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**GASIFICATION OF BLACK LIQUOR AS A WAY TO INCREASE POWER
PRODUCTION AT KRAFT PULP MILLS**

Examiners: Professor Kaj Henricson
Professor Ilkka Turunen

ABSTRACT

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The study is focused on the opportunity to improve the power performance from black liquor at Kraft pulp mills. The first part of the paper includes an overview of a traditional recovery system, its development and indication of the integral drawbacks which provoke the search for more efficient methods of black liquor treatment. The second part is devoted to the investigation of black liquor gasification as a technology able to increase electric energy generation at pulp mills. In addition, a description of two most promising gasification processes and their comparison to each other are presented. The paper is based on a literature review and interviews of specialists in this field.

The findings showed that while the modern recovery system meets demands of the pulp mills, pressurized oxygen-blown black liquor gasification has good potential to be used as an alternative technology, increasing the power output from black liquor.

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ABBREVIATIONS

| | |
|---------|---|
| BLG | Black liquor gasification |
| BLGCC | Black liquor gasification combined cycle |
| BLGMF | Black liquor gasification motor fuel |
| DP1 | Demonstration Plant 1 |
| Eq. | Equation |
| HRSG | Heat recovery steam generator |
| HTBLG | High-temperature black liquor gasification |
| HTBLGCC | High-temperature black liquor gasification combined cycle |
| LP | Low pressure |
| LTBLG | Low-temperature black liquor gasification |
| MP | Medium pressure |
| MTCI | Manufacturing Technology Conversion International Company |
| RB | Recovery boiler |
| TRI | ThermoChem Recovery International Company |

1 INTRODUCTION

The pulp industry is the most difficult branch of the forestry complex, associated with the mechanical handling and chemical processing of wood. The manufacture of pulp is characterized by high material, water and energy consumption.

Currently, an important objective entrusted to the pulp industry is to increase the competitiveness of its products. There are two ways to achieve this: improving the quality of pulp and reducing the cost of its production. [1]

For all industries associated with the processing of raw wood, the most important factor is the cost of raw wood material, including the cost of its transportation to consumers and the costs of fuel and energy. In the pulp's price structure, 50 % of costs belong to initial raw materials and approximately 40 % to energy. Consequently, in order to increase the efficiency of pulp mills, the priority is to reduce the consumption of raw wood material and energy. The works directed to the essential decrease of wood consumption during pulp production are unknown. In these circumstances, the only way to significantly improve the profitability of pulp manufacture is to reduce its energy costs. [1, 2]

One of the opportunities for reducing costs associated with the consumption of energy at the pulp mills is the use of renewable energy sources such as black liquor and bark, which are by-products of the pulp production. Indeed, modern pulp mills are energy self-sufficient due to using recovery systems in which black liquor combustion is carried out with the regeneration of chemicals and energy. However, the progress being made in research on how black liquor can be exploited as energy source has not stopped and as a result a more rational use for the black liquor gasification process was discovered.

The goals of this thesis were to show research on the necessity of new chemicals and energy regeneration methods at the Kraft pulp mills and to consider the gasification process as a worthy alternative to a conventional recovery system, allowing a significant increase the electric energy recovery from black liquor.

This thesis begins with the description of a traditional recovery system, its development and the identification of its shortcomings. The thesis continues by providing information about the black liquor gasification process as a new recovery system with a focus on energy generation based on the data obtained through the literature review. At the end of the thesis expert opinions about this technology are presented.

2 KRAFT PROCESS

Pulp production by cooking is the liberation of cellulose fibers from raw material in an undamaged state by the impact of chemicals under certain conditions. The main substance extracted from the plant is lignin, so the process of pulp cooking is called delignification. [3]

The cooking method based on the dissolution of lignin using sodium hydroxide and sodium sulfide is called sulfate cooking. Pulp obtained by this type of cooking is very strong and for this reason the process is commonly called Kraft, which means strong in translation from Swedish. [4]

Currently the Kraft process is the dominant method of alkaline cooking using wood as raw material and the most important method of pulp production. Today more than 90% of pulp in the world is produced by Kraft cooking. The main advantages of Kraft cooking before sulphite are the following [5]:

- lower demand for wood species and quality of wood raw materials, enabling the use of all types of wood and allowing the presence of significant amounts of extractive substances, rotten wood and bark residues,
- well-developed processes of recycling waste liquor, including the regeneration of cooking chemicals and generation of steam,
- excellent mechanical properties of pulp,
- production of valuable by-products, such as tall oil and turpentine in the cooking of pine wood, and
- relatively short cooking time.

The main disadvantages of Kraft cooking are the emission of malodorous gasses, reduced pulp yield as compared with sulfite cooking and the dark color of unbleached pulp.

2.1 The process stages of Kraft pulp production

The conventional process of pulp production from wood by the sulfate method consists of the following operations: preparation of wood, chips cooking, separation of cooked pulp from spent liquor, pulp bleaching and regeneration of chemicals and heat. Figure 1 shows the main stages of sulfate pulp production. [4]

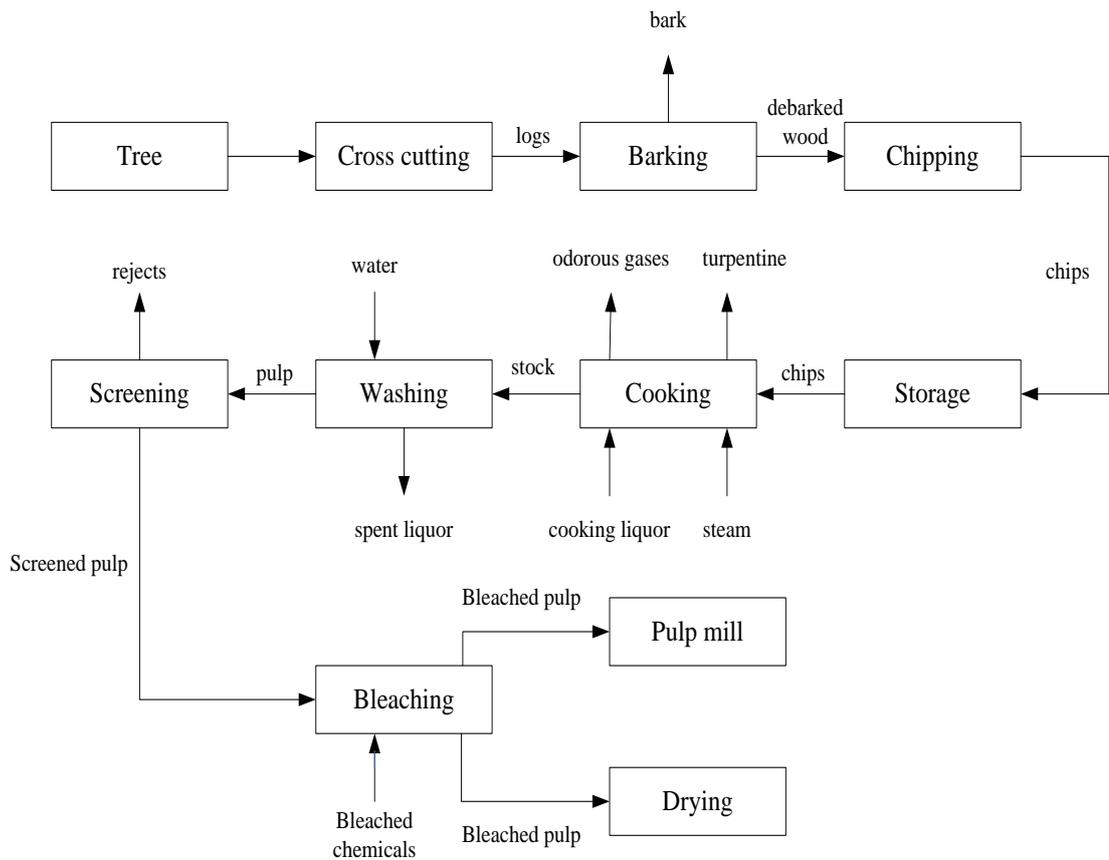


Figure 1. Technological scheme of the Kraft process of bleached pulp production [4]

The pulp sulfate cooking is carried out in a continuous or periodic manner. The required size wood chips are fed into a cooking digester working under pressure where steam is injected in order to heat the chips and remove air contained in the chips. Then the digester is filled with a hot cooking solution that penetrates the chips. This stage of chips impregnation by liquor is very important because it provides an even distribution of liquor into the chips. The cooking liquor is a mixture of white liquor and some quantity of black liquor. The white liquor includes two active reagents involved in the

isolation of cellulose fibers: sodium hydroxide and sodium sulfide. The pH of the cooking solution is 14. Black liquor is added at the beginning of the cooking process to adjust the liquor-to-wood ratio. [5]

The contents of the boiler are warmed by direct or indirect heating. In the former case, the steam goes straight to the digester and in the latter, steam enters a heat exchanger, through which the circulation pump continuously drives the cooking liquid. The cooking temperature of the sulfate process is about 160-170 °C, but delignification of wood material begins during the saturation stage and intensively continues at temperature above 140 °C [7]. During the rise in temperature, a turpentine vent is performed, which directs turpentine vapors, air remaining in the boiler, volatile organic products and water vapors to the heat recycling and turpentine production. When the final cooking temperature is achieved, the delignification process is continued until the desired pulp type is reached. After cooking completion, the pressure in the boiler is reduced by blowing and the cellulose mass with liquor enters the blow tank. [6]

The brown stock from the blow tank is transferred to the washing stage. The main goal of stock washing is to produce a clean pulp by removing black liquor, which comprises cooking chemicals and organic substances. A typical washing system is a continuous counter-current process based on the application of a series of drum filters. The separated black liquor is regenerated in the recovery system. Debris is detached from pulp by knotters, screens and centricleaners. Then the cellulose mass is bleached for fiber brightness improvement. [5]

3 RECOVERY SYSTEM

An internal part of the Kraft factory is the department of spent liquor regeneration. The following functions are performed by the regeneration system: recovery of chemicals, energy recovery and valuable by-products production. Figure 2 illustrates the basic stages of the regeneration process. [4]

