters, pulp quality, brown stock washing, black liquor evaporation, lime recausticizing or kiln operations (Kochesfahni and Bair 2002). The most apparent effect of autocausticizing on the liquor cycle is the increase in total inorganic salts in the system. This leads to an increase of the solids throughput for evaporators, concentrators and recovery boilers. Due to the endothermic nature of the autocausticizing reaction the black liquor heating value decreases. However, the evaporation load is not affected. Therefore the temperature may decrease in the recovery boiler. Even though Kochesfahni and Bair report the conversion of autocausticizing to be sensitive to operation conditions and especially temperature they claim the overall impacts on the recovery boiler to be manageable.

One mill trial with partial borate autocausticization has been carried out in Sweden. It started 2002 and proceeded for 15 months. The autocausticization level was typically 9-11%. The technology proved successful with little effect on mill operations and without any negative effects on pulp quality or properties. The pulp yield was enhanced during the trial, which might be because of the borate addition but this is not yet verified. No evidence was observed on corrosion or cracking in any equipment. (Björk et al. 2004)

Another mill trial in North America also showed that the technology of partial autocausticization worked well, with few operational problems, even though fouling in the evaporators was detected (Hoddenbagh et al. 2001). This was explained by an increase in pH in the evaporator feed.

Borates are naturally occurring minerals in soil (10-20 ppm B), rocks (5-100 ppm B) and at low concentrations in inland freshwater (typically < 1 ppm). The Swedish limit for boron in effluent to water recipient is 10 ppm (Timell 1965). Both Kochesfahni and Bair (2002) and

Björk et al. (2004) report the effluent of boron (from the treatment plant) to be below this value.

### Borate Autocausticization with Black Liquor Gasification

A first approximation of a thermochemical equilibrium model has been done on booster gasification with borate autocausticization (Leduc et al. 2004). According to this it seems like autocausticizing occurs in an atmospheric gasifier. The results were obtained with a thermodynamic equilibrium calculation where reaction restraints, i.e. reaction kinetics, were not considered.

In a gasifier there is no char bed where the solid carbon reacts with the present CO<sub>2</sub>, keeping the CO<sub>2</sub> pressure low. The gas phase characteristics are therefore important for the equilibrium of the autocausticization reactions. Reaction 2.6 is highly reversible (Yusuf and Cameron 2001, Lindberg et al. 2005) and consequently, especially in a pressurized gasifier, the high partial pressure of CO<sub>2</sub> may hinder the borate autocausticization. This is, however, still to be investigated.

### **2.3 Objective of this work**

The objective of this work is to compare the energy balance for a kraft pulp mill using black liquor gasification and partial borate autocausticization with a mill using gasification and extended lime causticizing and also with a mill having a conventional recovery cycle. Additionally, the cost of borate for autocausticizing is compared to the investment cost of a lime kiln.

### 3. Process Conditions and Assumptions

Three different mill systems have been studied in this work, which differ only in the recovery system: (1) a mill with conventional recovery system, (2) a mill with a black liquor gasifier and (3) a mill with a black liquor gasifier and partial borate autocausticization. The system boundary has in all cases been chosen from the wood to oxygen delignified pulp.

The calculations in all three cases are based on the updated reference mill in the MISTRA Research Program, “The Eco-Cyclic Pulp Mill” (1996-2002), abbreviated KAM2 with necessary changes due to the different recovery systems. The reference mill is a theoretical, generic mill with the most recent and commercially available technology in operation at pulp mills in Sweden or Finland. The kraft process with ECF (Elemental Chlorine Free) bleaching is used. It represents a development potential for both existing and new pulp mills and has therefore a very high technical and environmental standard. The mill produces 2,000 ADt (Air Dry ton, 10% damp) of bleached pulp per day. (KAM Final Report, 2003)

#### 3.1 The Reference Mill

Known data for the reference mill, which all the calculations are based upon, are listed in Table 3.1 and 3.2 and the process scheme of the reference mill is shown in Figure 3.1. On the basis of this information the mass and energy flows are determined. To be able to calculate the enthalpy of the flows, their temperatures are assumed as shown in Figure 3.1. The enthalpy calculations are based on information from Knacke et al. (1991) and Theliander and Grén (1989). Some restrictions are made in the model:

- The smelt withholds no NaOH
- The lime mud from the white liquor filter has a dry solids content of 75%, i.e. the same as the washed lime mud
- The lime mud wash has an efficiency of 100%, i.e. the liquid in the washed lime and lime sludge is assumed to be pure water
- Complete calcination of the solid material is achieved in the lime kiln
- No heat loss in smelt dissolver, slaker, lime wash, white liquor filter or lime kiln
- The dry solids content of the green liquor dregs is 50% (Young 2001)
- The mass flow of the ashes from the recovery boiler is neglected in the energy balance

*Table 3.1. Data for the reference mill (KAM Final Report 2003; Ledung et al. 2001)*

<b>Fiber line</b>	Bleached pulp production	2000	ADt/24h	
	Wood consumption	2087	kg/ADt	
	Water with chips	2000	kg/ADt	
	Kappa after cook	27		
	Alkali on wood, EA	18	% NaOH on wood	
	Pulp yield in digester (screened)	46	%	
	Reject from screening	2	% on wood	
	Yield in oxygen stage and washing	97	%	
	Bleached pulp concentration	35	%	
	Steam demand of cooking	1.6	GJ/ADt	
<b>White liquor</b>	Steam demand of oxygen delignification	0.14	GJ/ADt	
	Sulfidity	35	%	
	Reduction degree on sulfur	90	%	
	Causticizing efficiency	82	%	
	White liquor production	6924	m <sup>3</sup> /24h	
	Make-up chemicals to digester (NaOH)	14 (4)	kg/ADt	
	White liquor to bleaching	19	kg/ADt	
	<b>Evaporation</b>	Weak black liquor	10600	kg/ADt
		Steam demand	4.01	GJ/ADt
		Condensate	8628	kg/ADt
<i>to bleaching plant (90°C )</i>		4.4	ton/ADt	
<i>to white liquor preparation (75°C )</i>		4.1	ton/ADt	
<b>Recovery boiler</b>	Heat to production of warm water	4.01	GJ/ADt	
	Load	3420	t DS/24h	
	Steam production	17.7	GJ/ADt	
	DS of thick black liquor	80	%	
	Dry solids to recovery boiler	1710	kg/ADt	
	Ashes	16	kg/ADt	
	Sodium in ashes	2.9	kg/ADt	
	<b>Lime cycle</b>	DS of lime mud	75	%
		Burned lime	245	kg/ADt
		Active CaO in burned lime	90	%
Lime sludge		16	kg/ADt	
Make-up lime		16	kg/ADt	
<b>Residues</b>	Green liquor dregs	10	kg/ADt	
	Water leaving with solid residues	15	kg/ADt	

*Table 3.2. Water flows to and out of the delignification (KAM Final Report 2003)*

<b>Water flow</b>	<b>kg/ADt</b>
<b>In</b>	
Steam	600
OP-filtrate	4200
Miscellaneous water	800
<b>Out</b>	
Flash steam	400

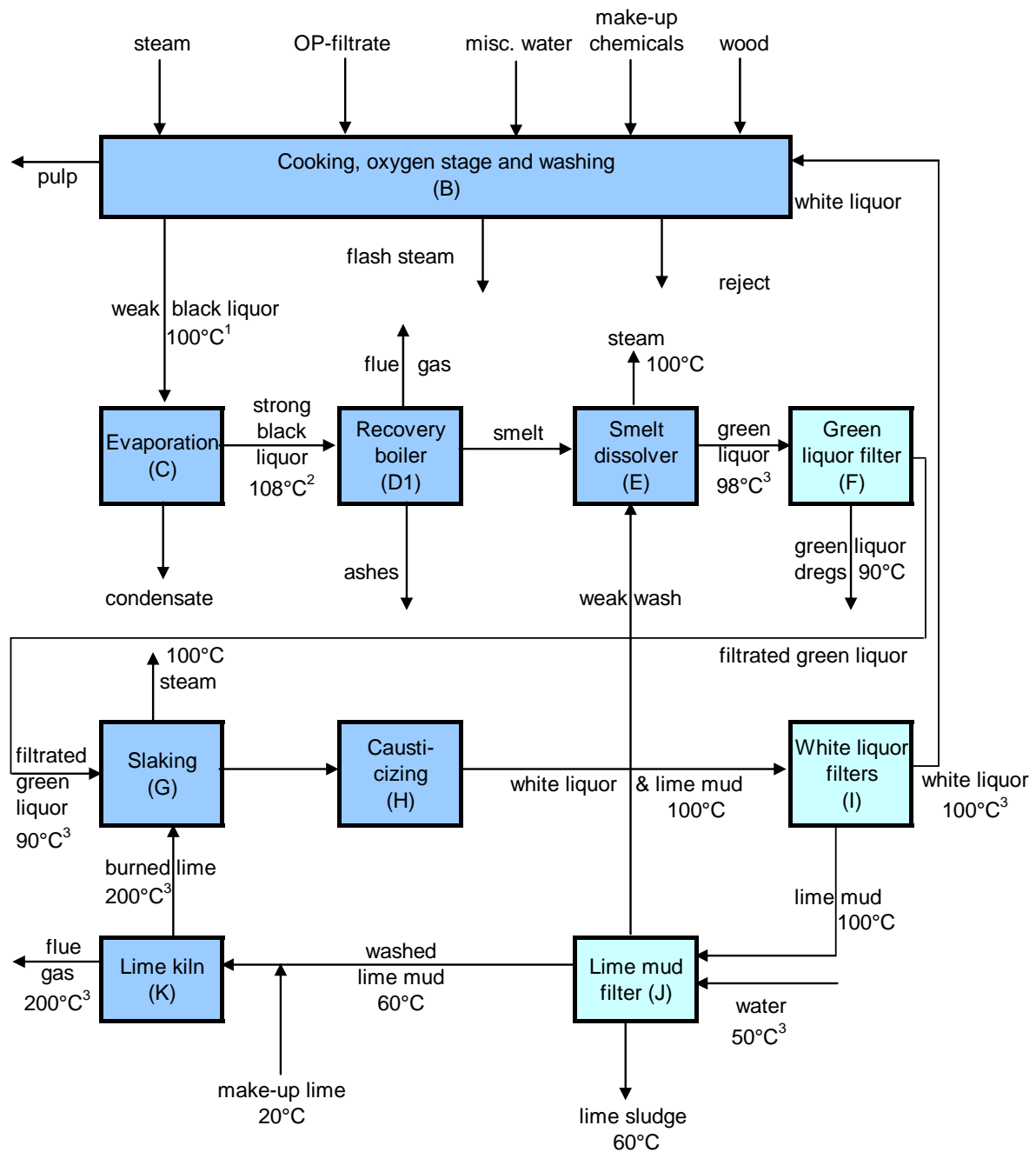


Figure 3.1. Process scheme of the reference mill with assumed temperatures of the flows

Note:

1. Based on data from Ledung et al. (2001)
2. Based on data from Adams et al. (1997)
3. Based on data from Richards et al. (2002)

Each process unit is denoted with a letter (shown in Figure 3.1). These letters are used to denote the flows in the system. For example, smelt from the recovery boiler to the smelt dissolver has the index D1E, indicating that the flow is coming from unit D1 and going to unit E. A stream entering the system is named “A” and a stream leaving the system is named “L”.

### 3.2 The Black Liquor Gasification Mill

The second mill model is set up with a gasification plant replacing the recovery boiler in the reference mill. The gasification plant holds an oxygen-blown, entrained flow gasifier and an absorption tower. In the latter, white liquor absorbs the  $H_2S$  in the gas. A process scheme of the mill model is shown in Figure 3.2.

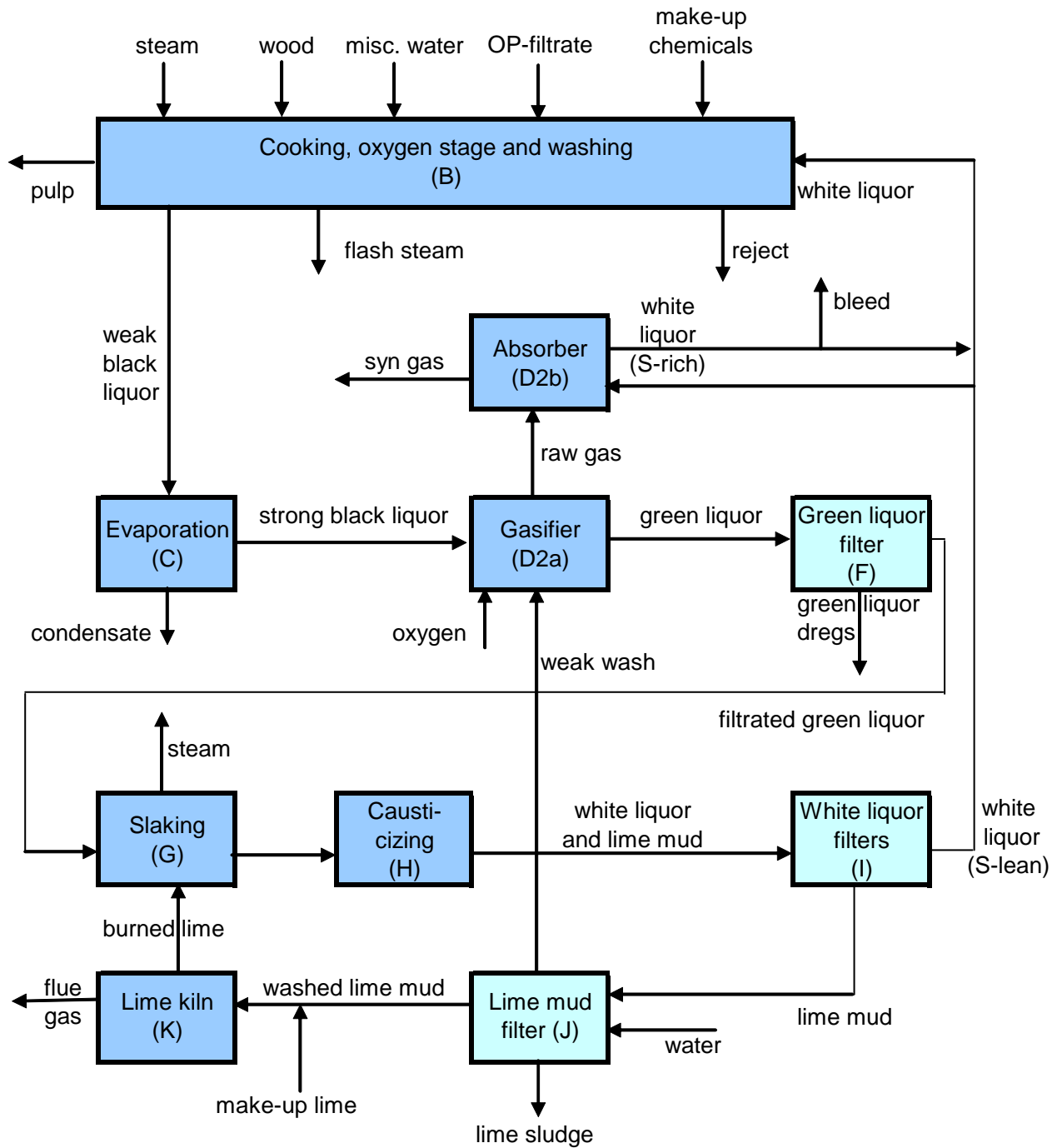


Figure 3.2. Process scheme of mill with black liquor gasification



All flows are assumed to have the same temperature as in the reference mill (Figure 3.1). Ekblom et al. (2003) concluded that the syn gas will have a lower heating value (LHV) of 19.4 MJ/kg and contain only 0.1% of the incoming H<sub>2</sub>S in the raw gas. However, since this is such a small amount it has, for simplification in this work, been assumed that all the H<sub>2</sub>S in the raw gas is absorbed by white liquor in the absorption unit, i.e. the syn gas will contain no H<sub>2</sub>S.

The selectivity for absorption of H<sub>2</sub>S from a gas stream containing both H<sub>2</sub>S and CO<sub>2</sub> depends on the absorption liquid but, the selectivity factor ( $k_{\text{H}_2\text{S}}/k_{\text{CO}_2}$ ) is generally 0.12-0.36 (Kohl 1987). In this work the selectivity is simplified to the assumption that one mole of CO<sub>2</sub> is absorbed per every 5 moles of absorbed H<sub>2</sub>S (Richards et al. 2002). All the restrictions in the reference mill holds in this model too, except for the first one that the smelt withholds no NaOH. Other assumptions in this model are:

- No energy loss in absorption
- 55% of the sulfur in the black liquor leaves the gasifier in the gas phase (Ekblom et al. 2003), which increases the lime demand with 32% (KAM Final Report, 2003)
- The green liquor dregs are assumed to have the same characteristics as in the reference mill
- It is assumed that the reaction efficiency is not affected, compared to the reference mill, by the change in amount of burned lime used in the slaking
- The raw gas has a temperature of 40°C (Ekblom et al. 2003)
- The gasifier is fed with 586 kg/ADt of oxygen and produces 1582 kg/ADt of raw gas (Ekblom et al. 2003)
- The oxygen, blown into the gasifier, is assumed to have a temperature of 20°C
- The delignification process is not affected by the change from a recovery boiler to a gasifier
- The same amount of white liquor, with the same concentrations, is produced except with the difference that no Na<sub>2</sub>SO<sub>4</sub> is present, since the sulfur reduction in the gasifier is assumed to be 100%

### ***3.3 The Black Liquor Gasification Mill with Partial Borate Autocausticization***

The third mill model is set up based on the gasification model in the last section but uses the same amount of lime as the reference mill. The additional causticizing demand is instead met with borate autocausticizing. The borates are added onto the streams in the model with gasification, contributing to the mass flow. The volume increase due to the borate addition is difficult to predict, therefore is the volume contribution from the borates neglected. However, the increase of the mass flow is of course included in the calculations.

The borates are added to the weak black liquor as Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> with a temperature of 20°C. The reaction efficiency in the gasifier (Reaction 2.6) is assumed to be 70% (Hoddenbagh et al. 2001) and the formation of hydroxide in the quench from the product borate (Na<sub>3</sub>BO<sub>3</sub>) (Reaction 2.7) is assumed to go to completion.

The borates are assumed to not affect the delignification process and to flow as the other soluble compounds in the liquors. The temperatures of the flows are the same as in the mill with gasification. The same basic restrictions are used in this model as for the reference mill

with conventional recovery system (Chapter 3.1) and for the mill model with black liquor gasifier (Chapter 3.2). Assumptions which are specific for this model are listed below:

- The maximum cooking temperature is assumed to be 160°C
- The effect of borates on the boiling point rise of black liquor is neglected (see Chapter 2)
- The effect of CO<sub>2</sub>/CO-shift in the produced gas due to formation of CO<sub>2</sub> from borate reactions (Reactions 2.6 and 2.9) is neglected
- The green liquor dregs are assumed to be similar to the dregs in the reference mill, with the exception of an addition of 9% of the boron in the green liquor (Hoddenbagh et al. 2001)
- The addition of borates is assumed to not affect the enthalpy of the rest of the streams, except for the addition of its own enthalpy (as dissolved)

### 3.4 Economic Evaluation

The two models with gasification are roughly compared economically. The investment cost of a new, larger lime kiln is compared to the cost of the added make-up borates in the mill with partial autocausticization. The calculation is based on the case where the reference mill is converted to each of the mills with gasification. A lime kiln in the size needed in the mill with partial causticizing is thus already available.

It is assumed that the additional investment cost of the larger lime kiln and bark dryer, compared to the reference mill, are proportional to the cost of each unit in the reference mill. Borax pentahydrate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·5H<sub>2</sub>O) is used as make-up borate, as suggested by Tran et al. (1999) (see Chapter 2.2.2). The economic evaluation is based on the costs shown in Table 3.3.

*Table 3.3 Costs in the mills with gasification used for economic evaluation*

	Cost	Unit	
<b>Gasification model</b>			
Investment for lime kiln	133 <sup>1</sup>	MSEK	(KAM Final Report, 2003)
<b>Partial autocausticization model</b>			
Borax pentahydrate	2540 <sup>2</sup>	SEK/ton	(Balci 2006, personal communication)

*Note:*

1. Recalculated to a value for 2005 using Swedish price level index (SCB, 2006)
2. Delivered to Sweden, exchange rate USD-SEK taken at 2006-11-08 (1 USD = 7.15 SEK)

## 4. Calculations

Explanations of the symbols in the following text are listed in Chapter 8. The index system of the flows was described in Chapter 3.1.

### 4.1 The Reference Mill

#### 4.1.1 Delignification

The mass flow of pulp ( $m_{\text{pulp}}^{\text{BL}}$ ) is calculated based on the wood consumption ( $m_{\text{wood}}^{\text{AB}}$ ), yield in cooking ( $\eta_{\text{digester}}$ ) and oxygen delignification ( $\eta_{\text{OO}}$ ) and the concentration of unbleached pulp ( $c_{\text{pulp}}^{\text{BL}}$ ) (Equation 4.1).

$$m_{\text{pulp}}^{\text{BL}} = \frac{\eta_{\text{digester}} \cdot m_{\text{wood}}^{\text{AB}} \cdot \eta_{\text{OO}}}{c_{\text{pulp}}^{\text{BL}}} \quad [4.1]$$

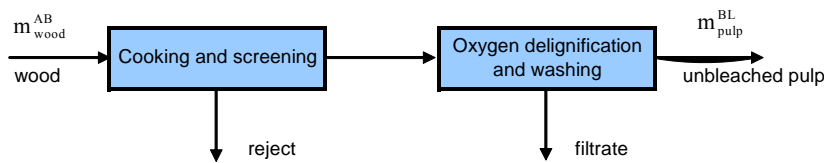


Figure 4.1. Fiber flow in delignification

The total mass of reject including water is calculated with a mass balance for the delignification. The flows in delignification containing only water are listed in Table 3.2. The energy demand of the delignification is the sum of steam demands from cooking and oxygen delignification (see Table 3.1).

#### 4.1.2 White Liquor

The concentration of the white liquor is calculated from the effective alkali (EA) on wood (Equation 4.2) and the sulfidity (Equation 4.3) together with consideration of the amount of make up NaOH. In addition, the reduction degree (Equation 4.4) gives the concentration of  $\text{Na}_2\text{SO}_4$  in the white liquor. Note that in Equations 4.2-4.4  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{SO}_4$  has to be expressed as NaOH in the calculations.

$$\text{EA} = \text{NaOH} + \frac{1}{2} \text{Na}_2\text{S} \quad [4.2]$$

$$\text{sulfidity} = \frac{\text{Na}_2\text{S}}{\text{NaOH} + \text{Na}_2\text{S}} \quad [4.3]$$

$$\text{reduction degree} = \frac{\text{Na}_2\text{S}}{\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}} \quad [4.4]$$

### 4.1.3 Lime Cycle

The lime cycle and the different solid calcium compounds in the lime cycle; lime (CaO and Ca(OH)<sub>2</sub>) and lime mud (CaCO<sub>3</sub>) are shown in Figure 4.1. The part of the flow of burned lime, which is active reacts in the slaker according to Reaction 2.1. The produced Ca(OH)<sub>2</sub> reacts further (Reaction 2.2) to generate NaOH and CaCO<sub>3</sub> in the causticizers.

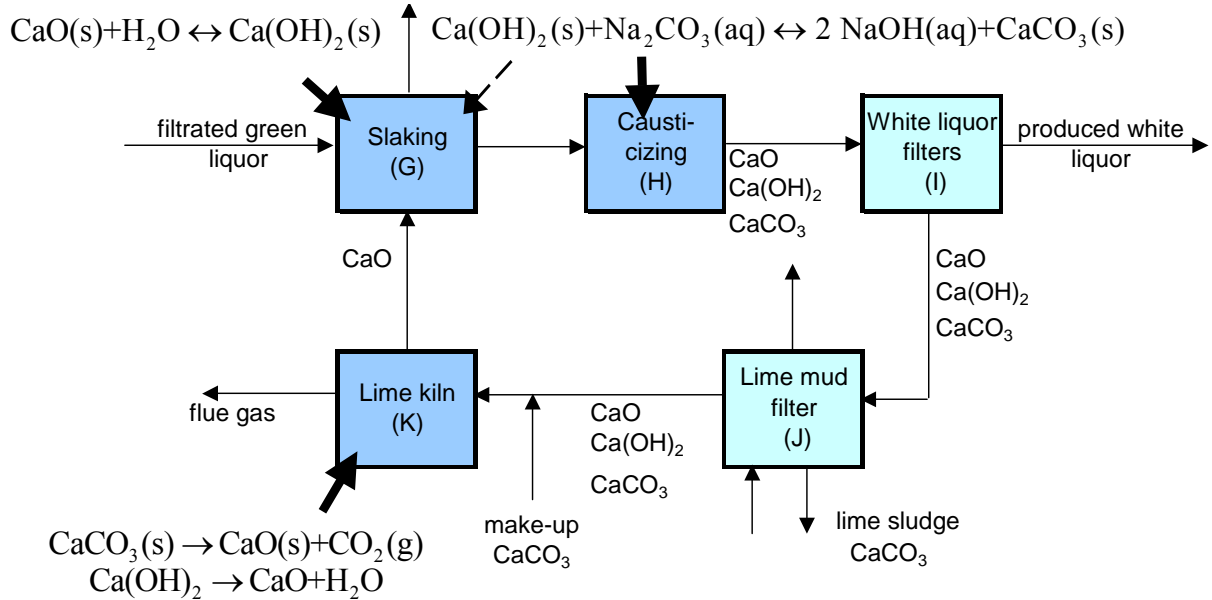


Figure 4.2. Process scheme of the lime cycle showing the different forms of lime compounds and their reactions

All solid material (i.e. CaCO<sub>3</sub>, unreacted CaO and Ca(OH)<sub>2</sub>) ends up in the washed lime mud when passing the lime mud filter, except for a small amount which exits as lime sludge. This loss is restored by a make up of lime mud before the lime kiln. The amount of separated lime sludge is determined in the KAM reference mill and is assumed to only contain CaCO<sub>3</sub>. The total amount of CaO ( $m_{\text{CaO}}^{\text{II}}$ ), Ca(OH)<sub>2</sub> ( $m_{\text{Ca(OH)}_2}^{\text{II}}$ ) and CaCO<sub>3</sub> ( $m_{\text{CaCO}_3}^{\text{II}}$ ) from the white liquor filter is determined by Equations 4.5-4.7. The dry solids concentration is known, which gives the total mass flow from the white liquor filter. The flow of white liquor and lime mud from causticizers is defined by a mass balance for the white liquor filter. The concentration of the liquor is maintained over the filter.

$$m_{\text{CaO}}^{\text{II}} = m_{\text{CaO}}^{\text{KG}} \cdot (1 - x_{\text{active lime}}) \quad [4.5]$$

$$m_{\text{Ca(OH)}_2}^{\text{II}} = \left( \frac{m_{\text{CaO}}^{\text{KG}}}{M_{\text{CaO}}} \cdot x_{\text{active lime}} - \frac{m_{\text{NaOH}}^{\text{IB}}}{2M_{\text{NaOH}}} \right) \cdot M_{\text{Ca(OH)}_2} \quad [4.6]$$

$$m_{\text{CaCO}_3}^{\text{II}} = \frac{m_{\text{NaOH react}}^{\text{G+H}}}{2M_{\text{NaOH}}} M_{\text{CaCO}_3} \quad [4.7]$$

where  $x_{\text{active lime}}$  is the fraction of lime that reacts in slaking

The amount of water leaving with solid residues is specified in Table 3.1, about 10 kg water per ADt of this water exists with the green liquor dregs (Young 2001) and the remaining part of the water follows the lime sludge. The concentration of solids is retained over the lime mud filter and the total mass flow of washed lime mud is thereby known. The flue gases are determined by mass balance for the lime kiln.

Since the smelt contains no sodium hydroxide, all the NaOH in filtrated green liquor, must originate from the weak wash. The amount of Na<sub>2</sub>CO<sub>3</sub> ( $m_{\text{Na}_2\text{CO}_3}^{\text{FG}}$ ) is determined in Equation 4.8 using the stoichiometry of Reaction 2.2, knowing the amount of NaOH generated ( $m_{\text{NaOH react}}^{\text{G+H}}$ ). The amounts of Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>4</sub> are not affected by the slaking or causticizing reactions and are the same as in the stream of white liquor and lime mud exiting the causticizing vessels.

$$m_{\text{Na}_2\text{CO}_3}^{\text{FG}} = m_{\text{Na}_2\text{CO}_3}^{\text{HI}} + \frac{m_{\text{NaOH react}}^{\text{G+H}}}{2M_{\text{NaOH}}} M_{\text{Na}_2\text{CO}_3} \quad [4.8]$$

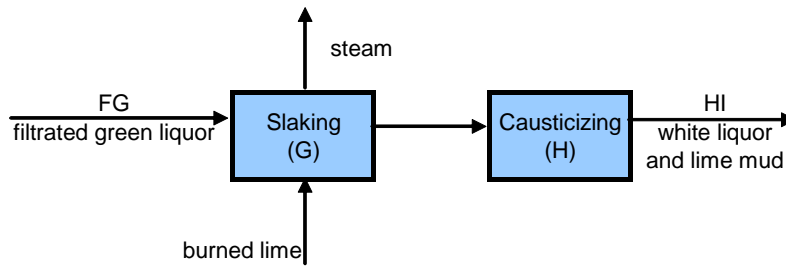


Figure 4.3. Process scheme of the slaking and causticizing

CO<sub>2</sub> gas is generated in the lime kiln according to Reaction 2.3 (Equation 4.9). The loss of CaCO<sub>3</sub> to lime sludge ( $m_{\text{CaCO}_3}^{\text{JL}}$ ) is restored before the lime kiln in form of make-up CaCO<sub>3</sub> ( $m_{\text{CaCO}_3}^{\text{AK}}$ ). All water in the washed lime mud, as well as the water formed when Ca(OH)<sub>2</sub> forms CaO (Reaction 4.1), is vaporized. The energy requirement of the lime kiln is calculated by an energy balance for the kiln.

$$m_{\text{CO}_2}^{\text{KL}} = \frac{m_{\text{CaCO}_3}^{\text{JK}} - m_{\text{CaCO}_3}^{\text{JL}} + m_{\text{CaCO}_3}^{\text{AK}}}{M_{\text{CaCO}_3}} M_{\text{CO}_2} \quad [4.9]$$

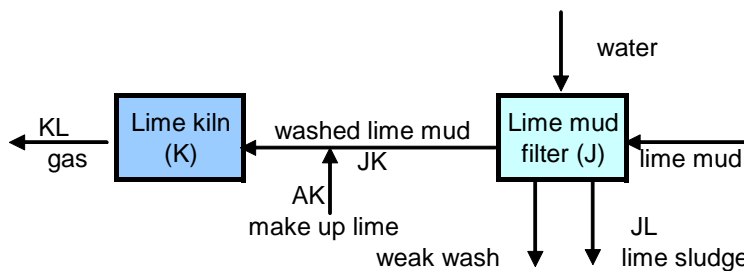


Figure 4.4. Process scheme of the lime mud filter and the lime kiln

The enthalpy of the stream from the causticizing unit is determined by an energy balance for the white liquor filter. Mass and energy balances for the slaking and causticizing have to be done simultaneously, since the amount of water evaporated is dependent on the energy entering the slaking vessels. The enthalpy of the green liquor is on the other hand dependent on its concentrations and thereby the mass balance, therefore, the calculations have to be performed by iteration. The determination of filtrated green liquor by iteration is described in Appendix A.

The calculation of the mass flows as well as the enthalpies of water added to the lime mud filter and weak wash leaving it will be described in the next section (Chapter 4.1.4).

#### 4.1.4 Liquor Cycle

A mass balance for the green liquor filter gives the mass flow of green liquor. In order to determine the energy content in the dregs an approximation of its composition has to be carried out, see Table 4.1. The concentration of the green liquor is kept over the green liquor filter, i.e. only the insoluble compounds are separated.

Table 4.1. Approximation of composition of green liquor dregs for calculating its enthalpy (Young 2001)

Compounds	kg/ADt	Weight-%
CaCO <sub>3</sub>	7.2	36
Na <sub>2</sub> CO <sub>3</sub>	1.2	6
MgCO <sub>3</sub>	1.2	6
Na <sub>2</sub> S	0.4	2
Liquor	10.0	50
<b>Total</b>	<b>20.0</b>	<b>100</b>

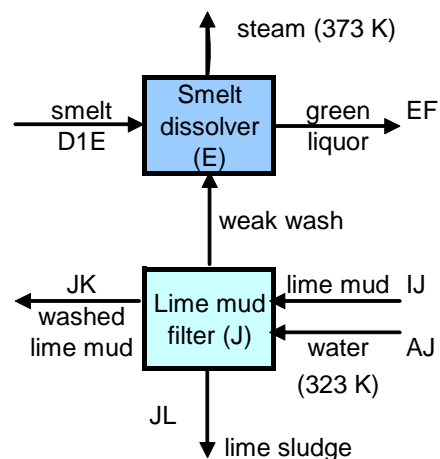


Figure 4.5. Process scheme of the smelt dissolver and the lime mud filter

The soluble compounds (e.g. Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>S) in the green liquor originate mainly from the smelt and a small part emanates from the weak wash. The mass and energy balances for the smelt dissolver and the lime mud filter together gives an expression for calculating mass of water added to the lime mud filter ( $m^{AJ}$ ).

$$m^{AJ} = \frac{(m^{D1E} + m^{IJ} - m^{EF} - m^{JK} - m^{JL}) \cdot h_{H_2O}^{373K} + H^{EF} + H^{JK} + H^{JL} - (H^{IJ} + H^{D1E})}{h_{H_2O}^{323K} - h_{H_2O}^{373K}} \quad [4.10]$$

Mass balances for the lime mud filter and the smelt dissolver determine the mass of weak wash and steam from the smelt dissolver. The enthalpy of weak wash is calculated by an

energy balance for the smelt dissolver. The amount of flue gas leaving the recovery boiler is determined by mass balance for the boiler.

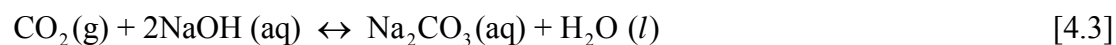
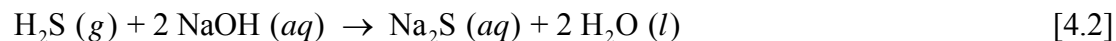
By mass balance the live steam mass flow used in the evaporation is determined. The calculation of the black liquor enthalpy is described in Section 4.2.3. An energy balance for the evaporation plant gives the energy released from it.

## 4.2 The Black Liquor Gasification Mill

### 4.2.1 White Liquor Preparation

During gasification of the black liquor, 55% of the sulfur ends up in the gas phase as H<sub>2</sub>S. The mass of sulfur in the black liquor is determined by an elemental mass balance for the recovery boiler in the reference mill. The black liquors should not differ between the models and consequently hold the same amount of sulfur.

The H<sub>2</sub>S is absorbed by some of the white liquor in the gas cleaner. NaOH is consumed during the process to convert the H<sub>2</sub>S to Na<sub>2</sub>S according to Reaction 4.2. NaOH will also react with CO<sub>2</sub> in the gas, Reaction 4.3.