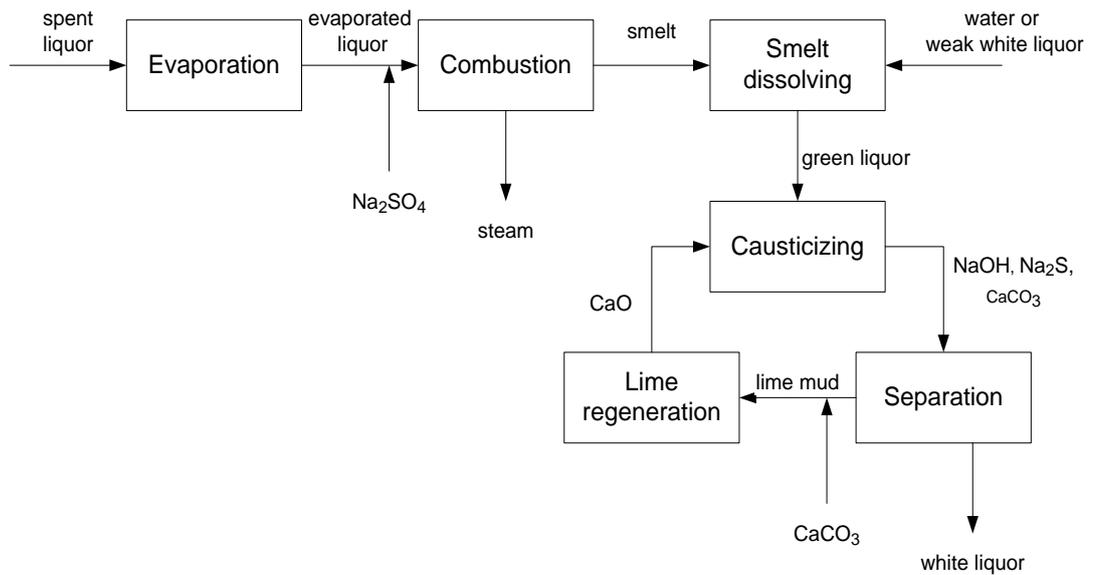


Figure 2. Chemical recovery system [4]

According to the figure above, the process of regeneration is composed of three operations:

- evaporation of black liquor,
- combustion of condensed liquor, which results in steam and mineral residue in the form of smelt, and
- causticizing of dissolved smelt (green liquor).

3.1 Evaporation

Evaporation is the process of thickening a solution in this case black liquor, by turning water into steam. The main sources of water in black liquor are: wood, condensed steam during cooking, white liquor and water used in brown stock washing. The target of the evaporation is to bring the dry solids content of spent liquor to a level that allows its efficient burning. Commonly, the liquor is evaporated until the concentration of dry matters is 65-75% while modern stations reach dry solids content of 80 %. [8]

Before feeding of the black liquor into the evaporation installation, it must be relieved of soap and small fibers. The fibers are separated by filtration, which is necessary to reduce scale formation on the surface of the vaporizer. The presence of soap in the liquor leads to foam formation in the vaporization process, which causes the loss of alkali from the foam moving from shell to shell. The removal of sulfate soap, which is a mixture of sodium salts of resin and fatty acids, is performed by settling. [5]

The evaporation of black liquor is executed in a multiple unit installation with the number of shells ranging from five to seven. The evaporator is a heat exchanger in which heat is transferred to the solution through the metallic surface warmed by steam. There are three types of evaporators usually exploited in the black liquor evaporation process: rising film, falling film and forced circulation. Presently, both falling film and forced circulation evaporators are used to reach final dry solids content in the liquor and they are defined as concentrators. Polluted condensate from evaporation is cleaned in the stripping column. [8]

3.2 Combustion

The evaporated black liquor is fed into a recovery unit for combustion. The inevitable alkali losses in the production cycle are compensated for by the addition of sodium sulfate before burning the liquor. Usually, the recovery unit used for liquor incineration is a boiler commonly known as the Tomlinson recovery boiler. Two main processes are carried out in the unit: the combustion of the organic substances in the

liquor accompanied by a release of heat and the regeneration of sulfur and sodium chemicals for reuse in the cooking after the recausticization stage. These separate processes are produced due to the division of the boiler into two zones: oxidation occurs in the upper part of the boiler, characterized by an excess of air when organic matter burns down, and reduction occurs in the lower part of the boiler, which is characterized by a lack of air when the components of sulfur and sodium are reduced in the form of smelt. Briefly, the burning process can be described by the following reaction [9]:



The heat produced by incinerating the liquor is spent on the transformation of water, contained in tubes in the furnace walls and floor, into the steam. This then leaves the boiler and moves to a turbine for the manufacture of electric power and steam for other technological needs [10]. Smelt removed from the bottom of the recovery unit goes to the recausticizing system. Black liquor combustion is described in detail in section 4.

3.3 Recausticization

Dissolved in weak white liquor, smelt (green liquor) is sent to the recausticization system, which is the last stage of chemical recovery.

Green liquor is mainly made up of carbonate and sodium sulfide, along with other compounds of sodium, including hydroxide. As mentioned above, sulfide and sodium hydroxide are active reagents applied in wood delignification. Hence, in order to acquire initial reagents for cooking from green liquor, it is necessary to transform sodium carbonate into hydroxide and this process is called recausticizing [11]. Figure 3 illustrates the recausticizing system.

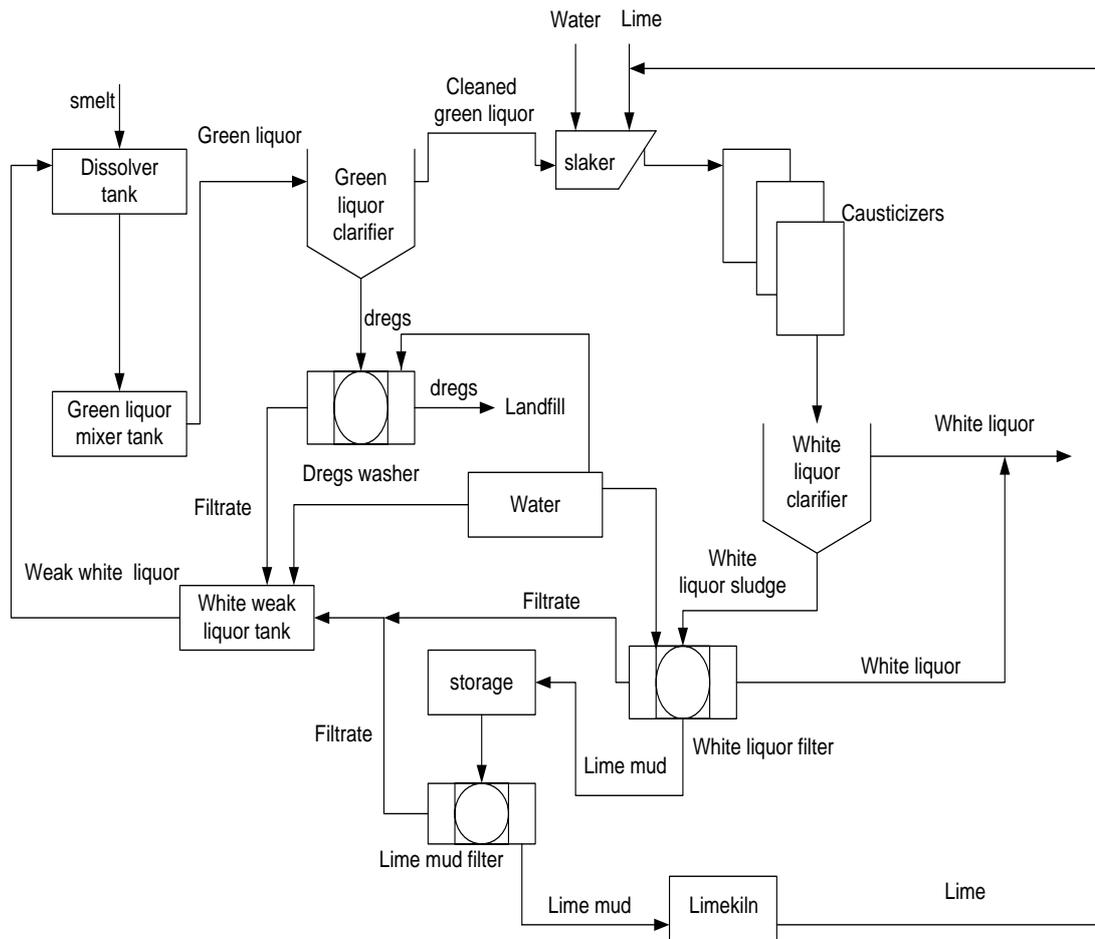


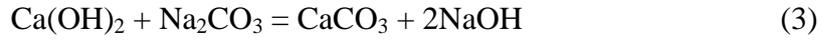
Figure 3. Recausticization process [9]

Green liquor contains along with sodium compounds insoluble substances, which can be serious obstacles in the recausticization process. These are soot and non-process elements (elements being removed from wood or going with chemicals and also oxides resulting from metals corrosion). These insoluble substances are removed from green liquor in the form dregs by sedimentation, using clarifiers or filtration. Free from the dregs, liquor is fed with lime in a lime slaker. A reaction occurring in the slaker between calcium oxide and water contained in the green liquor leads to the formation of calcium hydroxide and heat [9], as can be seen in the following reaction:



Simultaneously with the lime slaking process, the slaker separates sand and overburned or unburned lime. Then the green liquor moves to a line of causticizers, where the interaction of calcium hydroxide with sodium carbonate occurs. The

resulting products of this interaction are sodium hydroxide and calcium carbonate or caustic soda. [9]



The causticization efficiency characterizing the recausticizing reaction fullness equals to 80-85% and can be calculated by the following equation [7]:

$$\frac{\text{NaOH}}{\text{NaOH} + \text{Na}_2\text{CO}_3} \quad (4)$$

After the recausticizing reaction, the liquor contains reduced sodium hydroxide and sodium sulfide, so the green liquor becomes white liquor. Before further use of white liquor as a cooking solution it should be separated from the calcium carbonate, called lime mud, by sedimentation and filtration. The separated lime mud goes through an intermediate storage to water removal, in order to reduce the costs of its combustion in the furnace. Presently, mud can be dewatered to a dry solids content of 80-90 %. The filtrate from washing dregs and the filtrate from washing and dewatering of lime make up weak white liquor which is sent to the tank. [7, 10]

Thermal drying of the lime mud can be carried out in a cyclone, or directly in the furnace [8]. The aim of the incineration of lime sludge is the recovery of calcium oxide, which is again used in the slaking process. In most cases, calcium carbonate is burnt in a rotary lime kiln at a temperature of 1100-1200 °C. The burning is characterized by the following reaction [11]:



The lime leaves the kiln through a cooler to return heat to the burning process. The cooler also separates the large particles of lime, which are later crushed. The lime is reused in the cycle of sodium hydroxide recovery. [11]