Using the stoichiometry in these reactions, the demand of NaOH in the absorption unit can be calculated.

$$m_{\text{NaOH react}}^{\text{D2b}} = \frac{m_{\text{S}}^{\text{D2aD2b}}}{M_{\text{S}}} \cdot 2 \cdot M_{\text{NaOH}} \cdot 1.2 \quad [4.11]$$

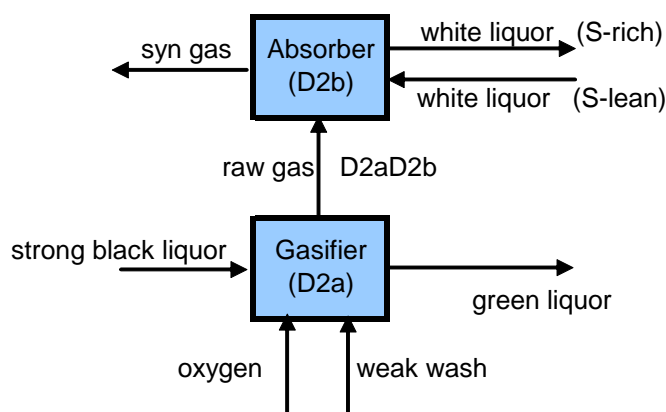


Figure 4.6. Process scheme of the gasifier and the absorber

When the white liquor has absorbed the sulfur, a part of the flow is bled off as an alternative to the purge of ashes in a recovery boiler, which cannot be done in a gasifier. Not to remove

too much sodium, the white liquor flow through the absorption is not larger than that all NaOH is consumed. The rest of the white liquor from the absorber is mixed with the white liquor that is not needed for the absorption to generate white liquor similar to the one in the reference mill.

#### 4.2.2 Lime Cycle

The mass and energy balances in the lime cycle are carried out as for the reference mill (Section 4.1.3), with only a few changes. The smelt from a gasifier is different from the smelt from a recovery boiler. It has a higher level of Na<sub>2</sub>CO<sub>3</sub>, leading to a higher causticization demand. To compensate for this the amount of burned lime used in slaking is increased by 32% to 324 kg/ADt (KAM Final Report, 2003).

The amount of NaOH in filtrated green liquor ( $m_{\text{NaOH}}^{\text{FG}}$ ) is determined in Equation 4.12, using that the amount of generated NaOH ( $m_{\text{NaOH react}}^{\text{G+H}}$ ) in causticizing (Reaction 2.2) is known. The amount of Na<sub>2</sub>CO<sub>3</sub> is calculated as in Equation 4.8.

$$m_{\text{NaOH}}^{\text{FG}} = m_{\text{NaOH}}^{\text{HI}} - m_{\text{NaOH react}}^{\text{G+H}} \quad [4.12]$$

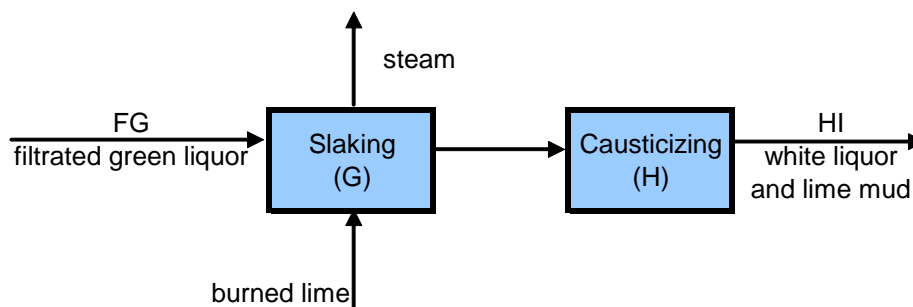


Figure 4.7. Process scheme of the slaking and causticizing

The amount of filtrated green liquor and water evaporated from the slaking and causticizing are determined with iteration similarly as for the reference mill. The calculations are described in more detail in Appendix A.

#### 4.2.3 Liquor Cycle

The delignification in the mill with a black liquor gasifier is essentially the same as the one in the reference mill, therefore, has the weak black liquor the same characteristics as in the reference mill. Furthermore, no changes are made in the evaporation process when the recovery boiler is replaced by a gasification plant.

A mass balance for the gasifier gives the flow of weak wash. A mass balance for the lime mud filter gives the demand of water added to the filter.



The flow of H<sub>2</sub>S in the raw gas was determined in Section 4.2.1. The gas also contains H<sub>2</sub>, CO, CO<sub>2</sub> and small amounts of other substances that are neglected here. The concentrations of these components are given in Table 4.2.

*Table 4.2. Flow and concentration of H<sub>2</sub>, CO and CO<sub>2</sub> in the raw gas (Ekbom et al. 2003)*

	kg/ADt	% by mass
H <sub>2</sub>	61.0	3.9
CO	823.2	52.0
CO <sub>2</sub>	646.7	40.9

Since no changes are made in the evaporation plant compared to the reference mill the energy released will be the same. The enthalpy of the weak black liquor is determined in Appendix C, using the calculated composition of smelt from the gasifier and the calorimetric heating value. The resulting enthalpy is also used in the other models.

The energy generated from the gasifier is known to be 4.9 GJ/ADt if the temperature of the green liquor is 87°C and that of the filtrated green liquor is 80°C (Berglin et al. 1999). The gasification model in this report has the respective temperatures of 98°C and 90°C in order to be similar to the reference mill model. To determine the enthalpy of the strong black liquor an extra mill model is calculated with the lower temperatures of green liquor and filtrated green liquor as the only differences from the ordinary gasification model. The calculation is further described in Appendix B and the determined enthalpy is used in all models calculated in this report. The enthalpy of strong black liquor is also calculated based on the composition of smelt and the calorimetric heating value in Appendix C for comparison. The energy release in the gasifier can then be calculated by an energy balance for the gasifier using the enthalpy of the strong black liquor.

### **4.3 The Black Liquor Gasification Mill with Partial Borate Autocausticization**

To get the delignification similar as in the reference mill the mass flows of NaOH, Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>S with the white liquor should be the same and the borates are assumed to be inert during delignification. However, the mass of the white liquor is higher than in the other models due to the extra mass of the borates in the white liquor. Since the borates are assumed not to affect the volume of the streams the concentrations per volume are not changed. The energy needed to raise the temperature of the borates during cooking is added to the steam demand of the delignification in the reference mill.

The make-up of borate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) is added to the system to the weak black liquor before the evaporation. The borates follow the liquor cycle: black liquor – green liquor – white liquor, since they are soluble in alkaline solutions. Borates exit the system with the green liquor dregs and with the white liquor bleed.

The borates react with Na<sub>2</sub>CO<sub>3</sub> in the gasifier according to Reactions 2.6 and 2.9 forming Na<sub>3</sub>BO<sub>3</sub> and CO<sub>2</sub> and when the salt (Na<sub>3</sub>BO<sub>3</sub>) dissolves in water NaBO<sub>2</sub> is formed according to Reaction 2.7. As mentioned, Reaction 2.6 and 2.9 generate CO<sub>2</sub>, which will affect the water-gas shift reaction (Reaction 4.4). However, in this work, this effect is neglected and it is

assumed that the generated CO<sub>2</sub> will increase only the amount of CO<sub>2</sub> in the raw gas and syn gas (i.e. not the amount of H<sub>2</sub>, H<sub>2</sub>O or CO).



The need of borate make-up is based on the demand in the gasifier and the losses to green liquor dregs as well as white liquor bleed, which are determined by mass balances for the units in the mill. This calculation is further described in Appendix D. Furthermore, the determination of mass and enthalpy for the flow of filtrated green liquor by iteration is described in Appendix A.

#### **4.4 Economic Evaluation**

The crystal water in borax pentahydrate is neglected in the mass and energy balances since the water addition from the borate is very small compared to the water flows in the mill. The make-up mass of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> is thus recalculated to the mass of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>•5H<sub>2</sub>O.

## 5. Results

### 5.1 Reference Mill

All the total mass flows calculated as described in Chapter 4 in this report are given in Figure 5.1 in the unit kg/ADt. The mass flows of CaO, Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> in the lime cycle are shown in Figure 5.2.

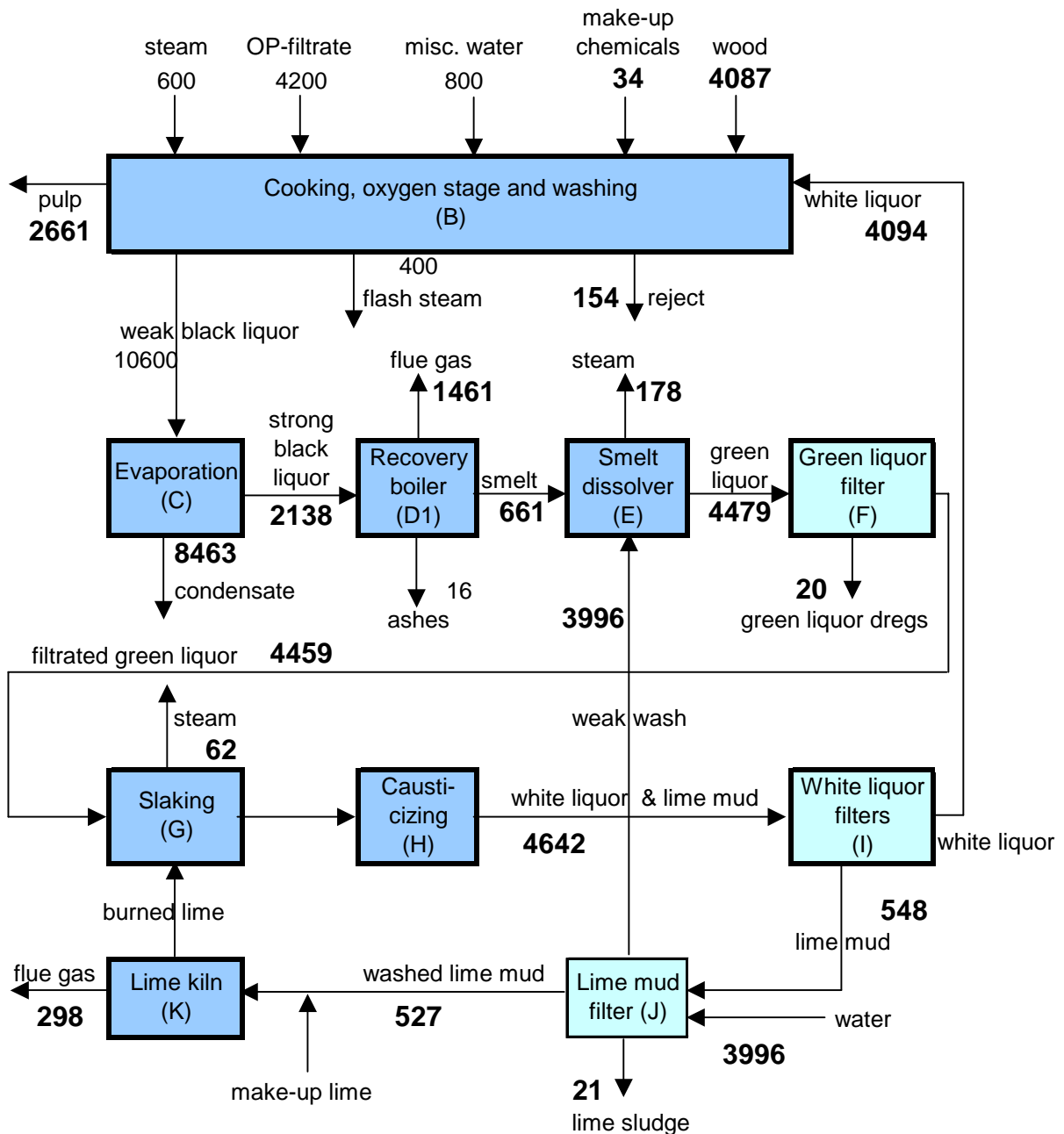


Figure 5.1. Total mass flows in the reference mill, [kg/ADt], (Calculated values are shown in bold)

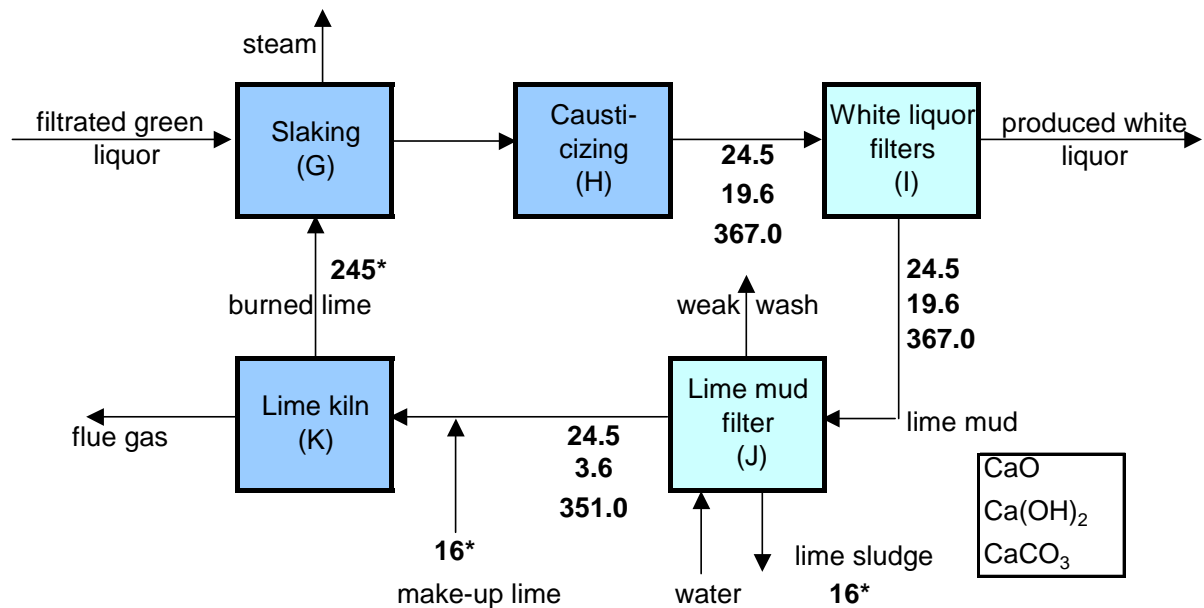


Figure 5.2. Mass flows of CaO, Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> in the lime cycle in the reference mill, [kg/ADt]

Note: \* (KAM Final Report 2003)

The concentrations in the produced white liquor are shown in Table 5.1, together with the concentrations in the filtrated green liquor. The NaOH in the green liquor originates from the weak wash.

Table 5.1. Concentration of the compounds in the white liquor and in the filtrated green liquor in the reference mill

Compound	White liquor			Filtrated green liquor		
	kg/ADt	g/kg	g/l	kg/ADt	g/kg	g/l
NaOH	293	72	85	10	2.2	2.5
Na <sub>2</sub> CO <sub>3</sub>	85	21	25	477	107	119
Na <sub>2</sub> S	156	38	45	161	36	40
Na <sub>2</sub> SO <sub>4</sub>	31	7.5	8.9	32	7.1	8.0

All enthalpies calculated for the streams in the reference mill are given in the unit GJ/ADt in Figure 5.3 and in the unit kJ/kg in Appendix E. Some enthalpy calculations are further described in Appendix F. No enthalpy calculations are needed for the streams entering or leaving the system via the fiber line since the energy demand of the cooking and oxygen delignification is defined in Table 3.1.

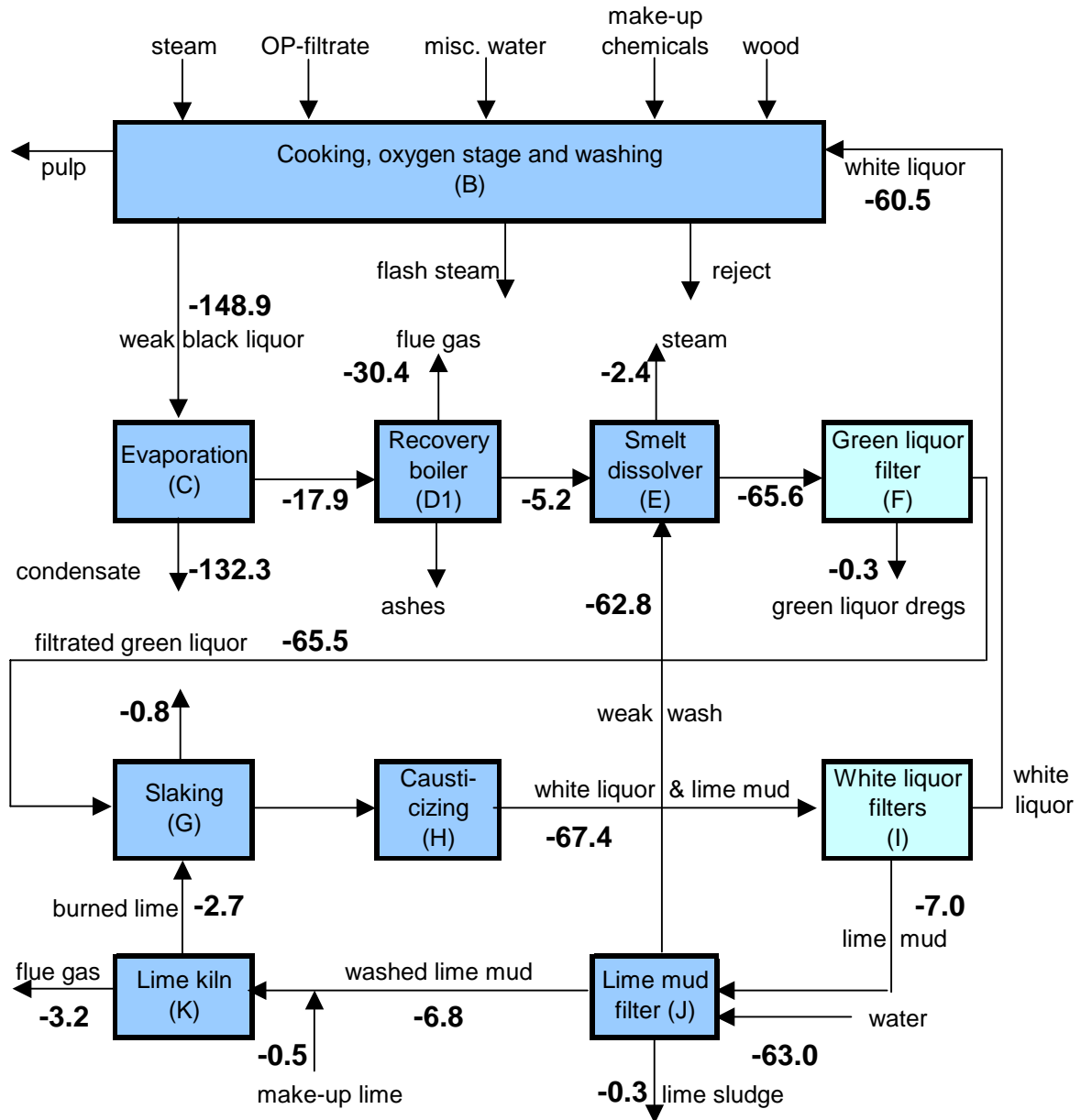


Figure 5.3. Calculated energy flows in the reference mill, [GJ/ADt]

The mill produces 61.6 kg/s of pulp, which is 5,300 ton per day. The steam demand in the delignification is 40.3 MW. The mass and energy balances for all the other units in the reference mill are shown in Table 5.2.

In evaporation 28.8 MW is lost to the surroundings. The energy loss in the green liquor filter is 3.3 MW. In the slaking the energy leaving with low temperature steam is 18.9 MW and in the smelt dissolver 54.7 MW. The lime kiln requires external fuel corresponding to 31.8 MW. The overall energy available in the chemical recovery of the reference mill is 410.0 MW, as illustrated in Table 5.3.

Table 5.2. Mass and energy balances for the unit operations in the reference mill

Stream name			Mass flow [kg/s]	Energy flow [MW]
<b>Evaporation</b>				
IN	Weak black liquor	BC	245.4 *	-3447.3
OUT	Strong black liquor	CD1	49.5	-414.1
	Condensate	CL	195.9	-3062.0
SUM			0.0	28.8
<b>Recovery boiler</b>				
IN	Strong black liquor	CD1	49.5	-414.1
OUT	Smelt	DE	15.3	-120.1
	Flue gas	D1L	33.8	-703.8
	Ashes	D1L	0.4 *	0
SUM			0.0	409.7
<b>Smelt dissolver</b>				
IN	Smelt	D1E	15.3	-120.1
	Weak wash	JE	92.5	-1454.3
OUT	Green liquor	EF	103.7	-1519.6
	Steam	EL	4.1	-54.7
SUM			0.0	0.0
<b>Green liquor filter</b>				
IN	Green liquor	EF	103.7	-1519.6
OUT	Filtrated green liquor	FG	103.2	-1516.8
	Green liquor dregs	FL	0.5	-6.1
SUM			0.0	3.3
<b>Slaking and causticizing</b>				
IN	Filtrated green liquor	FG	103.2	-1516.8
	Burned lime	KG	5.7	-63.4
OUT	White liquor and lime mud	HI	107.5	-1561.3
	Steam	GL	1.4	-18.9
SUM			0.0	0.0
<b>White liquor filters</b>				
IN	White liquor and lime mud	HI	107.5	-1561.3
OUT	Produced white liquor	IV	94.8	-1400.0
	Lime mud	B	12.7	-161.3
SUM			0.0	0.0
<b>Lime mud filter</b>				
IN	Lime mud	IJ	12.7	-161.3
	Water	AJ	92.5	-1457.5
OUT	Washed lime mud	JK	12.2	-158.2
	Weak wash	JD1	92.5	-1454.3
	Lime sludge	JL	0.5	-6.3
SUM			0.0	0.0
<b>Lime kiln</b>				
IN	Washed lime mud	JK	12.2	-158.2
	Make-up lime	AK	0.4 *	-11.2
OUT	Burned lime	KG	5.7 *	-63.4
	Flue gas	KA	6.9	-74.1
SUM			0.0	-31.8

Note: \* Based on data from KAM Final Report (2003) and Ledung et al. (2001)

*Table 5.3. Mass and energy balance for the recovery cycle in the reference mill*

<b>Stream name</b>			<b>Mass flow</b>	<b>Energy flow</b>
			<b>[kg/s]</b>	<b>[MW]</b>
IN	Weak black liquor	BC	245.4	-3447.3
	Make-up lime	AK	0.4	-11.2
	Water	AL	92.5	-1457.5
OUT	Condensate	CL	195.9	-3062.0
	Flue gas	D1L	33.8	-703.8
	Ashes	D1L	0.4	0.0
	Steam	EL	4.1	-54.7
	Green liquor dregs	FL	0.5	-6.1
	Steam	GL	1.4	-18.9
	White liquor	IB	94.8	-1400.0
	Lime sludge	JL	0.5	-6.3
	Flue gas	KL	6.9	-74.1
<b>SUM</b>			<b>0.0</b>	<b>410.0</b>

## **5.2 The Black Liquor Gasification Mill**

The calculated mass flows in the model with gasification are shown in Figure 5.4 in the unit kg/ADt. To absorb all the H<sub>2</sub>S in the gas 121.9 kg NaOH/ADt is needed. In the lime cycle 388.0 kg/ADt NaOH is produced in causticizing. The calculated mass flows of CaO, Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> are shown in Figure 5.5. The concentrations in the filtrated green liquor are listed in Table 5.4, together with the white liquor concentrations, which are the same as for the reference mill, except that Na<sub>2</sub>SO<sub>4</sub> is not present.

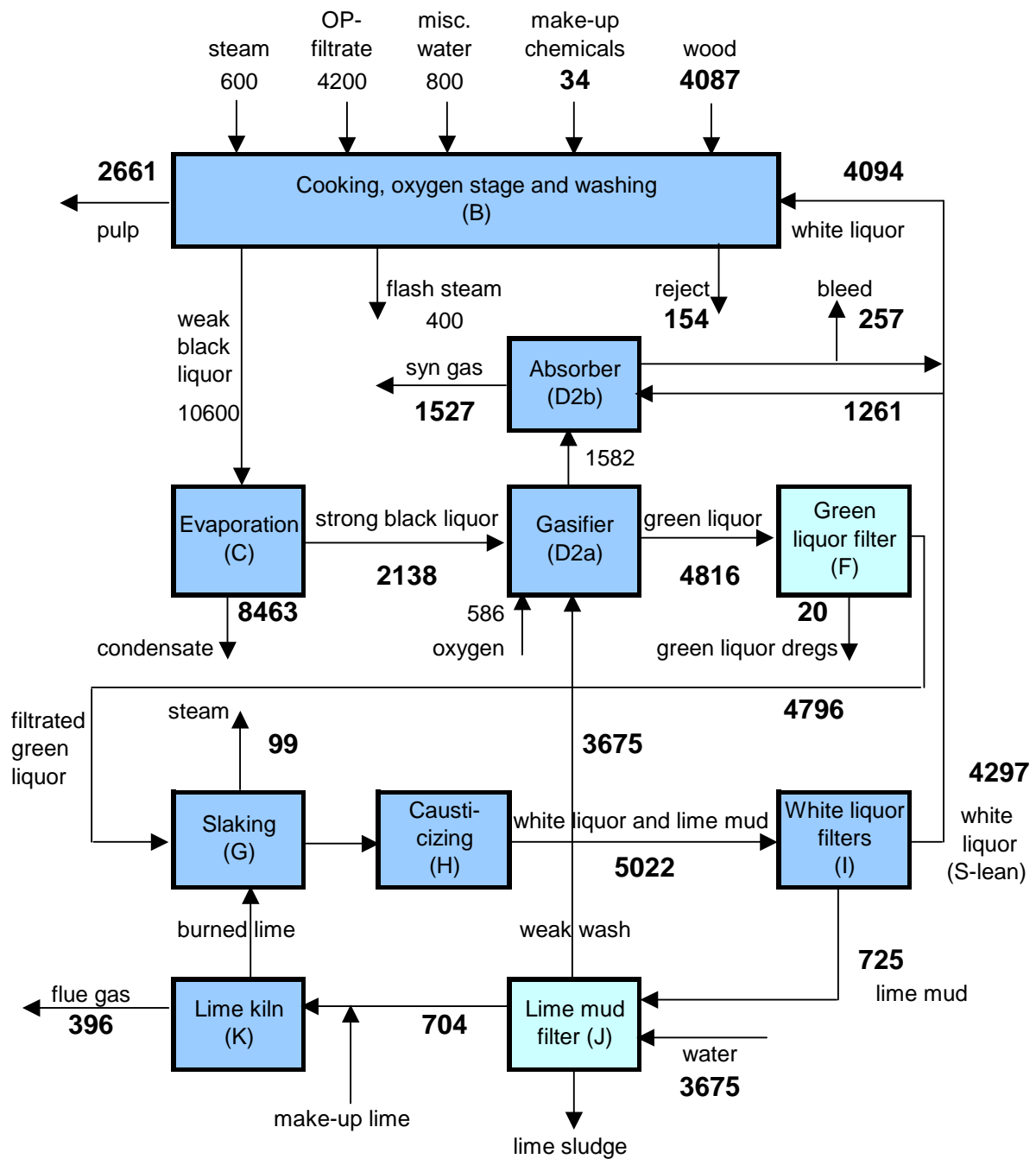


Figure 5.4. Total mass flows in the gasification model, [kg/ADt], (calculated values are shown in bold)



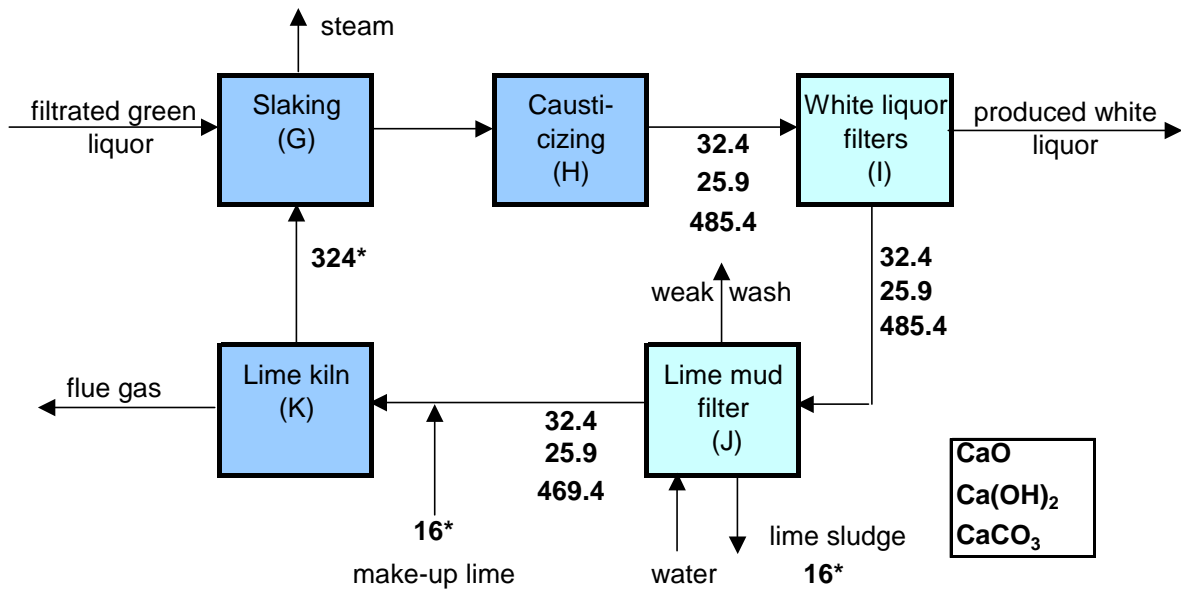


Figure 5.5. Mass flows of CaO, Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> in the lime cycle in the mill with gasification [kg/ADt]

Note: \* (KAM Final Report 2003)

Table 5.4. Concentration of the compounds in filtrated green liquor in the mill with gasification

Compound	White liquor			Filtrated green liquor		
	kg/ADt	g/kg	g/l	kg/ADt	[g/kg]	[g/l]
NaOH	293	72	85	45	9.3	10
Na <sub>2</sub> CO <sub>3</sub>	85	21	25	584	122	136
Na <sub>2</sub> S	156	38	45	84	18	20
Na <sub>2</sub> SO <sub>4</sub>	0.0	0.0	0.0	0.0	0.0	0.0

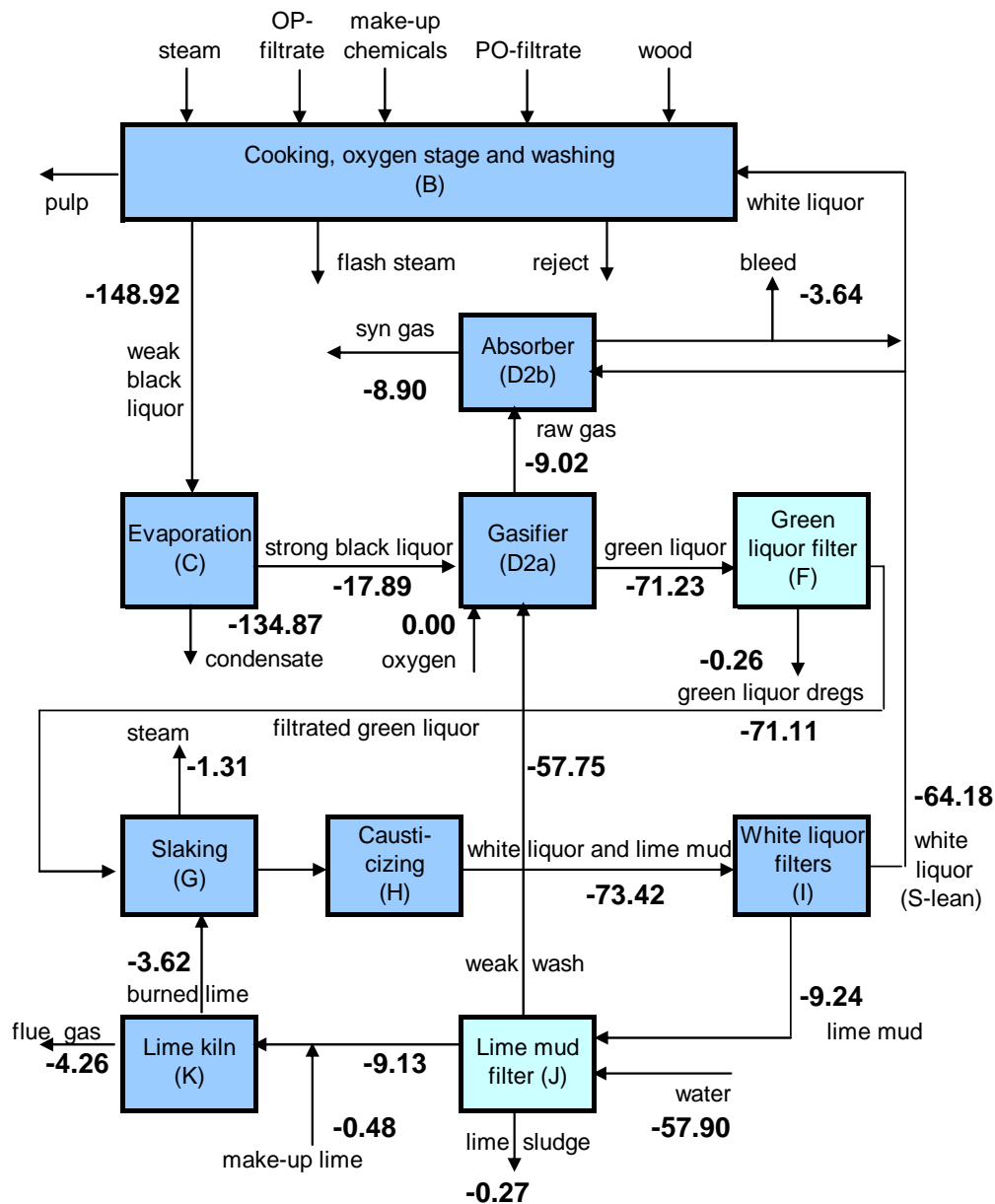


Figure 5.6. Calculated energy flows in the mill with gasification, [GJ/ADt]

The calculated enthalpies of the streams are shown in Figure 5.6 in the unit GJ/ADt and in Appendix E in the unit kJ/kg. The mass and energy balances for each unit are shown in Table 5.5. The mass balance as well as the energy demand for the delignification is by definition the same as in the reference mill. The gasifier releases 303 MW less than the recovery boiler in the reference mill, in both units the released energy is used to produce steam. This can be compared to the total lower heating value of the produced syn gas stream, which is 687 MW (calculated using the lower heating value of 19.4 MJ/kg from Ekbom et al. (2003)). The energy in the raw gas can be used to produce more steam and electricity, but would most likely be used to produce biofuels. The amount of low temperature steam formed in the slaking is high compared to the reference mill, even in relation to the amount of lime used. The energy loss in the green liquor filter is just slightly higher. Also the energy demand in the lime kiln is higher due to the higher lime load. A total mass and energy balance for the mill with gasification is shown in Table 5.6 and gives 99.0 MW. This is much lower than for the reference mill since less steam is produced in the same time as more energy is needed in the lime kiln.