4 BLACK LIQUOR

4.1 Composition of black liquor

The waste solution of sulfate cooking, the black liquor, includes minerals of white liquor spent during cooking and dissolved organic substances from wood. The liquor is an important by-product since its combustion results in not only chemical recovery but also a significant amount of heat, which covers the production costs of energy. The spent liquor segregated during pulp washing contains a large quantity of water that is removed by evaporation. The black liquor dry residue consists of 30-40% minerals and 60-70% of organic matters. Of the mineral residue, 18-25% of it is chemically connected with organic substances of dissolved wood, 1-2% of the mineral residue is in the form of free alkali, 1-4% in the form of sodium sulphide, 3-5% in the form of sodium sulphate, and 4-10% in the form of sodium carbonate. The organic part of the dry residue is made up of lignin (30-35%) and products of carbohydrates destruction (30-35%). The composition of this combustible mass includes 35-45% carbon, 3-5% hydrogen, 15-20% oxygen and 1-4% organic sulfur. [3]

Elemental composition of the liquor is determined by the type of wood and conditions of its delignification. [12]

4.2 Physical properties of black liquor

The physical properties of black liquor are directly dependent on its composition. The liquor properties which describe its behavior during the heat transfer processes are of interest to study [12]. The main physical parameters of sulfate black liquor considered during its evaporation and burning the following: density, viscosity, boiling temperature, surface tension and heat value. [9]

The liquor density characterizes the dry solids content. During the rise in temperature, density decreases due to volumetric expansion of water contained in the liquor. [13]

The viscosity of spent liquor depends on the amount of dry solids, their chemical composition and liquor temperature. An increase in the concentration of dry solids leads to increased viscosity, which in turn contributes to lower cost energy when burning liquor. On the other hand, a very high concentration of black liquor requires using medium steam pressure in the evaporation process, which demands additional energy consumption. Also the viscosity of black liquor is limited by the throughput of the pumps used for liquor transfer. An effective way to reduce viscosity is to keep the liquor under a temperature of 180 °C for 30 minutes since this destroys long organic molecules. [8]

The boiling temperature of black liquor is higher than the boiling temperature of water at the same pressure and varies with the composition of dissolved organic substances. This difference in temperature is called the boiling point rise. This parameter is the basis of the evaporation process.

The problems of foaming in the evaporation process are associated with the low value of surface tension of black liquor. Surface tension decreases with the increasing temperature and the decreasing concentration of the solution. The presence of turpentine and soap decrease surface tension therefore they should be removed from the liquor. [8]

The heat value is one of the most important parameters of black liquor because it shows the quantity of heat which can be obtained by burning. Organic and inorganic components of the liquor have different heat values as indicated in table I. [7]

Table I Heat values of spent liquor components [7]

| Component | MJ/kg | Btu/lb m |
|---------------------|-------|----------|
| Softwood lignin | 26.90 | 11.57 |
| Hardwood lignin | 25.11 | 10.80 |
| Carbohydrates | 13.56 | 5.83 |
| Resins, fatty acids | 37.71 | 16.22 |
| Sodium sulfide | 12.90 | 5.55 |
| Sodium thiosulfate | 5.79 | 2.49 |

Reactions taking place during burning also affect the liquor's heat value, for example the recovery reaction of sodium sulfate to sulfide consumes energy.

4.3 Physical and chemical conversions of black liquor in recovery boiler

The process of sulfate liquor combustion can be divided into three consecutive stages: drying; pyrolysis and devolatilization accompanied by alkali carbonization; char burning and mineral residue melting accompanied by the reduction of inorganic sulfur compounds (see figure 4). [7]

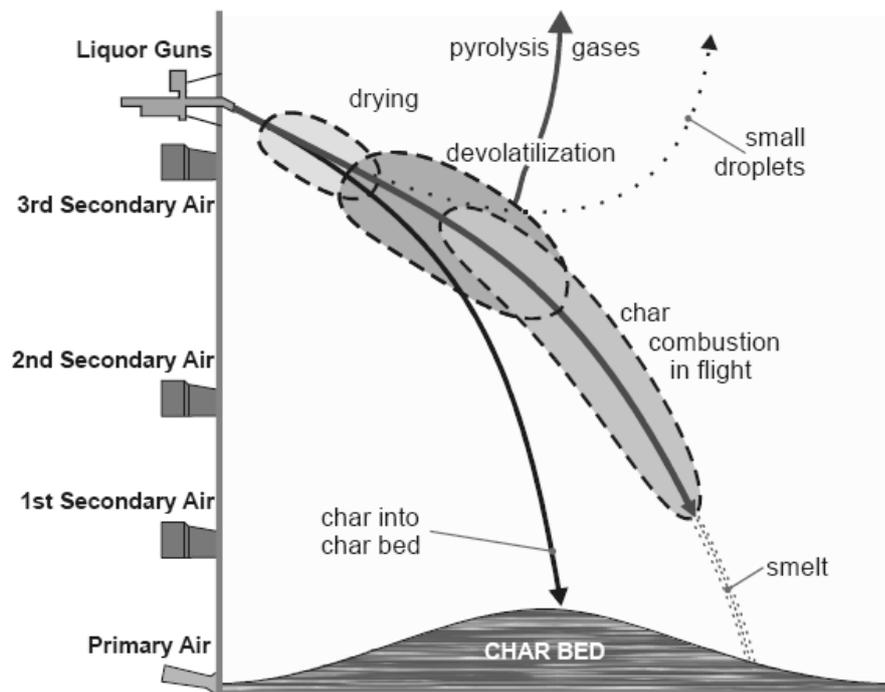


Figure 4. Stages of black liquor combustion [7]

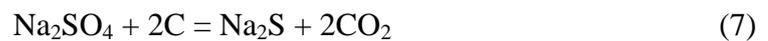
The liquor is fed into the recovery boiler in small droplets by spray guns in order to raise the efficiency of the burning process. Incoming particles are exposed to combustion gases and lose moisture. During drying, the size of the droplets increases. Black liquor drying time is determined by the speed of heat transfer to the droplet. As a result of chemical interaction of liquor with flue gases occurring in the first stage, all of the free sodium hydroxide and a substantial portion of the sodium sulfide turn into carbonate, sulfite, thiosulfate and sodium sulfate. [5]

As the droplet moves away from the distribution device, temperature grows and the droplet passes into the second stage of sulfate liquor combustion known as pyrolysis. Pending pyrolysis of the liquor organic part, devolatilization takes place where methane, phenols and other volatile products, as well as various sulfur compounds, are released. [14]

Most of them are ignited due to secondary air and burn into a stream of hot gases forming CO, CO₂, H₂, H₂O, H₂S and SO₂. After this stage the swollen particle, whose volume enlarges 30 times in comparison with its original volume [16], includes approximately 75% inorganic salts and 25% non-volatile organic substances. The main part of the mineral compounds is sodium carbonate. Carbonate and sulfate contained in the original liquor and fresh sulfate added to the liquor before burning remain unchanged in the first two stages. An extra amount of sulfate and other mineral sulfur compounds (Na₂S, Na₂SO₃, etc.) can appear within the second period of the liquor combustion due to the decomposition of organic matters composed of sulfur and sodium. [5]

The final stage of black liquor combustion is char burning and the melting of mineral salts. Complete burning of coal requires a certain amount of air. Primary and secondary air enter directly into a zone of burning and are intended to burning off the organic carbon (see figure 4).

The burning of carbon leads to the formation of smelt which mostly consists of inorganic material. The size of the droplet in the smelt is a half of its initial size. Sodium reduction reactions occur in the region of char bed [7]:



The degree of reduction in modern enterprise exceeds 90%, and defined as:

$$\text{Reduction, \%} = \frac{Na_2S}{Na_2S + Na_2SO_4} \times 100 \quad (9)$$

The major components of the sulfate smelt flowing from the furnace comprise sodium carbonate, sodium sulfide, and sodium sulfate. Other sodium compounds such as sulfite, thiosulfate and chloride are present in small amounts. In addition, various by-products of reactions and small particles of unburned coal can be found in the smelt. [3]

5 RECOVERY BOILER

After the evaporation process, concentrated black liquor goes into a recovery boiler for incineration. The first recovery unit was invented by G.H. Tomlinson in 1920, which effectively allowed the recovery and reuse of chemicals used for the delignification of wood. Eventually Tomlinson's boiler was further developed, becoming energy efficient. [15]

Currently, the recovery boiler has three chief objectives: energy (steam manufacture), technological (regeneration of alkali from black liquor and fresh sulfate) and environmental (exclusion of the basic share of useless by-products of pulp production). The recovery boiler differs from a traditional steam boiler by paying a big attention to the regeneration of sodium sulfide. [15]

5.1 Recovery boiler design

Various constructions of the recovery unit exist: one, two, and three drum boilers. Two drum type boilers have received primary distribution (see figure 5). Performance of the boiler is 1700 tons dry solids per day. The recovery boiler is divided by a bullnose or nose arch into two sections: the furnace section, where chemicals are recovered and the convective heat transfer section, whose function is to manufacture steam. The bullnose helps to create a uniform flow of flue gases passing through the superheater, as well as to protect the superheater from the direct effects of heat coming in from the furnace. [12]

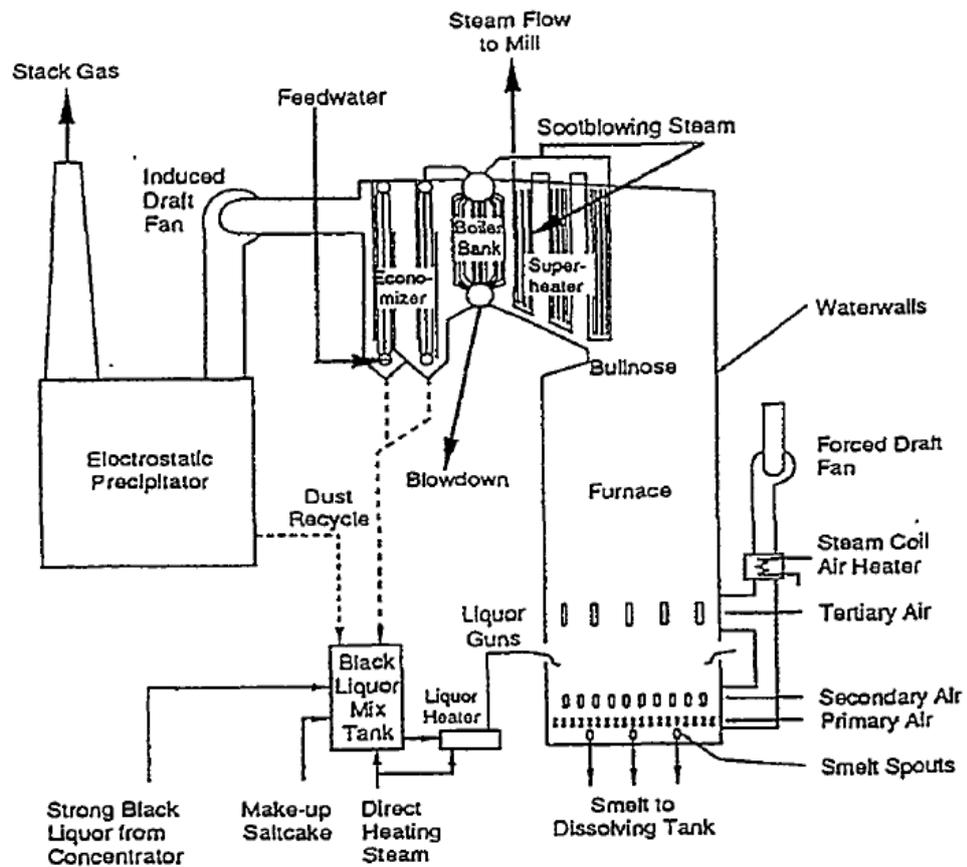


Figure 5. Two-drum recovery boiler arrangement [12]

5.1.1 Furnace section

Furnace

The furnace is a rectangular shaft, whose height depends on the size of the boiler and can be more than 60 m high. The walls and bottom of the furnace are completely shielded by boiler tubes, whose diameters vary from 6.4 to 7.6 cm and which are located 1.25 to 2.5 cm apart from each other, either linked by fins or are in contact with each other. The material used for pipe production is a carbon steel [16]. The temperature at the bottom of the furnace reaches 1000 °C, while the outlet gas temperature is about 100-200 °C. [17]

The liquor guns

The black liquor is injected into the burning chamber by means of liquor guns. This type of feed ensures the even distribution of the liquor onto the field of burning, the regulation of the amount of solution entered and also the uniform formation of the char bed at the bottom of the furnace. The guns are settled down directly into the walls of the furnace opposite to each other at a distance of 5 m above the floor. There are different types of spray gun nozzles, but the most widely used is the splash plate nozzle, which functions by forming a liquor sheet using a flat plate attached to the nozzle at an angle of 45 °C to the stream. [12]

Air burning system

Air is supplied to the furnace for the efficient combustion of the liquor. The air flow is subdivided into streams and introduced at different levels of height in the boiler, at different temperatures and pressures. The higher in the furnace the stream is introduced, the higher the stream's temperature and pressure. The number and size of air ports, as well as the distribution of the air-to-height ratio of the furnace can vary. [9]

Smelt spouts

Smelt is the resulting product of mixing and burning the liquor with air and mainly comprises reduced sulfide and sodium carbonate. This smelt is discharged from the boiler through water-cooled spouts into a dissolving tank and then it goes to causticization. The temperature of the smelt is approximately 850-900 °C. [18]

The spouts are located under the ports of primary air. If the floor of the burning chamber is inclined, they are situated in the lowest part of the furnace so the smelt can exit using gravity. If the floor horizontal, the smelt spouts are placed on one or two walls, 0.5 meters above the floor. [9]

5.1.2 The heat transfer section

During the burning of the black liquor, a significant amount of thermal energy is released and then used by the water-steam system of the boiler. This system is intended only for obtaining steam and includes an economizer, a boiler bank, a superheater and water pipes shielding the boiler furnace. The cycle of water to steam begins with the feed water being transferred to the economizer, where the water is heated to the boiling point. Steam formed during water heating is separated in a steam drum. Then the water flows through the tubes of furnace and of the boiler bank. The water from the boiler bank is used for cooling the recovery boiler walls. [12]

The energy released during the chemical reaction of the liquor burning transfers through the walls of tubes to the feed water, which converts it into steam. The steam then goes to the superheater in order to increase its temperature and pressure to correspond to the operation requirements of a turbine that produces electric energy. Some of the steam from the turbine is utilized for technological needs, for instance the steam with a pressure of approximately 12 bars is applied to heat the cooking digester, while the low pressure steam is suited for the evaporation process. [10]

The flow of flue gas generated by chemical reactions in the furnace boiler is a source of heat for the superheater, boiler bank and economizer. After heat transfer, the flue gases come into the tail part of the recovery unit to capture inorganic dust. The gases are cleaned using precipitators, cyclones and scrubbers. Cleaning raises the profitability of the boiler work thanks to saving chemicals and reducing gases emissions into the atmosphere. [19]

5.1.3 The soot blowers

One of the basic operations of boiler service is the cleaning of its heat transfer surfaces of pollution. As mentioned above, inorganic compounds present in black liquor are burnt in the recovery unit. At a certain temperature of combustion they evaporate and some of them move to a mass of the flue gases. Also particles of black liquor and coal are taken away by the gas flow. The chemical reactions occurring in the gas phase are the reason for the formation of deposits on the surface of the boiler. These include Na_2CO_3 , Na_2SO_4 , Na_2S , KCl and NaCl . [16] The deposit composition depends on deposit formation mechanics, black liquor type and conditions of burning. Different parts of the boiler have different composition of deposits. The scale in lower part of the boiler has more sodium carbonate and sodium sulfate and less sodium sulphide, sodium chloride and potassium chloride while deposits in the upper part of the boiler consist of less Na_2CO_3 , Na_2SO_4 and more Na_2S , KCl and NaCl .

Particles of dust generated in the combustion chamber stick to the surface of the pipe and form a deposit. The stickiness of dust is determined by state of the component particles. If the majority of the particle is molten it means that the dust is able to stick. A small quantity of the sodium and potassium salts, which appear in the liquor from the wood, dramatically raises the probability of dirt accumulation on the surface since it decreases the temperature at which sodium dust becomes sticky. [20]

The formation of the deposits leads to a deterioration of heat transfer from the flue gas to the feed water or to the generated steam [19]. To prevent fouling and plugging problems in the boiler, soot blowing is used. The blowers extract contaminations from the fouled surface by jet steam. The rejects from the surface can either be returned into the recovery unit along with the entering black liquor or fully taken out. There are about 50 soot blowers in the boiler located on the right and left sides of its convective zone. They take 5 to 12 % of the steam manufactured by the recovery unit. The effectiveness of cleaning depends on its frequency, the nozzle devise of the blowers, the cohesion degree of deposits with the surface of tubes and the pipe's design. [16]

5.2 Progress of the recovery boiler arrangement

The desire of enterprises to reduce costs per unit of pulp production, including those costs related to energy consumption, and increased demands to reduce environmental impacts drive the constant improvement of recovery boiler design. [21]

5.2.1 Modern recovery boiler

Performance of the modern recovery boiler is 3000 tds/d with a main steam pressure of 90 bars and a temperature of 490 °C. The increased productivity and steam data in comparison with the two-drum boiler require the following constructional changes: the transition from a two-drum design to a single drum, with a vertical steam generation bank, three-level air submission to the multilevel, and change of the device superheater. Figure 6 shows the arrangement of the modern recovery boiler. [22]

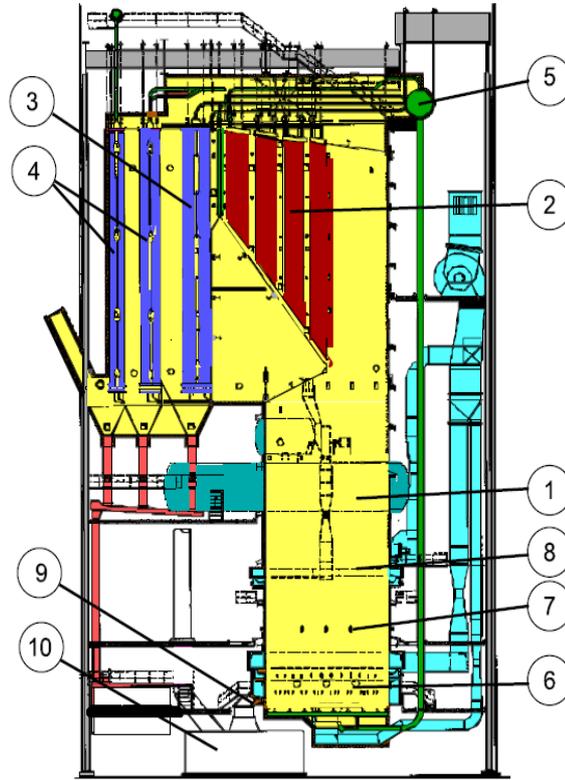


Figure 6. Arrangement of the modern recovery boiler: furnace-1, superheater-2, boiler generation tank-3, economizers-4, single steam drum-5, primary and secondary air ports-6, liquor guns-7, tertiary air-8, smelt ports-9, dissolving tank-10 [22]

The adoption of single-drum construction is safe and effective. The boiler becomes safer by improving the monitoring of water parameters and, as a consequence, the boiler can operate at higher levels of operational performance.

The multilevel system of air distribution is the reason for the temperature increase in the furnace that leads to use of liquor with higher concentration of dry solids, which increases productivity.

The emissions of flue gases decrease due to less water content in the liquor. The problems of surface pollution are partly solved by using the vertical steam generation bank, which resembles the economizer device accessible for cleaning, and by broadening the distance between the pipes of the superheater. [21]

5.2.2 Current and future recovery boiler

Presently, there are many boilers available for the combustion of black liquor working at a temperature of 520°C and a pressure of 104 bars. The capacity of such boilers is about 5000 tds/d. The most modern boilers for burning liquor are bigger than the boilers of 1990's. For example area of boiler floor can be reached 200 m^2 . Figure 7 shows a current recovery boiler. [22]

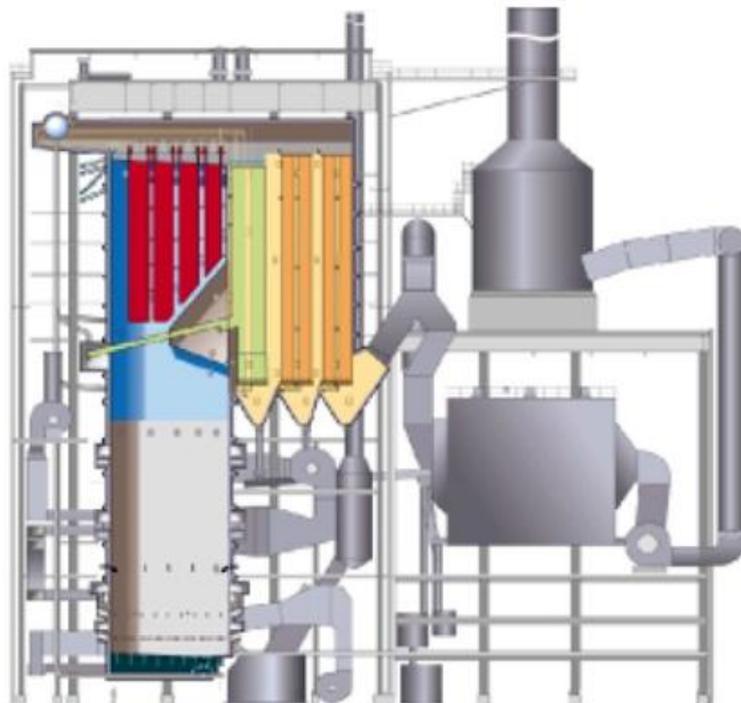


Figure 7. Current recovery boiler [22]