Table 5.5. Mass and energy balances for the unit operations in the mill with gasification

			Mass flow	Energy flow
Stream name			[kg/s]	[MW]
<b>Evaporation</b>				
IN	Weak black liquor	BC	245.4	-3447.3
OUT	Strong black liquor	CD2	49.5	-414.1
	Condensate	CL	195.9	-3062.0
SUM			0.0	28.8
<b>Gasifier</b>				
IN	Strong black liquor	CD2a	49.5	-414.1
	Oxygen	AD2a	13.6	-0.1
	Weak wash	JD2a	85.1	-1336.7
OUT	Raw gas	D2aD2b	36.6	-208.8
	Green liquor	D2F	111.5	-1648.9
SUM			0.0	106.8
<b>Absorber</b>				
IN	Raw gas	D2aD2b	36.6	-208.8
	White liquor (S-lean)	I-	99.5	-1485.7
OUT	syn gas	D2bL	35.4	-205.9
	Produced white liquor	-B	94.8	-1404.3
	White liquor bleed	D2bL	5.9	-84.3
SUM			0	0
<b>Green liquor filter</b>				
IN	Green liquor	D2aF	111.5	-1648.9
OUT	Filtrated green liquor	FG	111.0	-1646.2
	Green liquor dregs	FL	0.5	-6.1
SUM			0.0	3.4
<b>Slaking and causticizing</b>				
IN	Filtrated green liquor	FG	111.0	-1646.2
	Burned lime	KG	7.5	-83.9
OUT	White liquor and lime mud	HI	116.2	-1699.6
	Steam	GL	2.3	-30.4
SUM			0.0	0.0
<b>White liquor filters</b>				
IN	White liquor and lime mud	HI	116.2	-1699.6
OUT	White liquor (S-lean)	I-	99.5	-1485.7
	Lime mud	IJ	16.8	-213.9
SUM			0.0	0.0
<b>Lime mud filter</b>				
IN	Lime mud	IJ	16.8	-213.9
	Water	AJ	85.1	-1340.3
OUT	Washed lime mud	JK	16.3	-211.3
	Weak wash	JD2a	85.1	-1336.7
	Lime sludge	JL	0.5	-6.3
SUM			0.0	0.0
<b>Lime kiln</b>				
IN	Washed lime mud	JK	16.3	-211.3
	Make-up lime	AK	0.4	-11.2
OUT	Burned lime	KG	7.5	-83.9
	Flue gas	KL	9.2	-98.5
SUM			0.0	-40.0

*Table 5.6. Mass and energy balance for the chemical recovery in the mill with gasification*

Stream name			Mass flow [kg/s]	Energy flow [MW]
IN	Weak black liquor	BC	245.4	-3447.3
	Oxygen	AD2	13.6	-0.1
	Make-up lime	AK	0.4	-11.2
	Water	AL	85.1	-1340.3
OUT	Produced white liquor	IB	94.8	-1404.3
	Syn gas	D2bL	35.4	-205.9
	Condensate	CL	195.9	-3062.0
	Bleed	D2bL	5.9	-84.3
	Green liquor dregs	FL	0.5	-6.1
	Steam	GL	2.3	-30.4
	Lime sludge	JL	0.5	-6.3
	Flue gas	KL	9.2	-98.5
	<b>SUM</b>			<b>0.0</b>

### **5.3 Mill with Black Liquor Gasification and Partial Borate Autocauticization**

The concentrations in the sulfur-rich white liquor entering the delignification are assumed to not change per volume but per mass when adding the borates. The new concentrations are shown in Table 5.7, together with the concentrations in the filtrated green liquor.

*Table 5.7. Mass concentrations in the white liquor before delignification and in filtrated green liquor in the mill with gasification and partial autocauticization*

Compound	White liquor			Filtrated green liquor		
	kg/ADt	g/kg	g/l	kg/ADt	g/kg	g/l
NaOH	293	70	85	131	28	31
Na <sub>2</sub> CO <sub>3</sub>	85	20	25	458	96	109
Na <sub>2</sub> S	156	37	45	81	18	20
Na <sub>2</sub> SO <sub>4</sub>	0.0	0.0	0.0	0.0	0.0	0.0
NaBO <sub>2</sub>	87	21	24	94	20	22
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	3.9	0.9	1.1	4.3	0.9	1.0

The calculated total mass flows are given in kg/ADt in Figure 5.7. The mass flows in the lime cycle are lower in the mill with partial borate autocauticization than in the mill with only gasification, due to the lower throughput of lime. The mass flows of CaO, Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> are the same as for the reference mill (Figure 5.2).

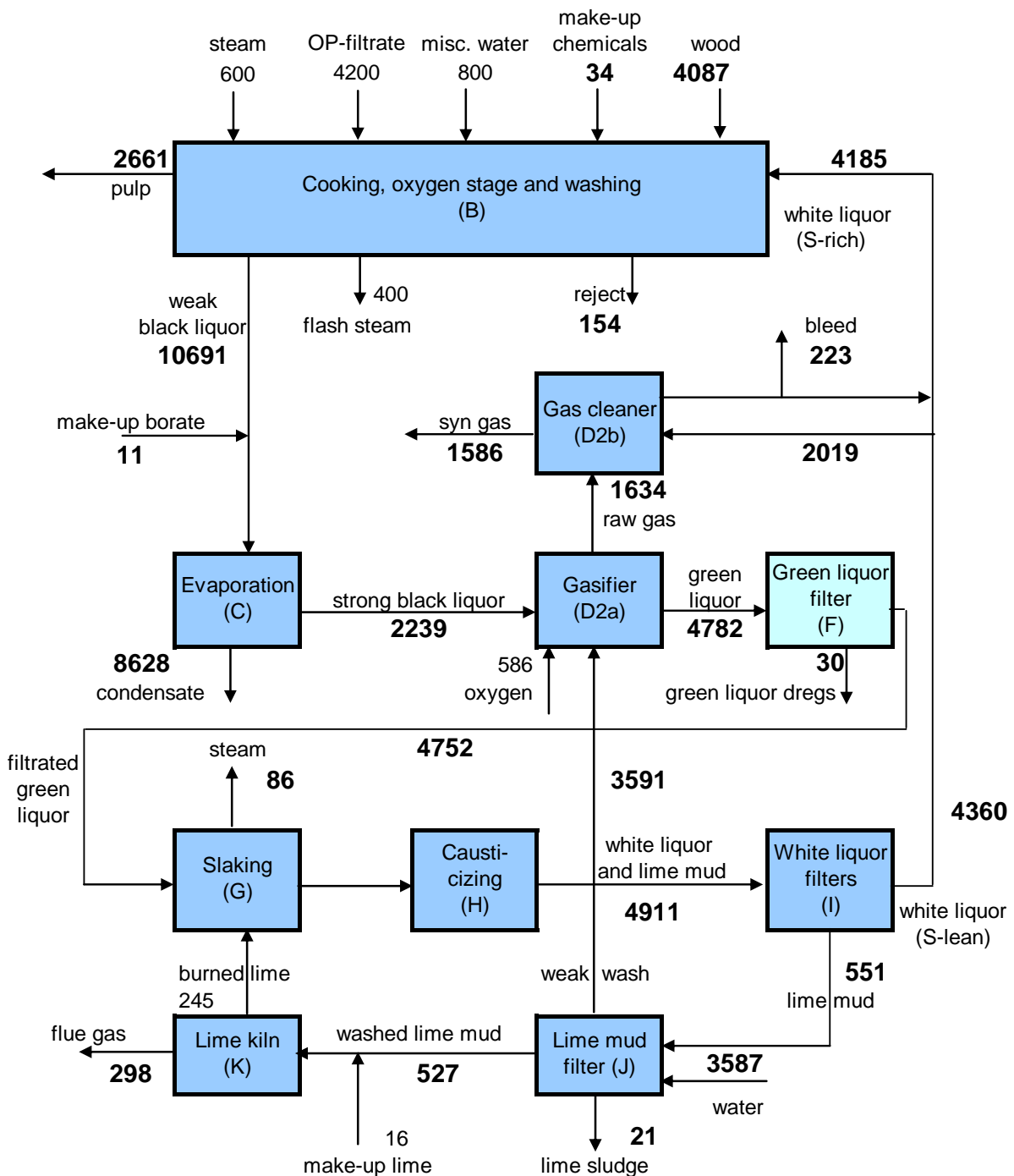


Figure 5.7. Calculated total mass flows in the mill with gasification and partial autocausticization, [kg/ADt], (calculated values are shown in bold)

The mass flows of the borates are given in the unit kg/ADt in Figure 5.8 and the raw gas composition is shown in Table 5.8. The autocausticization reactions increase the mass flow of CO<sub>2</sub> in the raw gas and syn gas with 8%.

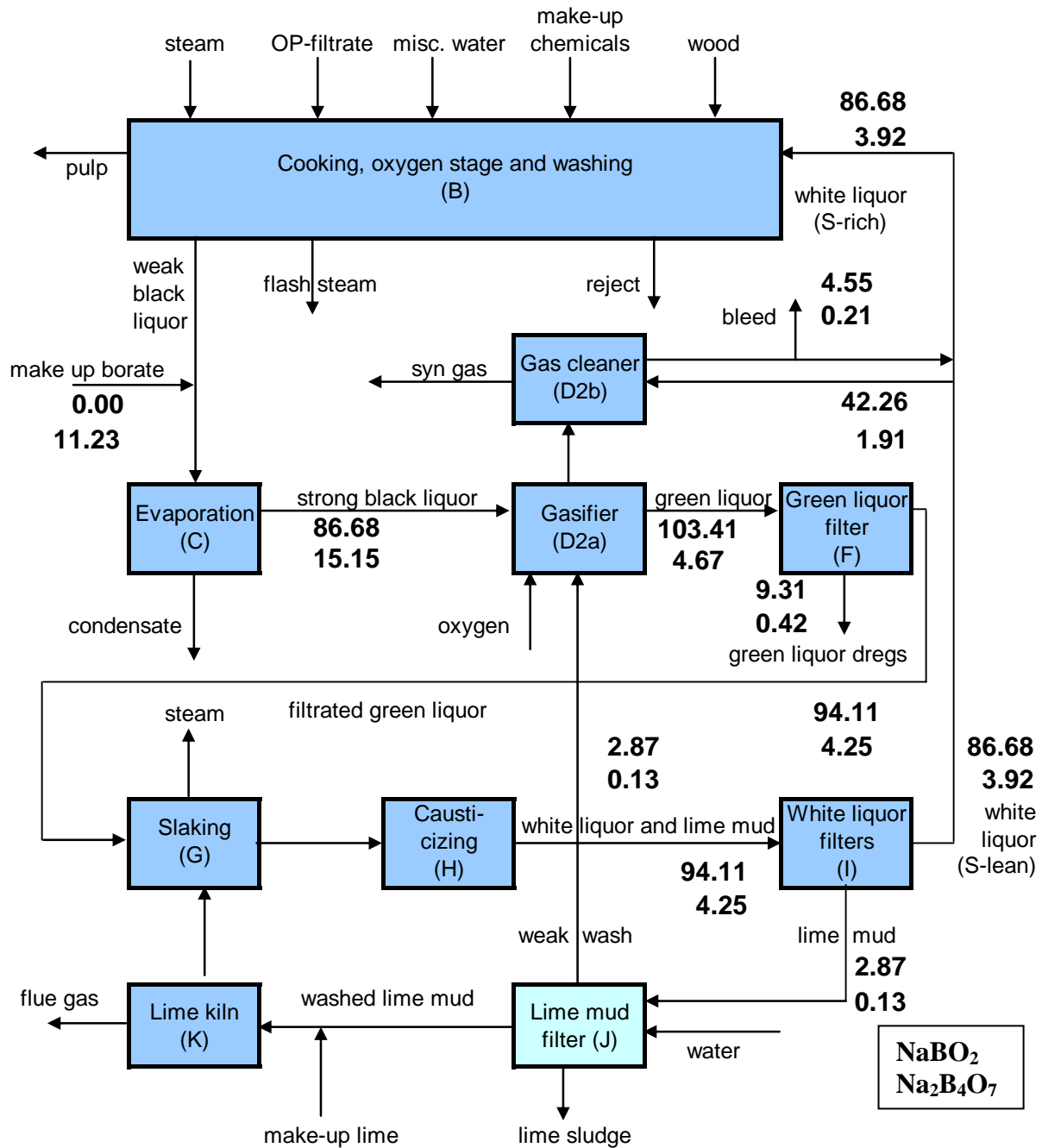


Figure 5.8. Mass flows of sodium borates in the mill with gasification and partial autocausticization, [kg/ADt] (calculated values are shown in bold)

Table 5.8. Composition of raw gas in the mill with gasification and partial autocausticization

	kg/ADt	Weight - %
H <sub>2</sub>	61	3.7
CO	823	50.4
CO <sub>2</sub>	698.9	42.8
H <sub>2</sub> S	43	2.7

The calculated enthalpies of the flows with borates are shown in Figure 5.9 in the unit GJ/ADt and in the unit kJ/kg in Appendix E. Some enthalpy calculations are further described in Appendix F.

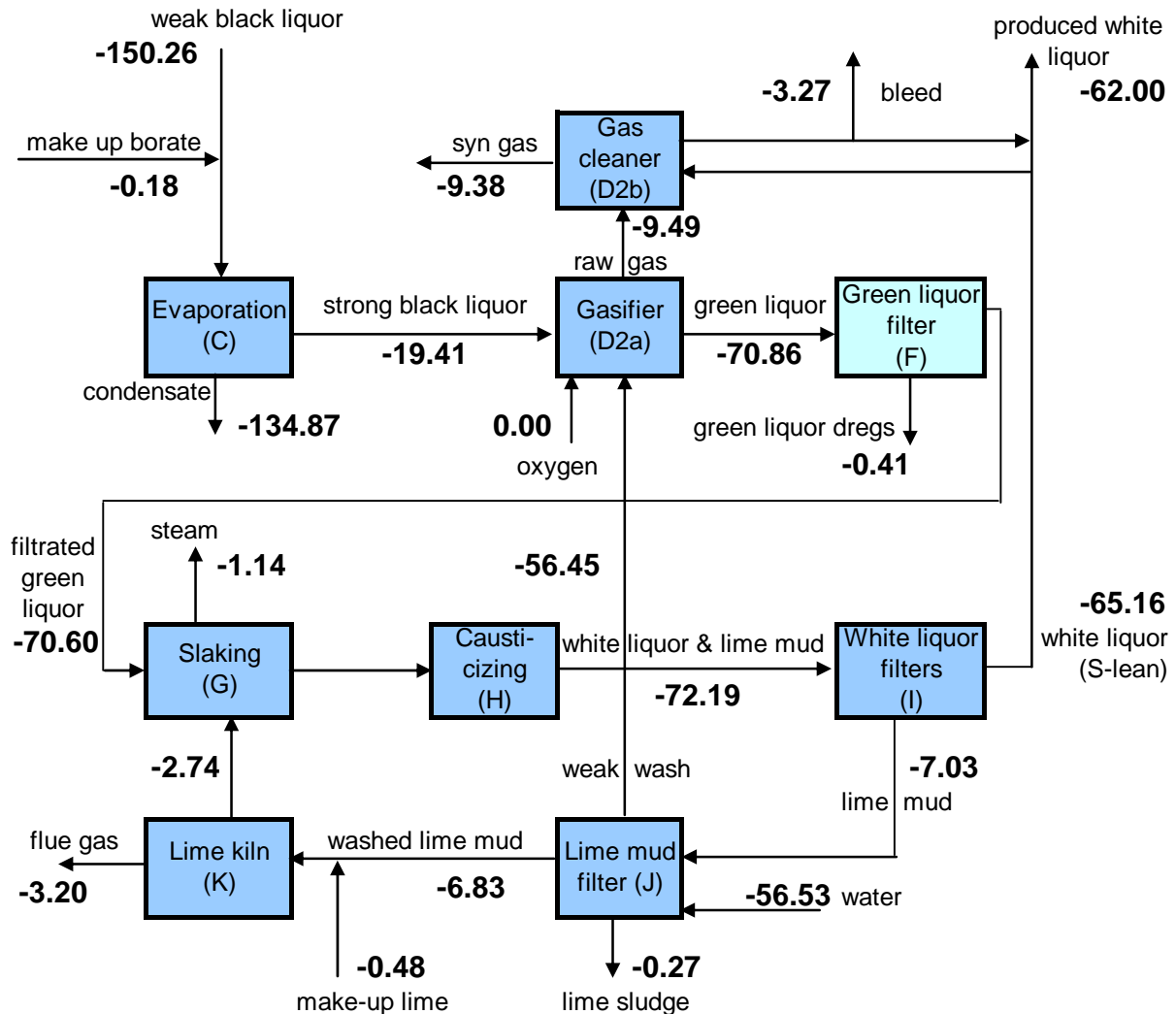


Figure 5.9. Calculated enthalpies of the flows in the mill with gasification and partial autocausticization, [GJ/ADt]

The extra load in the delignification gives a slightly higher energy demand, 40.4 MW. Mass and energy balances for the recovery units in the mill with borates are shown in Table 5.9.

*Table 5.9. Mass and energy balances for the unit operations in the mill with gasification and partial autocausticization*

Stream name			Mass [kg/s]	Energy [MW]
<b>Evaporation</b>				
IN	Weak black liquor	BC	247.5	-3478.2
	Make-up borate	AC	0.3	-4.2
OUT	Strong black liquor	CD2a	51.8	-449.3
	Condensate	CL	195.9	-3062.0
SUM			0.0	28.9
<b>Gasifier</b>				
IN	Strong black liquor	CD2a	51.8	-449.3
	Oxygen	AD2a	13.6	-0.1
	Weak wash	JD2a	83.1	-1306.8
OUT	Raw gas	D2a	37.8	-219.6
	Green liquor	D2aF	110.7	-1640.2
SUM			0.0	103.7
<b>Absorber</b>				
IN	Raw gas	D2aD2b	37.8	-219.6
	White liquor (S-lean)	I-	100.9	-1508.4
OUT	syn gas	D2bL	36.7	-217.0
	Produced white liquor	-B	96.9	-1435.2
	White liquor bleed	D2bL	5.2	-75.8
SUM			0	0
<b>Green liquor filter</b>				
IN	Green liquor	D2aF	110.7	-1640.2
OUT	Filtrated green liquor	FG	110.0	-1634.2
	Green liquor dregs	FL	0.7	-9.5
SUM			0.0	3.5
<b>Slaking and causticizing</b>				
IN	Filtrated green liquor	FG	110.0	-1634.2
	Burned lime	KG	5.7	-63.4
OUT	White liquor and lime mud	HI	113.7	-1671.1
	Steam	GL	2.0	-26.5
SUM			0.0	0.0
<b>White liquor filters</b>				
IN	White liquor and lime mud	HI	113.7	-1671.1
OUT	White liquor (S-lean)	I-	100.9	-1508.4
	Lime mud	IJ	12.8	-162.8
SUM			0.0	0.0
<b>Lime mud filter</b>				
IN	Lime mud	IJ	12.8	-162.8
	Water	AJ	83.0	-1308.5
OUT	Washed lime mud	JK	12.2	-158.2
	Weak wash	JD2a	83.1	-1306.8
	Lime sludge	JL	0.5	-6.3
SUM			0.0	0.0
<b>Lime kiln</b>				
IN	Washed lime mud	JK	12.2	-158.2
	Make-up lime	AK	0.4	-11.2
OUT	Burned lime	KG	5.7	-63.4
	Flue gas	KL	6.9	-74.1
SUM			0.0	-31.8



The lime kiln has the same energy demand as in the reference mill since the same amount of lime is used. The presence of borates decreases the energy output in the gasifier. The energy loss in the slaking is also decreased but the energy loss in evaporators and green liquor filter is slightly increased. In Table 5.10 a mass and energy balance is shown for the whole chemical recovery. The net energy release is 104.2 MW, which is slightly higher (5%) than in the mill with gasification, due to the lower energy demand in the lime kiln.