Figure 8 shows the average of recovery boilers and their capacity as a function of time. In accordance to the figure, the production of recovery boilers is decreasing, but their capacity is increasing. [23]

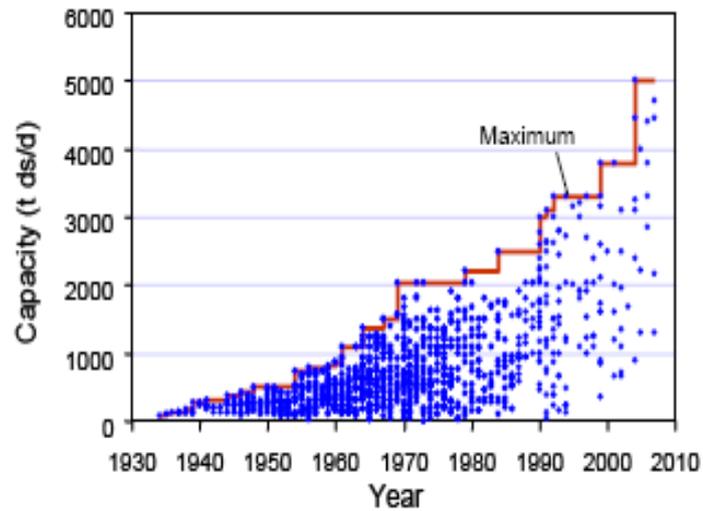


Figure 8. Change in recovery boiler capacity depending on its start-up year [23]

The constant change of parameters in the burning process has provoked some alterations to the design of the recovery boilers [22]:

- the temperature growth of the steam requires that the heat transfer surfaces are protected from thermal impact, therefore these surfaces should be installed behind the nose arch and made of high quality metals,
- the high output temperature of the steam increases superheater loading and it is reflected in its design,
- the pressure growth causes temperature to rise and hence the amount of entered air is decreased,
- the quality of the furnace's materials is improved,
- the boiler's volume is increased.

5.3 Changes in main operating conditions of burning liquor to get more power

The purpose of changing of the key parameters of burning liquor and as a consequence of the recovery boiler design is increasing steam and electrical energy generation.

Steam manufacture depends primarily on the content of dry solids in the black liquor. An increase of dry matter from 65 to 80% induces a growth in steam flow of 7 %, thus the increase of dry solids by 5 % gives a steam growth productivity of more than 2 %. Figure 9 shows the dependence of steam flow formation as a function of the dry solids content of black liquor. [21]

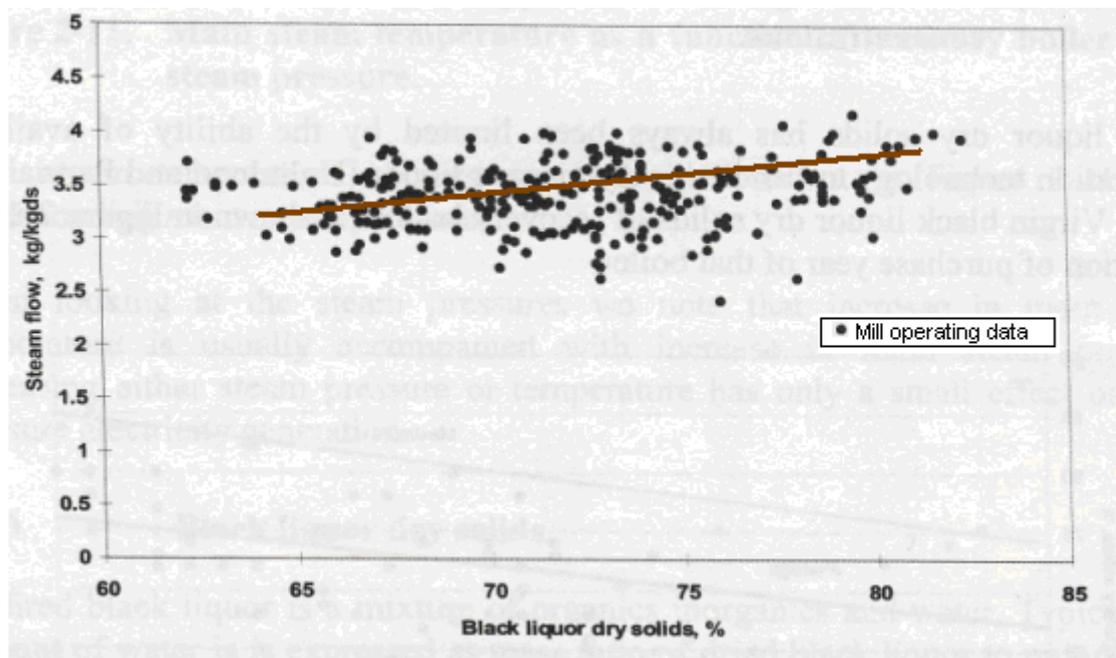


Figure 9. Change of steam manufacture in accordance with dry solids content of black liquor [21]

The second important factor affecting steam flow is the high heat value of black liquor, which increases steam flow (see figure 10). The main steam parameters of temperature and pressure, as well as sulfidity of black liquor, impact the manufacture of steam as well [24].

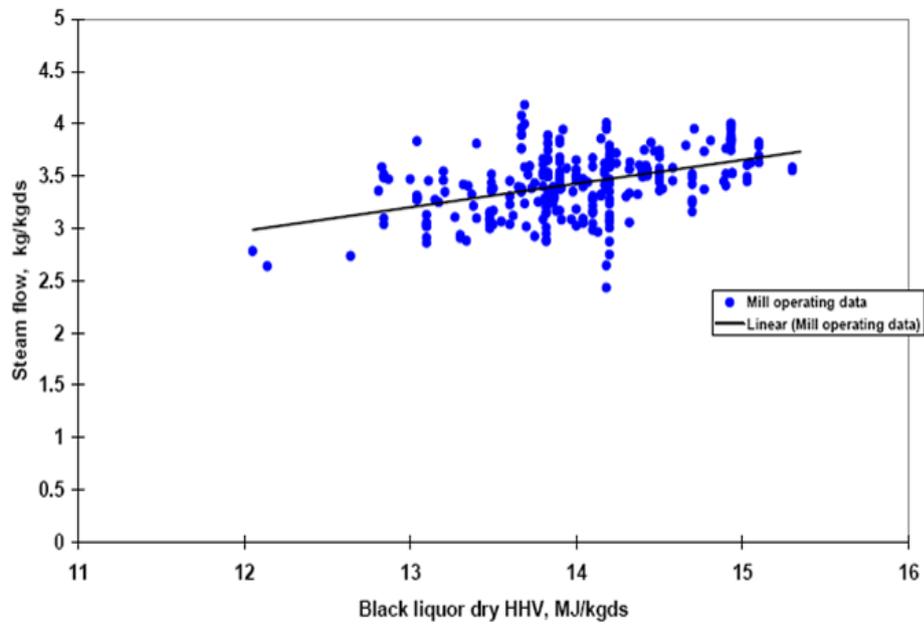


Figure 10. Change of steam manufacture in accordance with high heat value of black liquor [24]

In order to increase power production from the recovery boiler, three major parameters should be increased: dry solids content of the black liquor, steam pressure and temperature (see figure 11). [21]

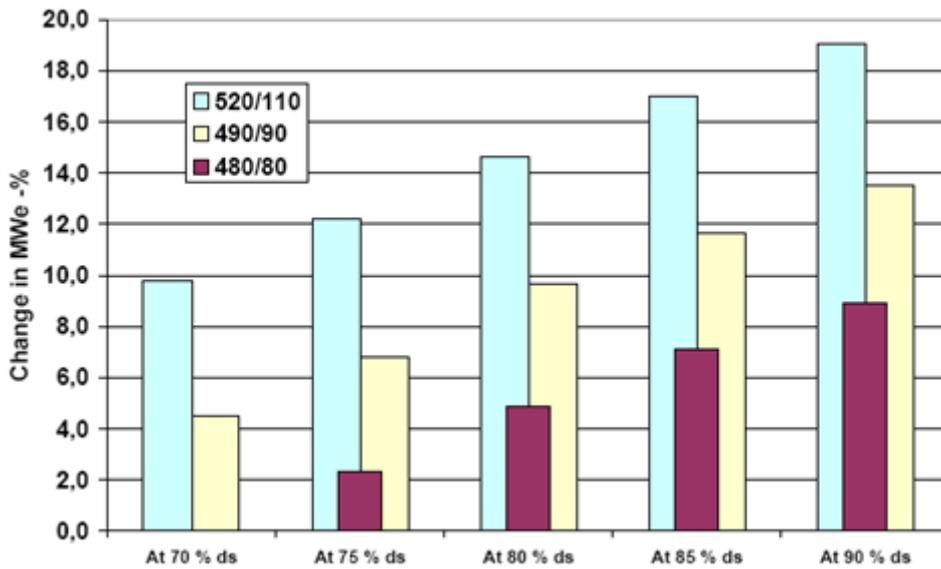


Figure 11. Impact of steam data and dry solids content of black liquor on electricity production from the recovery boiler [21]

As shown in the figure above, a rise in dry solids content of even 5 % and an increase of steam data result in a growth of power productivity from the recovery boiler. Appendix 1 (figure 1 and 2) illustrates changes in the concentration of liquor dry solids and main steam parameters as a function of time. [21, 23]

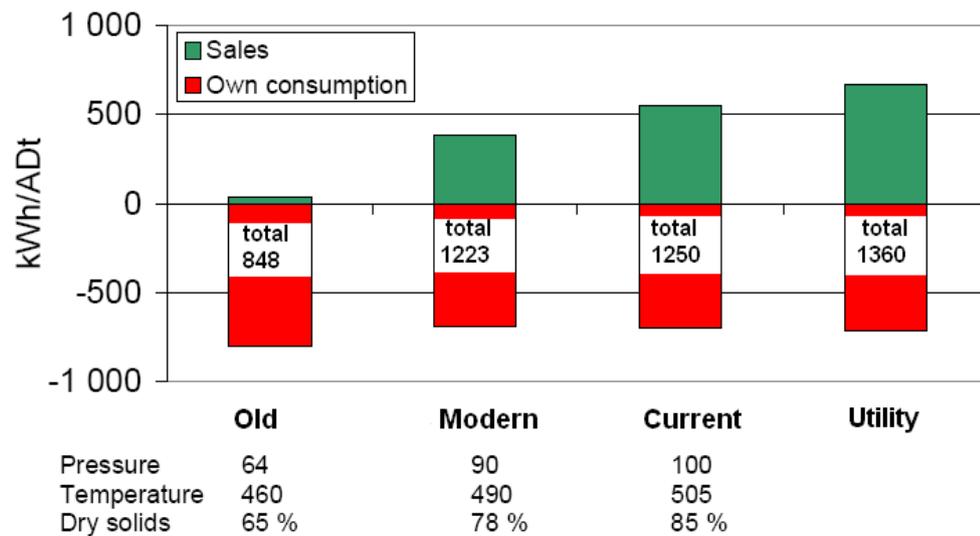
The results of rough calculations (see appendix 2, figures 1-3 and tables I-III), which were done on the basis of sources [25] and [26], are tabulated and indicate the amount of electric energy kWh/ADt produced by a recovery boiler depending on changes to the key parameters of black liquor burning (see table II).

Table II Electric energy generation of recovery boiler as function of combustion conditions of black liquor

| Main parameters of black liquor combustion | Electric energy generation by RB, kWh/ADt |
|--|---|
| T = 450 °C P = 60 bar Dry solids = 75 % | 662.4 |
| T = 480 °C P = 87.2 bar Dry solids = 80 % | 899.5 |
| T = 520 °C P = 104.5 bar Dry solids = 85 % | 1257.3 |

In accordance to the table, raising of the main steam parameters and concentration of black liquor leads to the significant increase in the produced power per ton of pulp.

Figure 12 also shows data on electric energy production by various types of recovery boiler as well as the amount of power which is used for its own needs and for sale. As one can see by figures, an increase of black liquor dry solids concentration and main steam parameters, the current and the future recovery system, the heart of which is recovery boiler, enables the production of extra power (approximately equal half of total produced electric energy) which can be sold.



* Total amount of energy is roughly calculated by author, kWh/ADt

Figure 12. Energy balance of pulp mill with using of different recovery boilers [27]

The following parameters, in addition to the ones listed above, having a positive impact on power production are:

- the application of combustion air with higher temperature and the regenerated heat of flue gas after ESP which produces an additional 5 MWe,
- the temperature increase of feed water which produces an additional 5 MWe,
- the use of reheating for steam with a pressure of 90 bars and temperature of 490 °C which promotes the generation of a supplementary 6 MWe, but further growth of steam data will give only an additional 1 MWe. [27]

To summarize one can conclude that the development of the recovery boiler and the liquor burning process will be directed towards the further increase of the concentration of dry solids, and the use of higher parameters of steam, combustion air and feed water for efficient electric energy generation. In turn, this will lead to a more aggressive environment, which will result in a more expensive material for the protection of the boiler, and a qualitative system for the removal of potassium and chlorine compounds must be used, which will accordingly require significant investments.

5.4 Disadvantages of recovery boiler operation and prerequisites to search for alternative technologies to liquor burning

The recovery system of Kraft mills is a mature technology with a long path of development. Currently, there are more than 500 black liquor burning boilers with a range of productivity from several hundred to 5000 tons of dry solids per day. [28]

Despite the fact that the development of the recovery boiler continues towards the improvement of its efficiency and safety, Tomlinson recovery boilers suffer from integral deficiencies, the main ones being:

- their relatively low power efficiency,
- a probability of smelt-water explosions,
- a problem of sulfur balance management,
- gas emissions,
- corrosion problems,
- a significant capital investment cost. [29]

Relatively low energy efficiency is a consequence of the relatively low steam data and the loss of energy with smelt and flue gases, together representing more than 15% of the heat which can be obtained from the burning of liquor. [8]

Smelt-water explosions are a very big problem in the existing recovery system. This is the result of the interaction between water and smelt, which leads to a rupture of boiler construction. Water can leak from the waterwall and furnace floor. An advanced boiler control system significantly reduces the number of smelt-water explosions, and now the frequency of explosions varies from 1 to 2 times a year. [30]

The problem of sulfur balance management associated with the inability to separate the flow of sodium and sulfur, which is desirable in the case of polysulfide cooking. [28]

Finally, the recovery boiler is a very capital-intensive unit at the pulp plant. An aggressive environment provokes the corrosion of interior parts of the boiler, leading to the destruction of its construction and therefore to avoid this, high quality protective

materials must be used. The demands of the materials increase with the desire to obtain more energy by creating more severe conditions of the liquor burning, and as a result, capital costs increase. The implementation of boiler modernization in order to raise capacity to 20 % or to reduce emissions means a new air system. Its installation will require about 15-45 million euros and about 45-60 days of plant shutdown. In the case of replacing the existing recovery boiler with a new one, the cost would be between 100 and 200 million euros and it would take between 3-7 days for its realization. [27]

All of the shortcomings mentioned above are the impetus for the introduction of alternative black liquor combustion technologies. Also it is the appropriate time to take action, since the service life of boilers which were built before 1980 and of reconstructed boilers is expiring or has already expired. Therefore there is a favorable economic climate today for the adoption of alternative technologies.

6 BLACK LIQUOR GASIFICATION

Black liquor gasification (BLG) is the process of converting organic compounds into combustible fuel gases comprising mainly hydrogen and carbon monoxide, and inorganic compounds into substances appropriate for recovery cooking chemicals. BLG technology has received great attention since 1960 and is currently under rapid development as alternative process of recovering chemicals and energy, thanks to its potential advantages compared to the existing recovery system, which include:

- an enlarged capacity for electric energy recovery,
- an enlarged capacity for chemicals recovery,
- a natural splitting of sulfur and alkali streams leading to the possibility of application in advanced pulping processes, increasing the yield of pulp,
- the exclusion of water-smelt explosions due to absence of water or steam tubes inside the reactor,
- cleaner production from an environmental point of view (emission reduction of NO_x and SO_x), and
- a cut in servicing expenditures.

Several variations of the gasification process of black liquor are at different stages of their development, all of which can be divided in two classes: high-temperature and low-temperature gasification. This classification is based on the operation temperature, which can be higher or lower depending on the melting point of inorganic substances found in black liquor or based on their physical state when they come out from the reactor. [31-33]

The most interesting attempts of accomplishing low-temperature and high-temperature black liquor gasification processes are summarized in table III.

Table III Attempts of development BLG technology [29, 33]

| | |
|-------------------------------|---|
| Low-temperature gasification | • Copeland process |
| | • SCA-Billerud process |
| | • DARS process (Direct Alkali Recovery system) |
| | • St. Regis hydrolysis process |
| | • VTT' circulating fluidized gasification process |
| | • ABB' circulating fluidized bed gasification process |
| | • MTCI/TRI's fluidized bed steam reforming process |
| High-temperature gasification | • NSP or "Ny Sodahus Process" |
| | • Champion/Rockwell molten salt gasification process |
| | • Chemrec' Entrained-flow gasification process |

Presently, the most promising and effective low-temperature and high-temperature gasification technologies under development are those of TRI and Chemrec companies respectively. [29, 33]

A detailed description of MTCI/TRI and Chemrec technologies and their comparison between each other are given below.

6.1 Low-temperature gasification of black liquor

Low-temperature black liquor gasification (LTBLG) is a gasification process which is carried out at a temperature below the melting temperature of inorganic chemicals present in black liquor. The most successful process of this was developed by the Manufacturing Technology Conversion International Company (MTCI) and commercialized by ThermoChem Recovery International Company (TRI). In this gasification technology, TRI applies the indirect heating of black liquor in a steam fluidized bed at a temperature of approximately 600 °C and at atmospheric pressure. As gasification equipment, TRI utilizes a steam reformer (see figure 13), which has two main output products: synthesis gas (syngas) and alkali salts as solids. Indirect

gasification creates conditions of organic substances converting into product gas in the absence of air or oxygen. Since steam plays a role of gasification and the fluidizing agent and transfers its energy to black liquor, the need of direct combustion of the feedstock in the presence of air or oxygen disappears. [34]

6.1.1 Status of indirect black liquor gasification

Two demonstrations of TRI's steam reformer on a commercial scale were carried out in North America: one of the units was installed at Georgia Pacific Mill in Big Island, Virginia, USA and the second one was installed at Norampac Paper Mill in Trenton, Ontario, Canada. [32]

Georgia Pacific Mill in Big Island, having a capacity of 1000 t/d of linerboard and 600 t/d of corrugating medium, uses a sodium carbonate process. The smelters used, which were initially installed, had the function of chemical recovery but energy recovery was not carried out. In 2001, the indirect gasification process was used instead of the smelters. Initially gas produced was cleaned and then burnt in pulse combustors. The capacity of the steam reformer was 200 t/d of black liquor dry solids. The system included two reformers and four pulse combustors (see appendix 3, figure 1). The process was shut down in 2007. During work the following weaknesses were identified: tar formation leading to plugging problems, incomplete conversion of carbon, and carburization problems. [34]

Norampac Paper Mill makes 500 tons per day of corrugated board and utilizes sodium carbonate pulping methods. Before the implementation of the gasification process at the mill, there was no recovery system and black liquor produced was bought by other countries, where it was applied as a road spray for dust suppression. In September 2003 a black liquor steam reformer was taken into use. The productivity of the unit is 115 tons of black liquor solids per day. Unlike in Big Island, Norampac uses only one steam reformer and an auxiliary boiler to burn off produced syngas. The first demonstration was completed in December 2003 (see appendix 3, figure 2). The main

issue during the gasification process was plugging problems. After numerous tests by TRI at both the Big Island and Ontario mills, the steam reformer was relaunched again in April 2004. The results of the gasification process are a 99 % recovery of sodium supplying the mill by process steam and with 100 % environmental technology. Currently Norampac's steam reformer prolongs its work. [34]

In spite of the headway done in the field of black liquor gasification, TRI has decided to return to the gasification of traditional biofuels and use its gasifier for these purposes because of the technical problems appearing during BLG process. [33]

6.1.2 Conversion of black liquor during indirect gasification

The indirect gasification of black liquor via the steam reformer is called liquor steam reforming because this process is based on the reaction of steam with organic carbon (see Eq. 10) instead of partial oxidation liquor as is usual in the gasification process. The steam reformation is an endothermic reaction [36]:



According to the reaction above, the primary products of liquor treatment by superheated steam are hydrogen and carbon monoxide. Then steam interacts with carbon monoxide and more hydrogen and carbon dioxide are obtained (see Eq. 11).