*Table 5.10. Mass and energy balance for the chemical recovery in the mill with gasification and partial autocausticization*

<b>Stream name</b>		<b>Mass flow</b>		<b>Energy flow</b>
			<b>[kg/s]</b>	<b>[MW]</b>
IN	Weak black liquor	BC	247.5	-3478.2
	Make-up borate	AC	0.3	-4.2
	Oxygen	AD2	13.6	-0.1
	Make-up lime	AK	0.4	-11.2
	Water	AL	83.0	-1308.5
OUT	Condensate	CL	195.9	-3062.0
	Syn gas	D2bL	36.7	-217.0
	Bleed	D2bL	5.2	-75.8
	Green liquor dregs	FL	0.7	-9.5
	Steam	GL	2.0	-26.5
	Produced white liquor	IB	96.9	-1435.2
	Lime sludge	JL	0.5	-6.3
	Flue gas	KL	6.9	-74.1
	<b>SUM</b>		<b>0.0</b>	<b>104.2</b>

## **5.4 Economic evaluation**

The costs for a new lime kiln are compared to the cost for borate make-up when using the lime kiln from the reference mill and exchanging a recovery boiler for a gasifier. Within five years the investment in a larger lime kiln has paid off in the savings on borax. A third of the borate losses exit the mill with the white liquor bleed. White liquor is bleed out of the system in order to keep the Na/S balance. If the balance can be kept in another fashion, the borate loss will be lower. Without this part of the losses it would take almost 7 years before the cumulative cost of the borates were at the level of the cost of the larger lime kiln.

## 6. Discussion

The results show that the recovery cycle releases less net heat when exchanging a recovery boiler for a black liquor gasifier. This is partly due to the higher energy demand in the lime kiln but mainly because the produced syn gas holds a significant amount of chemical energy. The syn gas can be used to produce electricity or products with high energy content, i.e. DME. However, the lower heating value (LHV) for the syn gas is higher than the heat loss from the gasifier to steam production compared to a recovery boiler, therefore, the energy efficiency is higher for the gasification case than for the conventional case if the use of the syn gas is taken into account. This is not clearly visible in the energy balances of this work since the syn gas leaves the system. In this work, the results are presented mainly as decreased steam production when the black liquor is partially combusted.

If the pulp mill is integrated with a paper mill the steam produced in the recovery boiler is generally used in the paper production. If all the syn gas, or a product from it, is sold the paper mill has to be compensated with another energy source than the black liquor.

As shown in Table 6.1, all energy needed for the autocausticizing reactions is released when the smelt is dissolved. All the released energy is recovered since the gasifier does not purge steam during dissolving. However, the temperature elevation demands some energy, resulting in lower energy release in the gasifier in the mill with partial autocausticization. In the conventional cycle, 40% of the energy absorbed during calcination is released in the slaking and causticizing reactions. The released energy is used to heat the liquor to its boiling point and to vaporize some water, which then leaves the system. In both processes, energy is required at high temperature and released at low temperature but the reactions with borates are more endothermic respective exothermic than the lime reactions. However, the borates are dissolved in the quench, at a pressure of 30 bar, which makes the energy recovery somewhat more effective. It should be noted that the heat of reaction for dissolving the borates in the quench is not available at the relevant temperature in the quench (i.e. 220°C), therefore, the value in Table 6.1 is at 100°C which is the best available approximation.

*Table 6.1. The heats of reaction and temperatures for the key-reactions (Richards et al. 2002)*

<b>Process/Reaction</b>	<b>Temperature °C</b>	<b>Heat of reaction kJ/mol NaOH</b>
<b>Lime</b>		
Calcination	850	+85
Slaking	100	-32.5
Causticizing	100	-2.1
<b>Borate</b>		
Causticizing, NaBO <sub>2</sub>	950	+125.3 <sup>1</sup>
Dissolving	100	-125.3

*Note:* 1. Based on data from Backman (2006, oral)

The recovery cycle with gasification and partial autocausticization releases more net heat (5%) than the recovery cycle with gasification and conventional causticizing (Table 5.6 and 5.10). The main reason is the lower energy demand in the lime kiln because of the decreased lime load. The autocausticizing reactions give a lower release of heat in the gasifier, but that heat loss is only about a third of the energy saved in the lime kiln.

By simplification of the model with autocausticization, the temperature elevation of the additional load of borates does not affect the temperature in the gasifier, compared to the model with conventional causticization. In the model, only the release of heat is affected. In practice the temperature would most likely decrease. To maintain the temperature, more oxygen would be needed. This would lead to more combustion and less chemical energy in the syn gas, rather than less energy to the cooling water. Thus the value of the produced syn gas would decrease. On the other hand, external energy is saved in the lime cycle.

The reference mill generates low temperature energy streams in the form of steam during smelt dissolving and slaking and in gaseous form during calcination in the lime kiln. The low temperature streams are generally used for production of warm water with a temperature of 60-100°C. No low temperature stream is generated during smelt dissolving in the gasifier. As illustrated in Table 6.2, this is compensated in the mill with conventional causticization by the higher amount of flue gases from the lime kiln. The mill with gasification and partial autocausticization has the same lime load as the reference mill and therefore gives less energy in the form of low temperature streams than the other mills.

*Table 6.2. Generation of low temperature energy streams, energy in MW ( $H-H_{298K}$ )*

<b>Stream</b>		<b>Reference mill</b>	<b>The gasification mill</b>	<b>The gasification mill with autocausticization</b>
Steam	EL	0.57	-	-
Steam	GL	0.20	0.32	0.28
Flue gas	KL	1.69	2.25	1.69
<b>SUM</b>		<b>2.46</b>	<b>2.57</b>	<b>1.97</b>

It has been stated that the dead load of borates decreases the overall energy efficiency (Chapter 2.2.2). The heat losses in the digester, evaporators and green liquor filter become somewhat higher when adding borates but in the gasifier, where the autocausticization reactions occur, the energy loss due to the borate load is small. This is of course dependent on the assumptions of no heat losses in some units and of the reaction efficiency.

In a conventional mill, electrostatic precipitator (ESP) dust is purged from the recovery boiler to control the sulfur level in the white liquor. The dust also contains sodium and to recover that loss, NaOH is used as make-up to the delignification. The same kind of purge can not be made in a gasifier but the control can be made by the degree of absorption of sulfur from the gas. In a mill with gasification the need of make-up for sodium will thus be much smaller. There might even be necessary to exchange the  $\text{Na}_3\text{H}(\text{SO}_4)_2$ , added in the tall oil production, to e.g.  $\text{H}_2\text{SO}_4$  to not obtain too much sodium in the process. In practice, the separation of sulfur and sodium in the gasifier gives a possibility for advanced pulping methods (see Chapter 2.2.1). In this work, the comparison between the different mill models was made based on the assumption that the same white liquor was produced in all the mill models. Therefore white liquor was bled off to also purge sodium.

The alternative with partial autocausticization does not show a great advantage, when comparing the different costs for partial autocausticizing and conventional causticizing for a gasification system. It takes only five years for the investment of a larger lime kiln to repay the costs for the alternative make-up borate. These results also depend on the causticizing efficiency as well as on the amount of borate loss in the process. If no borates are lost with the white liquor bleed the payback time is extended with two years, which makes the alternative of borate autocausticization somewhat more attractive. If the pulp yield is enhanced by the

presence of sodium borates, as proposed in the literature, the product profit will be higher for the alternative of autocausticizing. This would also prolong the pay-back time for a new lime kiln. However, in this comparison the cost for the additional fuel demand in a larger lime kiln is not included.

The enthalpy of the strong black liquor is calculated in two ways. Determination by a mill model where the heat released in the gasifier is known (Appendix B), which is used in the energy balances, gives a lower enthalpy than determination from the heating value (Appendix C). An energy balance using the latter enthalpy would give 17% higher release of heat from the gasifier (without borate autocausticization). The former-mentioned determination is chosen as more accurate since the released heat should agree to other values known for the gasifier.

The results of the calculations for the mill with partial autocausticization are strongly dependent on the reaction efficiency of the autocausticizing reactions. However, the experimental work carried out in the BLG Program shows that very little or no autocausticization is taking place in a pressurized high temperature gasifier.

## 7. Conclusions

This thesis work shows that black liquor gasification under high temperature and pressure is more energy efficient than conventional recovery of black liquor. When a recovery boiler is replaced by a gasifier the steam production decreases. However, the lower heating value (LHV) of the produced syn gas is higher than the energy decrease to the steam production. Also, the syn gas is a more attractive energy form than the steam.

Partial borate auto-causticization is shown to be inferior to the conventional causticization with lime. Using partial borate auto-causticizing to compensate for the extra causticizing demand, caused by replacement of a recovery boiler for a gasifier, gives a lower energy demand. However, the chemical costs for the partial auto-causticization is high, even at high reaction efficiency.

## 8. Nomenclature

Symbol	Unit	Explanation
$c_{\text{pulp}}^{\text{BL}}$	%	Bleached pulp concentration
EA	%NaOH	Alkali on wood
$M_X$	g/mol	Molar mass of compound X
$m^{\text{XY}}$	kg/ADt	Total mass flow from unit X to unit Y
$m_Z^{\text{XY}}$	kg/ADt	Mass flow of compound Z from unit X to unit Y
$m_{\text{NaOH react}}^{\text{D2b}}$	kg/ADt	Mass of NaOH produced in the autocausticizing reaction
$m_{\text{NaOH react}}^{\text{G+H}}$	kg/ADt	Mass of NaOH produced in the causticizing reaction
$\text{Na}_2\text{S}$	g/l as NaOH	Concentration of $\text{Na}_2\text{S}$
$\text{Na}_2\text{SO}_4$	g/l as NaOH	Concentration of $\text{Na}_2\text{SO}_4$
NaOH	g/l	Concentration of NaOH
$H^{\text{XY}}$	kJ/ADt	Enthalpy of total stream from unit X to unit Y
$h_{\text{H}_2\text{O}}^{\text{XK}}$	kJ/kg	Enthalpy of water at X Kelvin
$x_{\text{active lime}}$	-	Fraction of lime that reacts in slaking
$\eta_{\text{digester}}$	-	Pulp yield in digester (screened)
$\eta_{\text{OO}}$	-	Yield in oxygen stage and washing

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# Appendices

## Appendix A

### Mass and Energy Balance for Slaking and Causticizing

Mass and energy balances for slaking and causticizing have to be done simultaneously. The mass balance is shown in Equation A.1. The masses of both filtrated green liquor and evaporated water are unknown. The energy balance for slaking and causticizing is given in Equation A.2. The total energy of burned lime and of white liquor and lime mud are both known, as well as the enthalpy (per mass) of steam. If the enthalpy of the filtrated green liquor would also be known, the mass of liquor could be calculated by putting Equations A.1 and A.2 together (Equation A.3). The flows of soluble compounds with filtrated green liquor are shown in Table 5.1, 5.4 and 5.7 for the respective mill models. The concentrations of the compounds could then be calculated and from that the enthalpy could be determined.

$$m^{FG} + m^{KG} = m^{GL} + m^{HI} \quad [A.1]$$

$$m^{FG} \cdot h_{363K}^{FG} + H^{KG} = m^{GL} \cdot h_{373K}^{H_2O} + H^{HI} \quad [A.2]$$

$$m^{FG} = \frac{(m^{KG} - m^{HI})h_{373K}^{H_2O} + H^{HI} - H^{KG}}{h_{363K}^{FG} - h_{373K}^{H_2O}} \quad [A.3]$$

Iteration is done by choosing an enthalpy of the filtrated green liquor and checking it as described above. The mass of steam evaporated can then be calculated by Equation A.4 and its enthalpy by Equation A.5.

$$m^{GL} = m^{FG} + m^{KG} - m^{HI} \quad [A.4]$$

$$H^{GL} = m^{GL} \cdot h_{373K}^{H_2O} \quad [A.5]$$

### The Reference Mill

Equation A.3 is rewritten with numbers:

$$m^{FG} = \frac{(245 - 4,642.4) \cdot (-13,282) - 67,447,189 - (-2,739,312)}{h_{363K}^{FG} - (-13,282)}$$

Starting with an enthalpy of filtrated green liquor at  $-14,700$  kJ/kg, only two iterations are needed and the enthalpy is determined to  $-14,695$  kJ/kg and the mass flow of filtrated green liquor is determined to  $4,459$  kg/ADt. The calculated values are shown in Table A.1.

*Table A.1. Iterated values for the enthalpy of filtrated green liquor in the reference mill*

<b>Iteration</b>	<b>1</b>	<b>2</b>	<b>unit</b>
Chosen enthalpy	-14700	-14695	kJ/kg
Filtrated green liquor	4444	4459	kg
Concentration			g/kg
NaOH	2.21	2.20	
Na <sub>2</sub> CO <sub>3</sub>	107.30	106.94	
Na <sub>2</sub> S	36.31	36.19	
Na <sub>2</sub> SO <sub>4</sub>	7.16	7.14	
Calculated enthalpy	-14691	-14694	kJ/kg
Difference	-0.06	-0.01	%

The mass and enthalpy of the steam flow are calculated by Equations A.4 and A.5:

$$m^{GL} = 4,458.9 + 245 - 4,642.4 = 61.6 \text{ kg/ADt}$$

$$H^{GL} = 61.55 \cdot (-13,282) = -817,507 \text{ kJ/ADt}$$

### **Mill with Black Liquor Gasification**

Equation A.3 is rewritten with numbers:

$$m^{FG} = \frac{(324 - 5,021.5) \cdot (-13,282) - 73,422,696 - (-3,622,601)}{h_{363K}^{FG} - (-13,282)}$$

Starting with an enthalpy of filtrated green liquor at  $-14,830 \text{ kJ/kg}$ , three iterations are needed and the enthalpy is determined to  $-14,826.4 \text{ kJ/kg}$  and the mass flow of the filtrated green liquor is determined to  $4,796.5 \text{ kg/ADt}$ . The calculated values are shown in Table A.2.

*Table A.2. Iterated values for the enthalpy of filtrated green liquor in the mill with gasification*

<b>Iteration</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>unit</b>
Chosen enthalpy	-14830.0	-14826.9	-14826.4	kJ/kg
Filtrated green liquor	4785.4	4795.1	4796.5	kg
Concentration				g/kg
NaOH	9.36	9.34	9.3	
Na <sub>2</sub> CO <sub>3</sub>	122.12	121.87	121.8	
Na <sub>2</sub> S	17.65	17.62	17.6	
Na <sub>2</sub> SO <sub>4</sub>	0.00	0.00	0.0	
Calculated enthalpy	-14823.7	-14826.0	-14826.5	kJ/kg
Difference	-0.04	-0.01	0.00	%

The mass and enthalpy of the flow of vaporized steam are calculated by Equations A.4 and A.5:

$$m^{GL} = 4,796.5 + 324 - 5,021.5 = 98.9 \text{ kg/ADt}$$

$$H^{GL} = 98.9 \cdot (-13,282) = -1,314,155 \text{ kJ/ADt}$$

## Mill with Gasification and Borate Autocausticization

Equation A.3 is rewritten to also include the mass and enthalpy of the borates in Equation A.6, which is then rewritten in numbers.

$$m^{FG} = \frac{(m^{KG} - m^{HI}) \cdot h_{373K}^{H_2O} - (m_{NaBO_2}^{FG} + m_{Na_2B_4O_7}^{FG}) \cdot h_{363K}^{FG}}{h_{363K}^{FG} - h_{373K}^{H_2O}} + \frac{H^{HI} - [H^{KG} + H_{NaBO_2}^{FG} + H_{Na_2B_4O_7}^{FG}]}{h_{363K}^{FG} - h_{373K}^{H_2O}} \quad [A.6]$$

$$m^{FG} = \frac{(245 - 4,910.9) \cdot (-13,282) + (94.1 + 4.3) \cdot h_{363K}^{FG}}{h_{363K}^{FG} - (-13,282)} + \frac{-72,193,365 - [-2,739,312 - 1,380,049 - 70,012]}{h_{363K}^{FG} - (-13,282)}$$

The iteration starts with the enthalpy of  $-14,860 \text{ kJ/kg}$  for the filtrated green liquor and is shown in Table A.3. Two iterations are needed and the resulting enthalpy is  $14,858.8 \text{ kJ/kg}$ . The mass flow of the filtrated green liquor is calculated to  $4,752.0 \text{ kg/ADt}$ , including the load of borates.

Table A.3. *Iterated values for the enthalpy of filtrated green liquor in the mill with gasification and autocausticization*

Iteration	1	2	unit
Chosen enthalpy	-14860.0	-14858.8	kJ/kg
Filtrated green liquor	4748.5	4752.0	kg/ADt
Concentration			g/kg
NaOH	28.19	28.17	
Na <sub>2</sub> CO <sub>3</sub>	98.50	98.43	
Na <sub>2</sub> S	17.99	17.98	
Na <sub>2</sub> SO <sub>4</sub>	0.00	0.00	
Calculated enthalpy	-14857.6	-14858.1	kJ/kg
Difference	-0.02	0.00	%

The mass flow of vaporized steam and the enthalpy leaving with it is calculated using Equation A.4 and A.5 respectively:

$$m^{GL} = 4,752.0 + 245 - 4,910.9 = 86.1 \text{ kg/ADt}$$

$$H^{GL} = 86.1 \cdot (-13,282) = -1,143,640 \text{ kJ/ADt}$$



## Appendix B

### ***Enthalpy Calculation for Strong Black Liquor with New Model***

If the temperature of the green liquor is 87°C and that of the filtrated green liquor is 80°C the energy generated from the gasifier is 4.9 GJ/ADt (Berglin et al. 1999). A new gasification model is made with the lower green liquor temperatures to determine the enthalpy of the strong black liquor. All other temperatures are the same as in the ordinary model.

The mass and energy balance for the slaking and causticizing is determined by iteration as in Appendix A. The iteration is started with an enthalpy of -14,850 kJ/kg and the calculated values in the procedure are shown in Table B.1. The enthalpy flow of the filtrated green liquor is shown to be -14,851.1 kJ/kg. The flow of filtrated green liquor is 4,724.3 kg/ADt and the evaporated water is 23.5 kg/ADt (Equation A.4). The liquor concentration is given in Table B.2.

*Table B.1. Iterated values for the enthalpy of filtrated green liquor at 80°C in the mill with gasification*

<b>Iteration</b>	<b>1</b>	<b>2</b>	<b>unit</b>
Chosen enthalpy	-14850.0	-14851.1	kJ/kg
Filtrated green liquor Concentration	4724.3	4724.3	kg g/kg
NaOH	9.48	9.48	
Na <sub>2</sub> CO <sub>3</sub>	123.70	123.78	
Na <sub>2</sub> S	17.88	17.89	
Na <sub>2</sub> SO <sub>4</sub>	0.00	0.00	
Calculated enthalpy	-14852.2	-14851.8	kJ/kg
Difference	0.01	0.00	%

*Table B.2. Filtrated green liquor concentration at 80°C in the mill with gasification*

<b>Compound</b>	<b>g/l</b>
NaOH	10.66
Na <sub>2</sub> CO <sub>3</sub>	139.16
Na <sub>2</sub> S	20.12
Na <sub>2</sub> SO <sub>4</sub>	0.00

The green liquor flow is determined to 4,741.0 kg/ADt by mass balance for the green liquor filter. The concentrations of soluble compounds are not changed over the green liquor filter but the green liquor also contains the solids ending up in the green liquor dregs. The enthalpy of the green liquor is calculated in Table B.3.

*Table B.3. Enthalpy calculation for green liquor at 87°C*

<b>Compound</b>	<b>kg/ADt</b>	<b>Enthalpy [kJ/ADt]</b>
Liquor	4,731.0	-70,137,369
CaCO <sub>3</sub>	7.2	-86,521
Na <sub>2</sub> CO <sub>3</sub>	1.2	-12,721
MgCO <sub>3</sub>	1.2	-15,521
Na <sub>2</sub> S	0.4	-1,850
<b>Total</b>	<b>4741.0</b>	<b>-70,253,982</b>

All other flows around the gasifier are similar as in the ordinary model with gasification. An energy balance for the gasifier gives the total enthalpy of the strong black liquor.

$$\begin{aligned}
 H^{CD2a} &= E_{D2a} + H^{D2aD2b} + H^{D2aF} - (H^{AD2a} + H^{JD2a}) = \\
 &= 4,900,000 - 9,021,522 - 70,253,982 - (-2,650 - 56,482,916) = -1,7889,937 \text{ kJ/ADt} \quad [B.1]
 \end{aligned}$$

The enthalpy of the strong black liquor is thus  $-8,370$  kJ/kg liquor. This value is used in all mill models in this report.

## References

Berglin. N., Eriksson. H. and Berntsson. T. (1999). Performance Evaluation of Competing Design for Efficient Cogeneration from Black Liquor, *2<sup>nd</sup> Biennial Johan Gullichsen Colloquium, Optimal utilization of wood fiber: energy and paper products*. Espoo. Finland. 9-10 September 1999, p. 55-67

## Appendix C

### Enthalpy Calculation for Black Liquor Using its Heating Value

#### Strong Black Liquor

##### Standard Enthalpy

The smelt composition is determined from the flows of the components in green liquor and the addition of the components from the weak wash by component mass balances (Table C.1). Elemental mass balances for the gasifier then give the composition of dry black liquor solids listed in Table C.2.

Table C.1. Calculated composition of smelt from the gasifier

Smelt	kg/ADt	
NaOH	27	4%
Na <sub>2</sub> CO <sub>3</sub>	582	84%
Na <sub>2</sub> S	81	12%
Na <sub>2</sub> SO <sub>4</sub>	0	0.0%
<b>Sum</b>	<b>690</b>	<b>100%</b>

Table C.2. Composition of black liquor solids

Element	kg/ADt		mol/kg bls
C	595	34.8%	29.5
H	64	3.8%	37.9
S	74	4.3%	1.4
O	629	36.8%	23.4
Na	316	18.5%	8.2
Others	32	1.9%	
<b>Sum</b>	<b>1,710</b>	<b>100%</b>	

The calorimetric heating value of the black liquor is -14,500 kJ/black liquor solids (Ekbohm et al. 2003). Combustion in oxygen gives the products listed in Table C.3, which also shows the enthalpy calculation for the products at standard temperature (25°C) and pressure.

Table C.3. Enthalpy calculation for the products of black liquor solids combustion

	mol/kg bls	kJ/kg bls
CO <sub>2</sub>	26.8	-10,554
H <sub>2</sub> O	19.0	-5,423
Na <sub>2</sub> SO <sub>4</sub>	1.4	-1,908
Na <sub>2</sub> CO <sub>3</sub>	2.7	-3,077
<b>Sum</b>		<b>-20,958</b>

The standard enthalpy of the black liquor solids is calculated in Equation C.1. The strong black liquor contains 20% water and the enthalpy of this is also calculated in Equation C.2, where x is the mass fraction of dry solids. The total enthalpy at standard temperature is determined in Equation C.3.

$$h_{\text{bls}}^{\circ} = h_{\text{products}} - \text{HHV} = -20958 + 14500 = -6458 \text{ kJ/bls} \quad [\text{C.1}]$$

$$h_{\text{water}}^{\circ} = \frac{m^{\text{CD2a}}(1-x)}{m^{\text{CD2a}} \cdot x \cdot M_{\text{H}_2\text{O}}} h_{\text{H}_2\text{O}}^{\circ} =$$

$$= \frac{2,137.5 \cdot (1-0.8)}{2,137.5 \cdot 0.8 \cdot 18.02} (-285,829) = -3,965 \text{ kJ/kg bls} \quad [\text{C.2}]$$

$$h_{298\text{K}}^{\text{SBL}} = (h_{\text{bls}}^{\circ} + h_{\text{H}_2\text{O}}^{\circ}) \cdot x = (-6,458 - 3,965) \cdot 0.8 = -8,338.4 \text{ kJ/kg liquor} \quad [\text{C.3}]$$

## Heat Capacity

The heat capacity of the black liquor is estimated with Equation C.4 (Masse et al.).

$$c_{\text{PBL}} = (1-x) \cdot c_{\text{pW}} + x \cdot c_{\text{pS}} + c_{\text{pE}} \quad [\text{C.4}]$$

where:

x is the mass fraction of solids

$c_{\text{pW}}$  is the heat capacity of water, 4,216 J/(kg K)

$$c_{\text{pS}} = 1,684 + 4.47 \cdot T$$

$$c_{\text{pE}} = (4,930 - 29 \cdot T)(1-x) \cdot x^{3.2}$$

T is the temperature in °C

The variable T is set to the mean value of the standard temperature and the actual temperature, which is  $T = 66.5^{\circ}\text{C}$  and equation C.4 gives a heat capacity of 2,722 kJ/(kg K).

$$c_{\text{PBL}} = (1-0.8) \cdot 4,216 + 0.8 \cdot (1,684 + 4.47 \cdot 66.5) + (4,930 - 29 \cdot 66.5)(1-0.8) \cdot 0.8^{3.2} = 2,722 \text{ J/(kg K)}$$

## Heat of Dilution

At  $80^{\circ}\text{C}$  and 80% dry solids a black liquor in Stoy and Fricke (1994), similar to the one in this report, has the enthalpy of 179.7 kJ/kg. The enthalpy was determined by Equation C.5. Then the heat of dilution for the strong black liquor (80%) is  $-141 \text{ kJ/kg dry solids}$ . In this study it is assumed that the heat of dilution is independent of temperature.

$$h_x = (1-x)h_w - x \cdot Q^{\infty} \quad [\text{C.5}]$$

where:

x is the mass fraction of solids

$h_w$  is the specific enthalpy of water at  $80^{\circ}\text{C}$ , given as 334.5 kJ/kg

$Q^{\infty}$  is the heat of dilution per unit mass of solids at  $80^{\circ}\text{C}$  for solution containing x mass fraction of solids

## Enthalpy of Strong Black Liquor

The enthalpy per mass of black liquor is determined in Equation C.6 to  $-8,000$  kJ/kg.

$$\begin{aligned} h_{381}^{\text{SBL}} &= h_{298\text{K}}^{\text{SBL}} + c_{\text{pBL}} \cdot (T_{\text{SBL}} - T_{\text{ref}}) - Q^{\infty} \cdot x = \\ &= -8,338.4 + 2.722 \cdot (381 - 298) + 141 \cdot 0.8 = -8,000 \text{ kJ/kg liquor} \end{aligned} \quad [\text{C.6}]$$

## Weak Black Liquor

### Standard Enthalpy

The standard enthalpy of black liquor solids is the same for weak as strong black liquor. The solids content in the weak black liquor is 16% and the enthalpy of the water part is calculated as in Equation C.2 to  $-82,475$  kJ/kg solids. The standard enthalpy of the weak black liquor is then calculated as in Equation C.3 to  $-14,345$  kJ/kg liquor.

### Heat Capacity

The heat capacity of the weak black liquor is calculated with Equation C.4. The temperature of the weak black liquor is  $100^{\circ}\text{C}$  which gives a mean temperature of  $62.5^{\circ}\text{C}$ . The heat capacity is estimated to  $3.86$  kJ/kg liquor.

$$\begin{aligned} c_{\text{pBL}} &= (1 - 0.1613) \cdot 4,216 + 0.1613 \cdot (1,684 + 4.47 \cdot 62.5) + (4,930 - 29 \cdot 62.5)(1 - 0.1613) \cdot 0.1613^{3.2} = \\ &= 3,860 \text{ J/(kg K)} \end{aligned}$$

### Heat of Dilution

At 16.2% and  $80^{\circ}\text{C}$  the enthalpy of a similar black liquor to the one in this report is  $286.5$  kJ/kg (estimated by linearization) according to Stoy and Fricke (1994). The heat of dilution is determined in the same way as above to  $-36.9$  kJ/kg dry solids.

## Enthalpy of Weak Black Liquor

The enthalpy of the weak black liquor is  $-14,050$  kJ/kg, determined in Equation C.7.

$$\begin{aligned} h_{373}^{\text{WBL}} &= h_{298\text{K}}^{\text{WBL}} + c_{\text{pBL}} \cdot (T_{\text{WBL}} - T_{\text{ref}}) - Q^{\infty} \cdot x = \\ &= -14,345 + 3.860 \cdot (373 - 298) + 36.9 \cdot 0.1613 = -14,050 \text{ kJ/kg liquor} \end{aligned} \quad [\text{C.7}]$$

## References

Ekbom. T., Lindblom. M., Berglin. N. and Ahlvik. P., (2003). "*Technical and Commercial Feasibility Study of Black Liquor Gasification with Methanol/DME Production as Motor Fuels for Automotive Uses – BLGMF*", Altener Contract No 4.1030/Z/01-087/2001, 2003

Masse. M. A., Kiran. F. and Fricke. A. L., (1987). "A Thermodynamic Model of the Heat Capacity of Compositionally Complex Multi-Component Polymer Solutions: Kraft Black Liquor", *Chemical engineering communications*, Vol. 50(1-6), p. 81-91

Stoy. M. A., Fricke. A. L., (1994) "Enthalpy Concentration Relations for Black Liquor", *Tappi Journal*, Vol. 77(9), p. 103-110

## Appendix D

### Borate Mass Balances

Component mass balances for  $\text{NaBO}_2$  and  $\text{Na}_2\text{B}_4\text{O}_7$  are done for the whole recovery cycle in Equation D.1 and D.2 respectively. In the gasifier  $\text{NaBO}_2$  is produced from  $\text{Na}_2\text{B}_4\text{O}_7$  according to Equation 2.9. In the green liquor filter 9% of the borates are lost with the green liquor dregs. Some borate is also lost with the bleed of sulfur-rich white liquor. The concentrations of  $\text{NaBO}_2$  and  $\text{Na}_2\text{B}_4\text{O}_7$  in the weak wash are calculated in Equation D.3 and D.4 respectively. The need of make-up borate is determined with an elemental mass balance for boron in the recovery cycle in Equation D.5.

$$\begin{aligned} \text{NaBO}_2^{\text{WBL}} &= \\ &= \left[ \text{NaBO}_2^{\text{WBL}} + \eta \cdot (\text{M} + \text{Na}_2\text{B}_4\text{O}_7^{\text{WBL}}) \frac{4 \cdot \text{M}_{\text{NaBO}_2}}{\text{M}_{\text{Na}_2\text{B}_4\text{O}_7}} + \text{NaBO}_2^{\text{WW}} \right] \frac{0.91}{\text{WL}_1 + \text{WL}_2} \left[ \text{WL}_2 - \frac{\text{WL}_3 \cdot \text{WL}_4}{\text{WL}_3 + \text{m}_{\text{rxn}}} \right] \quad [\text{D.1}] \end{aligned}$$

$$\begin{aligned} \text{Na}_2\text{B}_4\text{O}_7^{\text{WBL}} &= \\ &= \left[ (1 - \eta) (\text{Na}_2\text{B}_4\text{O}_7^{\text{WBL}} + \text{M}) + \text{Na}_2\text{B}_4\text{O}_7^{\text{WW}} \right] \frac{0.91}{\text{WL}_1 + \text{WL}_2} \left[ \text{WL}_2 - \frac{\text{WL}_3 \cdot \text{WL}_4}{\text{WL}_3 + \text{m}_{\text{rxn}}} \right] \quad [\text{D.2}] \end{aligned}$$

$$\text{NaBO}_2^{\text{WW}} = \left[ \text{NaBO}_2^{\text{WBL}} + \eta \cdot (\text{Na}_2\text{B}_4\text{O}_7^{\text{WBL}} + \text{M}) \frac{4 \cdot \text{M}_{\text{NaBO}_2}}{\text{M}_{\text{Na}_2\text{B}_4\text{O}_7}} \right] \cdot 0.91 \frac{\text{WL}_1}{\text{WL}_1 + \text{WL}_2} \quad [\text{D.3}]$$

$$\text{Na}_2\text{B}_4\text{O}_7^{\text{WW}} = \left[ (1 - \eta) (\text{Na}_2\text{B}_4\text{O}_7^{\text{WBL}} + \text{M}) + \text{Na}_2\text{B}_4\text{O}_7^{\text{WW}} \right] \cdot 0.91 \frac{\text{WL}_1}{\text{WL}_1 + \text{WL}_2} \quad [\text{D.4}]$$

$$\begin{aligned} \text{M} &= \left( 0.09 + 0.91 \frac{\text{WL}_3 \cdot \text{WL}_4}{(\text{WL}_1 + \text{WL}_2)(\text{WL}_3 + \text{m}_{\text{rxn}})} \right) \cdot \\ &\left[ \text{M} + \text{Na}_2\text{B}_4\text{O}_7^{\text{WBL}} + \text{Na}_2\text{B}_4\text{O}_7^{\text{WW}} + (\text{NaBO}_2^{\text{WBL}} + \text{NaBO}_2^{\text{WW}}) \frac{\text{M}_{\text{Na}_2\text{B}_4\text{O}_7}}{4 \cdot \text{M}_{\text{NaBO}_2}} \right] \quad [\text{D.5}] \end{aligned}$$

A mass balance is made for the white liquor from the lime cycle to the delignification. In the gas cleaner some mass is absorbed from the gas and then a part of the sulfur-rich white liquor is bled off. The mass of white liquor entering the delignification is the same as in the reference mill with the addition of the mass of borates. It is assumed that there is no loss of borates in the delignification.

$$\text{WL}_4 + \text{WL}_5 = \text{m}_{\text{rxn}} + \text{WL}_2 \quad [\text{D.6}]$$

$$\text{WL}_5 = 4094.2 + \text{NaBO}_2^{\text{WBL}} + \text{Na}_2\text{B}_4\text{O}_7^{\text{WBL}} \quad [\text{D.7}]$$

The total mass of absorbed compounds ( $\text{H}_2\text{S}$  and  $\text{CO}_2$ ) is calculated with the earlier stated assumption that one mole of  $\text{CO}_2$  is absorbed per every five absorbed moles of  $\text{H}_2\text{S}$  in Equation D.8.

$$m_{\text{rxn}} = \left( H_2S^{\text{RG}} - H_2S^{\text{SG}} \right) \left( 1 + 0.2 \frac{M_{\text{CO}_2}}{M_{\text{H}_2\text{S}}} \right) \quad [\text{D.8}]$$

Without the autocausticization reactions the green liquor should have the same concentrations as in the model with gasification and only conventional causticization. The mass flow of these compounds with the white liquor produced in the recovery cycle should also be the same. In the slaker the same amount of NaOH and Na<sub>2</sub>CO<sub>3</sub> is produced and consumed respectively as in the reference model since the same amount of lime is used.