During the drying and heating of black liquor, a significant amount of hydrogen, carbon monoxide, carbon dioxide and methane is formed via the release of volatile components [37]. Over 90 % of the sulfur compounds in black liquor are converted into sulfide gas under the influence of the superheated steam [34].

The typical composition and heating value of syngas achieved by black liquor steam reforming after its separation from hydrogen sulphide is shown in table IV. Carbon dioxide produced during liquor steam reforming combines with potassium and sodium hydroxide to obtain their carbonates (Na_2CO_3 and K_2CO_3) in the form of solids. [37]

Table IV The typical composition and heating value of cleaned syngas produced by indirect gasification [38]

| | |
|-------------------------------------|-------|
| Hydrogen (H_2), % | 61.9 |
| Carbon monoxide (CO), % | 23.7 |
| Carbon dioxide (CO_2), % | 10.5 |
| Methane (CH_4), % | 3.5 |
| Heating value, MJ/kg | 20.95 |

In summary, the results of the conversion of black liquor in the steam reformer are: the production of hydrogen-rich and medium Btu synthesis gas (syngas) and the almost complete segregation of sulphur compounds from alkali.

6.1.3 Description of the indirect black liquor gasification process and equipment

As mentioned above, the indirect gasification is based on converting the organic components of black liquor into syngas without direct combustion and executed by means of the steam reformer used as gasifier. The layout of the steam reformer is shown in figure 13.

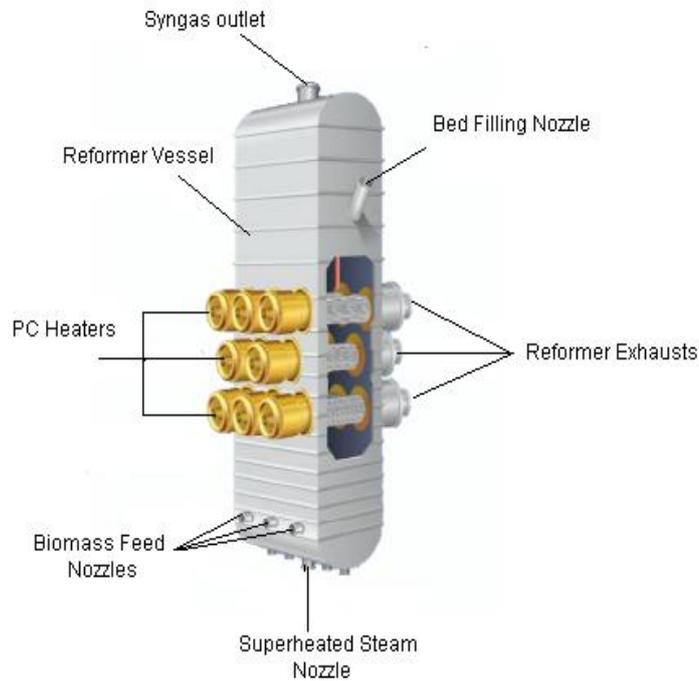


Figure 13. Steam reformer layout [36]

The bed material, which in the gasification technology of black liquor is sodium carbonate, is introduced in the steam reformer first. The size of sodium carbonate particles varies within the limits of 100-600 microns. The bed material serves as a catalyst promoting a more intensive interaction of the gasifier agent (steam) with the feedstock (liquor) by increasing the reaction surface area and thus raising the reformer capacity. After filling the reformer vessel with sodium carbonate, superheated steam is fed into the vessel, preliminary going through the superheater. The steam has two functions: the first is fluidizing bed material and the second is heat transfer from the source of heat to the feedstock. [36]

Pulsed combustion heat exchangers (PC heaters) are the source of indirect heating (see figure 14).

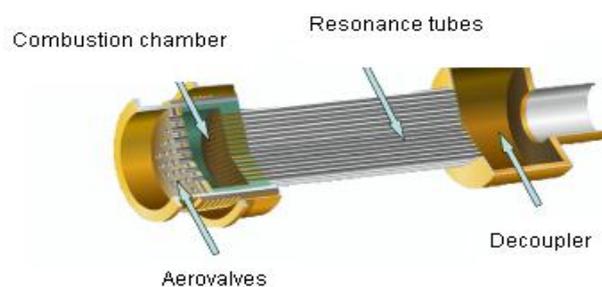


Figure 14. Arrangement of pulsed combustion heater [36]

A mixture of fuel and air, the flow rate of which is adjusted by aerovalves, enters into the combustion chamber and is ignited by a pilot flame. The incineration of this mixture leads to its expansion and fuel gases are pushed into resonance tubes and then leave the heater. When fuel gases leave the combustion zone, a vacuum is formed bringing more fuel and air into the chamber and also the phenomenon of the reverse motion of gases remaining in the tubes. A fresh mixture is ignited by returning hot gases and the process repeats itself. The frequency of the process (pulsations) is 60 times a second. The heat transfer efficiency of the heater is provided by perpendicular arrangement of its pipes to the streams of bed materials and steam, and also by a permanent change of the direction of flue gases. [36]

Black liquor is fed into the vessel after the bed reaches operation temperature, which is lower than the slugging temperature of liquor components. As soon as the feedstock enters the reformer, water contained in the liquor evaporates and then volatile components are liberated. [36]

Inorganic salts in the form of sodium carbonate and calcium (present in a small amount) are discharged from the reformer as dry solids. Cyclones installed at the top of the reformer are intended to separate solids taken away by produced gases. Figure 15 illustrates the work of the reformer. [36]

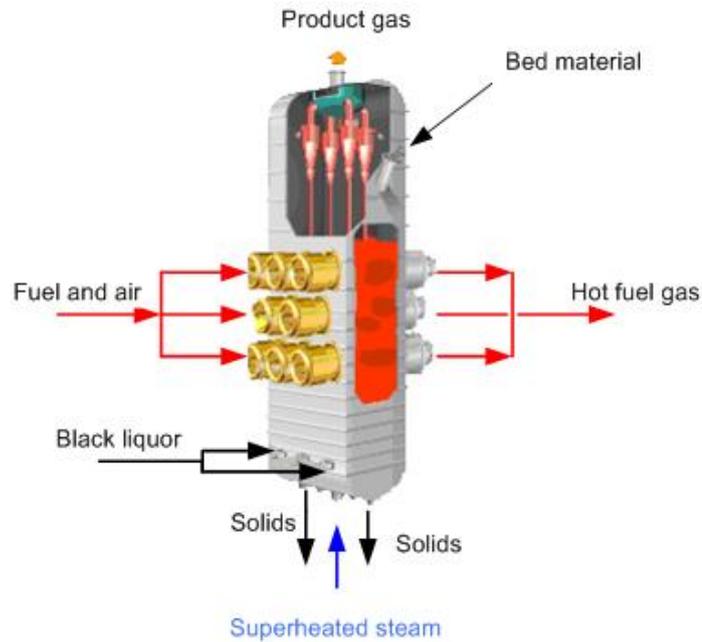


Figure 15. Black liquor steam reforming process [36]

In addition to carbonates, the outgoing solids contain non-process elements (calcium and silicon) and unburnt carbon, which are removed by counter current washing and filtering after solids dissolution. The cleaned alkali solution is used in pulp mills for the preparation of white liquor and undesired elements are discharged as dregs. Figure 16 illustrates a simplified cleaning system of syngas and green liquor generation. [37]

The syngas leaving the gasifier passes through a cleaning and sulfur recovery system. Firstly, the gas is quenched and impregnated with water in a heat recovery steam generator (see figure 16). Then undesired particles are moved off by scrubbing and the gas goes to cooling. Purified of solids and chilled gas is sent to the multistage counter current scrubber where it loses sulfur hydroxide by absorption in a mixture of sodium carbonate and caustic solution producing green liquor. [37]

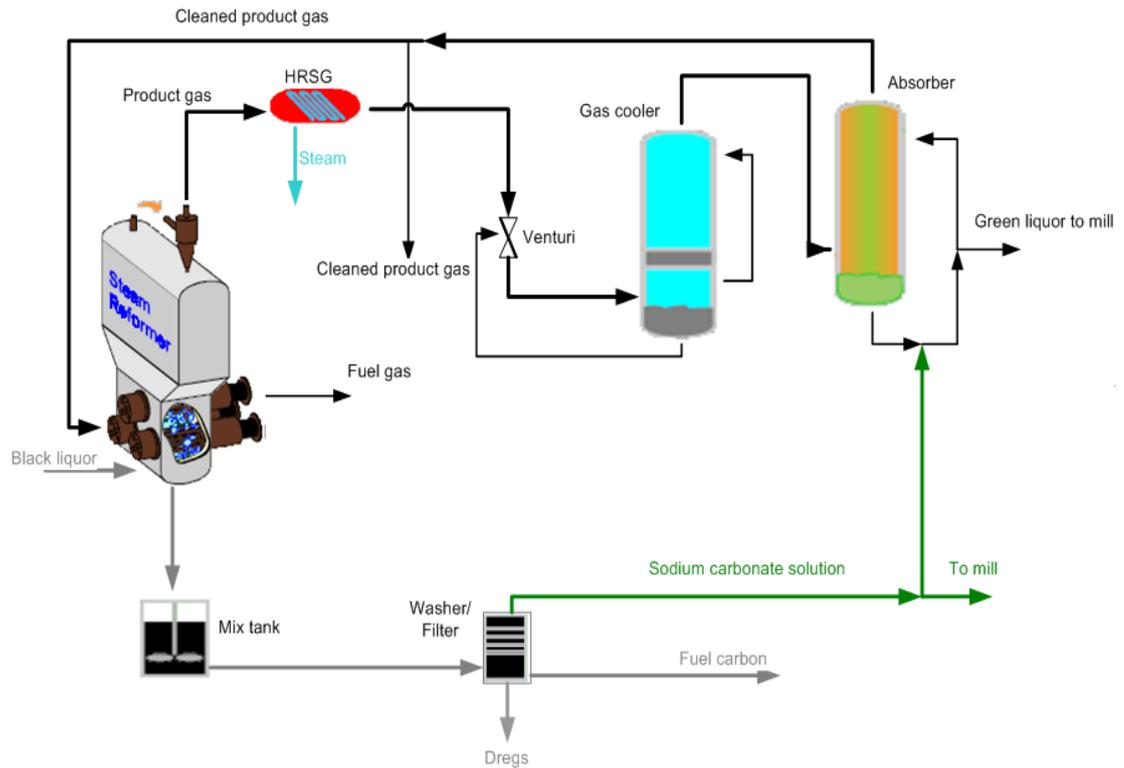


Figure 16. Production scheme of cleaned syngas and green liquor [39]

The indirect gasifier is self energy efficient since the syngas and steam produced during the process are the main inputs needed for the reformer work. Product gas and fuel gases are sent to the reformer boiler for steam generation. [37]

The main issue of the steam reformer working properly is keeping the required temperature, which in turn decreases the probability of tar formation that causes clogging and plugging and avoids the agglomeration of bed material. [34]

6.2 High-temperature black liquor gasification

The technology, in which black liquor is gasified resulting in synthetic gas and smelt is called high-temperature black liquor gasification (HTBLG). The current state-of-the-art process of HTBLG is a Chemrec's process was developed and commercialized by Swedish Chemrec AB Company. This technology is an analogue of biomass entrained-flow gasification and concerns direct methods of BLG.