The amounts of NaOH generated by the autocausticization in the gasifier and in the absorption unit are determined in Equation D.9 and D.10 respectively. In the absorption unit, NaOH is actually consumed and therefore the expression should be negative. The component mass balance for NaOH in the recovery cycle is shown in Equation D.11.

$$\text{NaOH}^{\text{D2a}} = \left( 2 \cdot \frac{\text{NaBO}_2^{\text{WBL}}}{M_{\text{NaBO}_2}} + 8 \cdot \frac{\text{Na}_2\text{B}_4\text{O}_7^{\text{WBL}} + M}{M_{\text{Na}_2\text{B}_4\text{O}_7}} \right) \cdot \eta \cdot M_{\text{NaOH}} \quad [\text{D.9}]$$

$$\text{NaOH}^{\text{D2b}} = -2.4 \cdot \frac{H_2S^{\text{RG}} - H_2S^{\text{SG}}}{M_{\text{H}_2\text{S}}} M_{\text{NaOH}} \quad [\text{D.10}]$$

$$\begin{aligned} & \text{NaOH}^* + \text{NaOH}^{\text{D2a}} + \text{NaOH}^{\text{G}} + \text{NaOH}^{\text{D2b}} = \\ & = \left( \left( \text{NaOH}^* + \text{NaOH}^{\text{D2a}} + \text{NaOH}^{\text{G}} \right) \frac{\text{WL}_3}{\text{WL}_2} + \text{NaOH}^{\text{D2b}} \right) \frac{\text{WL}_4}{\text{WL}_3 + m_{\text{rxn}}} + \text{NaOH}^{\text{WL}} \end{aligned} \quad [\text{D.11}]$$

The amounts of Na<sub>2</sub>CO<sub>3</sub> generated by the autocausticization in the gasifier and in the absorption unit are determined in Equation D.12 and D.13 respectively. The mass balance for Na<sub>2</sub>CO<sub>3</sub> in the recovery cycle is shown in Equation D.14 and that for Na<sub>2</sub>S in Equation D.15.

$$\text{Na}_2\text{CO}_3^{\text{D2a}} = - \left( \frac{\text{NaBO}_2^{\text{WBL}}}{M_{\text{NaBO}_2}} + 5 \cdot \frac{\text{Na}_2\text{B}_4\text{O}_7^{\text{WBL}} + M}{M_{\text{Na}_2\text{B}_4\text{O}_7}} \right) \cdot \eta \cdot M_{\text{Na}_2\text{CO}_3} \quad [\text{D.12}]$$

$$\text{Na}_2\text{CO}_3^{\text{D2b}} = 0.2 \cdot \frac{H_2S^{\text{RG}} - H_2S^{\text{SG}}}{M_{\text{H}_2\text{S}}} \cdot M_{\text{Na}_2\text{CO}_3} \quad [\text{D.13}]$$

$$\begin{aligned} & \text{Na}_2\text{CO}_3^* + \text{Na}_2\text{CO}_3^{\text{D2a}} - \text{Na}_2\text{CO}_3^{\text{G}} + \text{Na}_2\text{CO}_3^{\text{D2b}} = \text{Na}_2\text{CO}_3^{\text{WL}} + \\ & + \left( \left( \text{Na}_2\text{CO}_3^* + \text{Na}_2\text{CO}_3^{\text{D2a}} - \text{Na}_2\text{CO}_3^{\text{G}} \right) \frac{\text{WL}_3}{\text{WL}_2} + \text{Na}_2\text{CO}_3^{\text{D2b}} \right) \frac{\text{WL}_4}{\text{WL}_3 + m_{\text{rxn}}} \end{aligned} \quad [\text{D.14}]$$

$$\begin{aligned} & \text{Na}_2\text{S}^* + \frac{H_2S^{\text{RG}} - H_2S^{\text{SG}}}{M_{\text{H}_2\text{S}}} M_{\text{Na}_2\text{S}} = \\ & = \left( \text{Na}_2\text{S}^* \frac{\text{WL}_3}{\text{WL}_2} + \frac{H_2S^{\text{RG}} - H_2S^{\text{SG}}}{M_{\text{H}_2\text{S}}} M_{\text{Na}_2\text{S}} \right) \frac{\text{WL}_4}{\text{WL}_3 + m_{\text{rxn}}} + \text{Na}_2\text{S}^{\text{WL}} \end{aligned} \quad [\text{D.15}]$$



Equations D.1-D.15 are solved simultaneously and the result is shown in Table D.1. The need of make-up borate is 11.23 kg/ADt.

*Table D.1. Result of Equations D.1-D.15*

<b>Variable</b>	<b>Symbol</b>	<b>Mass [kg/ADt]</b>
NaBO <sub>2</sub> in weak wash	x <sub>1</sub>	2.87
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> in weak wash	x <sub>2</sub>	0.13
NaBO <sub>2</sub> in weak black liquor	y <sub>1</sub>	86.68
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> in weak black liquor	y <sub>2</sub>	3.92
Make-up Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	M	11.23
H <sub>2</sub> S in syn gas	H <sub>2</sub> S <sup>SG</sup>	4.53
White liquor from the lime cycle	WL <sub>2</sub>	4360
White liquor to the gas cleaner	WL <sub>3</sub>	2019
White liquor bleed	WL <sub>4</sub>	222.7
Absorbed mass in the gas cleaner	m <sub>rxn</sub>	47.84

## Nomenclature

m <sub>rxn</sub>	Absorbed mass from the gas to the white liquor
M	Mass flow of make-up Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>
NaBO <sub>2</sub> <sup>WBL</sup>	Mass flow of NaBO <sub>2</sub> in the weak black liquor
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> <sup>WBL</sup>	Mass flow of Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> in the weak black liquor
NaBO <sub>2</sub> <sup>WW</sup>	Mass flow of NaBO <sub>2</sub> in the weak wash
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> <sup>WW</sup>	Mass flow of Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> in the weak wash
NaOH <sup>D2a</sup>	Generated mass of NaOH in the gasifier
NaOH <sup>D2b</sup>	Generated mass of NaOH in the absorption unit
NaOH <sup>G</sup>	Generated mass of NaOH in the lime cycle
NaOH <sup>*</sup>	Mass flow of NaOH in the green liquor if no autocausticizing reactions (fictive)
Na <sub>2</sub> CO <sub>3</sub> <sup>D2a</sup>	Generated mass of Na <sub>2</sub> CO <sub>3</sub> in the gasifier
Na <sub>2</sub> CO <sub>3</sub> <sup>D2b</sup>	Generated mass of Na <sub>2</sub> CO <sub>3</sub> in the absorption unit
Na <sub>2</sub> CO <sub>3</sub> <sup>G</sup>	Generated mass of Na <sub>2</sub> CO <sub>3</sub> in the lime cycle
Na <sub>2</sub> CO <sub>3</sub> <sup>*</sup>	Mass flow of Na <sub>2</sub> CO <sub>3</sub> in the green liquor if no autocausticizing reactions fictive)
Na <sub>2</sub> S <sup>*</sup>	Mass flow of Na <sub>2</sub> S in the green liquor if no autocausticizing reactions (fictive)
WL <sub>1</sub>	White liquor mass flow in lime mud (IJ)
WL <sub>2</sub>	Mass flow of S-rich white liquor ready for delignification
WL <sub>3</sub>	Inflow of white liquor to the gas cleaner
WL <sub>4</sub>	Bleed of sulfur-rich white liquor
WL <sub>5</sub>	Mass flow of white liquor produced in the recovery cycle
η	Efficiency of Reactions 2.6 and 2.9

## Appendix E

### Enthalpies

*Table E.1. Enthalpies of the streams in the reference mill*

<b>Stream</b>		<b>T</b> °C	<b>Enthalpy</b> kJ/kg
Burned lime	KG	200	-11,181
Condensate	CL	90/75	-15,631
Filtrated green liquor	FG	90	-14,695
Flue gas	D1L	-	-20,816
Flue gas	KL	200	-10,749
Green liquor	EF	98	-14,657
Green liquor dregs	FL	90	-13,177
Lime mud	IJ	100	-12,707
Lime sludge	JL	60	-12,916
Make-up lime	AK	20	-30,158
Smelt	D1E	850	-7,848
Strong black liquor	CD1	108	-8,370
Washed lime mud	JK	60	-12,971
Weak black liquor	BC	100	-14,049
Weak wash	JE	57.7	-15,722
White liquor	IB	100	-14,773
White liquor and lime mud	HI	100	-14,529

*Table E.2. Enthalpies of the streams in the mill with gasification*

<b>Stream</b>		<b>T</b> °C	<b>Enthalpy</b> kJ/kg
Burned lime	KG	200	-11,181
Condensate	CL	90/75	-15,631
Filtrated green liquor	FG	90	-14,826
Raw gas	D2aD2b	40	-5,703
Flue gas	KL	200	-10,760
Green liquor	EF	98	-14,789
Green liquor dregs	FL	90	-13,242
Lime mud	IJ	100	-12,748
Lime sludge	JL	60	-12,916
Make-up lime	AK	20	-30,158
Oxygen	D2aF	20	-5
Strong black liquor	CD2a	108	-8,370
Washed lime mud	JK	60	-12,971
Weak black liquor	BC	100	-14,049
Weak wash	JE	58.7	-15,714
White liquor (S-lean)	IB	100	-14,938
White liquor and lime mud	HI	100	-14,622

*Table E.3. Enthalpies of the streams in the mill with gasification and partial autocausticization*

<b>Stream</b>		<b>T</b> <b>°C</b>	<b>Enthalpy</b> <b>kJ/kg</b>
Burned lime	KG	200	-11 181
Condensate	CL	90/75	-15 631
Filtrated green liquor	FG	90	-14 856
Raw gas	D2aD2b	40	-5 806
Flue gas	KL	200	-10 749
Green liquor	EF	98	-14 818
Green liquor dregs	FL	90	-13 773
Lime mud	IJ	100	-12 758
Lime sludge	JL	60	-12 916
Make-up borate	AC	20	-16 329
Make-up lime	AK	20	-30 158
Oxygen	D2aF	20	-5
Strong black liquor	CD2a	108	-8 667
Washed lime mud	JK	60	-12 969
Weak black liquor	BC	100	-14 055
Weak wash	JE	58.3	-15 723
White liquor (S-lean)	IB	100	-14 946
White liquor and lime mud	HI	100	-14 701

## Appendix F

### Enthalpy Calculations

Some of the flows in the different mill models in this report consist of a mixture of different compounds. The enthalpies of the different compounds in these mixed streams are presented below, as well as of the total flows.

#### The Reference Mill

*Table F.1. Enthalpy calculation for washed lime mud in the reference mill*

Washed Lime Mud	Mass		Enthalpy	
	kg/ADt	kg/s	kJ/ADt	kJ/kg
CaO	24.5	0.57	-276,775	-11,297
Ca(OH) <sub>2</sub>	19.6	0.45	-260,278	-13,265
CaCO <sub>3</sub>	351.0	8.13	-4,226,935	-12,041
Water	131.7	3.05	-2,070,114	-15,716
<b>Total</b>	<b>526.9</b>	<b>12.20</b>	<b>-6,834,102</b>	<b>-12,971</b>

*Table F.2. Enthalpy calculation for the flow of lime mud in the reference mill*

Lime Mud	Mass		Enthalpy	
	kg/ADt	kg/s	kJ/ADt	kJ/kg
CaO	24.5	0.57	-275,992	-11,265
Ca(OH) <sub>2</sub>	19.6	0.45	-259,286	-13,215
CaCO <sub>3</sub>	367.0	8.50	-4,406,310	-12,005
Liquor	137.1	3.17	-2,024,604	-14,773
<b>Total</b>	<b>548.2</b>	<b>12.69</b>	<b>-6,966,193</b>	<b>-12,707</b>

*Table F.3. Calculation of enthalpy for green liquor dregs in the reference mill*

Green liquor dregs	Mass		Enthalpy	
	kg/ADt	kg/s	kJ/ADt	kJ/kg
CaCO <sub>3</sub>	7.2	0.17	-86,502	-12,014
Na <sub>2</sub> CO <sub>3</sub>	1.2	0.03	-12,717	-10,597
MgCO <sub>3</sub>	1.2	0.03	-15,518	-12,932
Na <sub>2</sub> S	0.4	0.01	-1,848	-4,621
Liquor	10.0	0.23	-146,950	-14,695
<b>Total</b>	<b>20.0</b>	<b>0.46</b>	<b>-263,535</b>	<b>-13,177</b>

*Table F.4. Enthalpy calculation for green liquor in the reference mill*

Green liquor	Mass		Enthalpy	
	kg/ADt	kg/s	kJ/ADt	kJ/kg
Liquor	4468.9	103.45	-65,530,008	-14,664
CaCO <sub>3</sub>	7.2	0.17	-86,450	-12,007
Na <sub>2</sub> CO <sub>3</sub>	1.2	0.03	-12,706	-10,588
MgCO <sub>3</sub>	1.2	0.03	-15,508	-12,924
Na <sub>2</sub> S	0.4	0.01	-1,845	-4,613
<b>Total</b>	<b>4478.9</b>	<b>103.68</b>	<b>-65,646,518</b>	<b>-14,657</b>

## Mill with Black Liquor Gasification

*Table F.5. Enthalpy calculation for the flow of washed lime mud in the mill with gasification*

Washed Lime Mud	Mass		Enthalpy	
	kg/ADt	kg/s	kJ/ADt	kJ/kg
CaO	32.4	0.75	-366,021	-11,297
Ca(OH) <sub>2</sub>	25.9	0.60	-344,204	-13,265
CaCO <sub>3</sub>	469.4	10.87	-5,652,029	-12,041
Water	175.9	4.07	-2,764,648	-15,716
<b>Total</b>	<b>703.6</b>	<b>16.29</b>	<b>-9,126,902</b>	<b>-12,971</b>

*Table F.6. Enthalpy calculation for the flow of lime mud in the mill with gasification*

Lime Mud	Mass		Enthalpy	
	kg/ADt	kg/s	kJ/ADt	kJ/kg
CaO	32.4	0.75	-364,986	-11,265
Ca(OH) <sub>2</sub>	25.9	0.60	-342,892	-13,215
CaCO <sub>3</sub>	485.4	11.24	-5,827,120	-12,005
Liquor	181.2	4.20	-2,707,378	-14,938
<b>Total</b>	<b>725.0</b>	<b>16.78</b>	<b>-9,242,376</b>	<b>-12,748</b>

- *The enthalpy of the green liquor dregs is the same as in the reference mill*

*Table F.7. Enthalpy calculation for the green liquor in the mill with gasification*

Green liquor	Mass		Enthalpy	
	kg/ADt	kg/s	kJ/ADt	kJ/kg
Liquor	4806.5	111.26	-71,113,875	-12,007
CaCO <sub>3</sub>	7.2	0.17	-86,450	-10,588
Na <sub>2</sub> CO <sub>3</sub>	1.2	0.03	-12,706	-12,924
MgCO <sub>3</sub>	1.2	0.03	-15,508	-4,613
Na <sub>2</sub> S	0.4	0.01	-1,845	-14,796
<b>Total</b>	<b>4816.5</b>	<b>111.5</b>	<b>-71,230,385</b>	<b>-14,789</b>

Table F.8. Enthalpy calculation for the raw gas in the mill with gasification

Raw gas	Mass		Enthalpy	
	kg/ADt	kg/s	kJ/ADt	kJ/kg
H <sub>2</sub>	61.0	1.41	12,995	213
CO	823.2	19.05	-3,235,402	-3,930
CO <sub>2</sub>	646.7	14.97	-5,773,746	-8,928
H <sub>2</sub> S	43.3	1.00	-25,369	-586
<b>Total gas</b>	<b>1581.9</b>	<b>36.62</b>	<b>-9,021,522</b>	<b>-5,703</b>

### Mill with Black Liquor Gasification and Borate Autocausticization

The enthalpy for the washed lime mud is the same as in the reference mill

Table F.9. Enthalpy calculation for the flow of the lime mud in the mill with gasification and autocausticization

Lime Mud	Mass		Enthalpy	
	kg/ADt	kg/s	kJ/ADt	kJ/kg
CaO	24.5	0.57	-275,992	-11,265
Ca(OH) <sub>2</sub>	19.62	0.45	-259,286	-13,215
CaCO <sub>3</sub>	367.04	8.50	-4,406,310	-12,005
Liquor	137.05	3.17	-2,048,411	-14,946
NaBO <sub>2</sub>	2.9	0.07	-42,000	-14,654
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	0.1	0.00	-2,107	-16,458
<b>Total</b>	<b>551.20</b>	<b>12.76</b>	<b>-7,034,106</b>	<b>-12,761</b>

Table F.10. Calculation of enthalpy for the green liquor dregs in the mill with gasification and autocausticization

Green liquor dregs	Mass		Enthalpy	
	kg/ADt	kg/s	kJ/ADt	kJ/kg
CaCO <sub>3</sub>	7.2	0.17	-86,502	-12,014
Na <sub>2</sub> CO <sub>3</sub>	1.2	0.03	-12,717	-10,597
MgCO <sub>3</sub>	1.2	0.03	-15,518	-12,932
Na <sub>2</sub> S	0.4	0.01	-1,848	-4,621
Liquor	10.0	0.23	-148,564	-14,856
NaBO <sub>2</sub> (aq)	9.3	0.22	-137,452	-14,768
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> (aq)	0.4	0.01	-6,841	-16,270
<b>Total</b>	<b>29.7</b>	<b>0.69</b>	<b>-409,442</b>	<b>-13,773</b>

Table F.11. Enthalpy calculation for green liquor in the mill with gasification and autocausticization

Green Liquor	Mass		Enthalpy	
	kg/ADt	kg/s	kJ/ADt	kJ/kg
Liquor	4663.6	107.95	-69,147,450	-14,827
CaCO <sub>3</sub> (s)	7.2	0.17	-86,450	-12,007
Na <sub>2</sub> CO <sub>3</sub> (s)	1.2	0.03	-12,706	-10,588
MgCO <sub>3</sub> (s)	1.2	0.03	-15,508	-12,924
Na <sub>2</sub> S (s)	0.4	0.01	-1,845	-4,613
NaBO <sub>2</sub> (aq)	103.4	2.39	-1,515,626	-14,656
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> (aq)	4.7	0.11	-76,899	-16,460
<b>Total</b>	<b>4781.7</b>	<b>110.69</b>	<b>-70,856,484</b>	<b>-14,818</b>

Table F.12. Enthalpy calculation for the raw gas in the mill with gasification and autocausticization

Raw Gas	Mass		Enthalpy	
	kg/ADt	kg/s	kJ/ADt	kJ/kg
H <sub>2</sub>	61.0	1.41	12,995	213
CO	823.2	19.05	-3,235,402	-3,930
CO <sub>2</sub>	698.9	16.18	-6,239,596	-8,928
H <sub>2</sub> S	43.3	1.00	-25,364	-586
<b>Total</b>	<b>1626.3</b>	<b>37.65</b>	<b>-9,487,367</b>	<b>-5,834</b>