Chemrec BLG, which application depends on operational conditions, can be utilized as booster to a traditional recovery boiler or for its full replacement. In the first case, liquor is gasified using air under high temperature and pressure close to that of atmospheric. In the second case, the process is supported under high temperature and high pressure using oxygen as a gasifier agent. [32]

6.2.1 Status of direct black liquor gasification

There are four Chemrec gasification technology demonstrations, which were performed in the United States and in Sweden. Development of direct gasification began with high temperature, low pressure (near atmospheric) technology in which air was supplied to the system for liquor atomization. The capacity of the first air-blown gasifier installed at the Assi Domän Mill in Frövifors, Sweden was 75 t/d of black liquor solids (see figure 17). The gasifier operated during 1991-1996 and was removed from manufacture due to lack in need for additional power. [34]

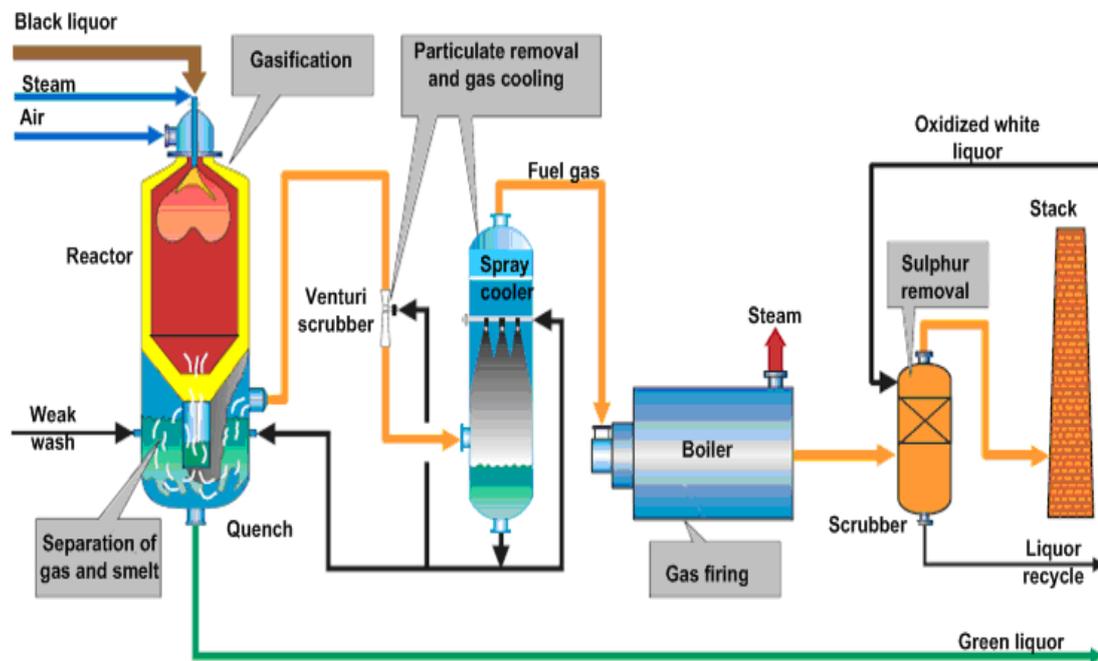


Figure 17. Chemrec air-blown gasification system, Assi Domän Mill, Frövifors [40]

The first demonstration using a Chemrec's gasifier as a booster system was performed at Weyerhaeuser Mill in New Bern, North Carolina, USA in 1996. The booster operated in parallel with the recovery boiler and its productivity was 300 tons of black liquor solids per day (see figure 18). Within the gasifier, many problems were observed and the majority of which were refractory problems that were the reason for its shut down in 2000. During the booster reconstruction, the following major changes to the shell effectuated: a shell made of carbon steel was installed instead of made of stainless steel, refractory alumina was introduced as the lining, the distance between the shell and the lining was filled by metal foam. In 2003, the booster was reintroduced to the process and capacity increased by 4 % in the period of 2003-2004 in comparison with 1999. [34]

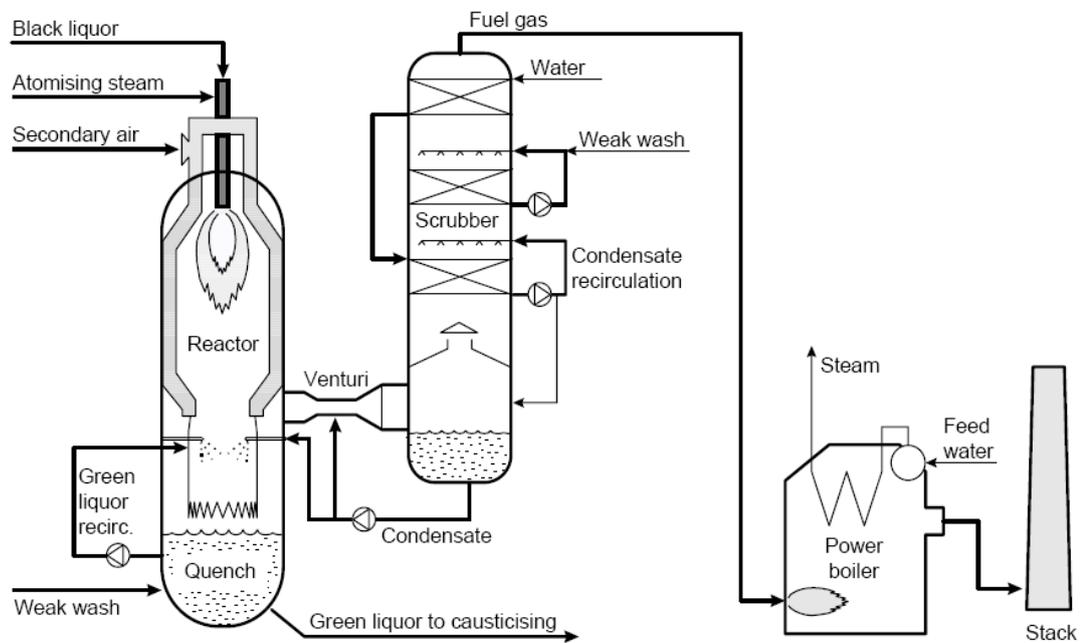


Figure 18. Chemrec booster gasification system, Weyerhaeuser Mill, New Bern, North Carolina, USA [30]

A trial of the air-blow gasifier under pressure conditions was performed at the Stora Enso Mill in Skoghall, Sweden, in 1994. The capacity of the gasifier was 6.6 tons of black liquor solids per day. In 1997 oxygen was used instead of air as an oxidizing agent (see figure 19). The capacity of the unit grew up to 11 tons of black liquor solids per day. The results illustrated that under pressure conditions it is possible to achieve a high quality of green liquor along with high carbon conversion. [34]

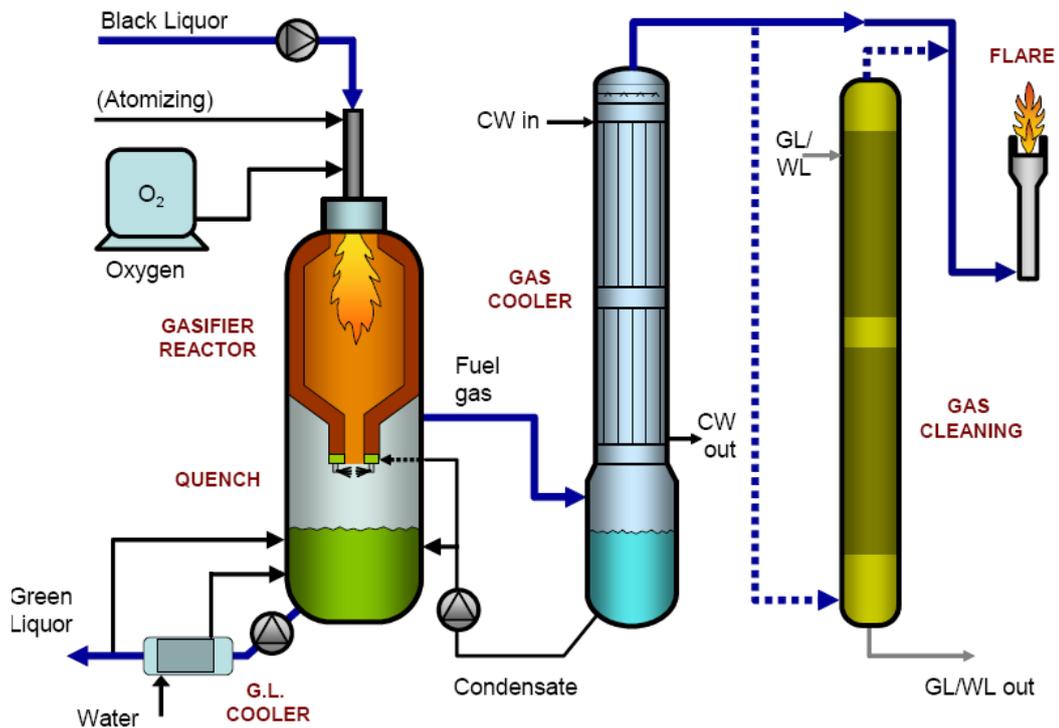


Figure 19. Chemrec gasification system, Stora Enso Mill, Skoghall, Sweden [35]

Development of the pressurized gasification technology has led to the construction of a demonstration plant (DP1) with a capacity of 22 tons of black liquor solids per day in Piteå, Sweden. The plant's process conditions are a pressure of 30 bar and temperatures of 1000 °C. This project is very promising as the replacement for the traditional system of recovery chemicals. Therefore, the description of direct gasification technology presented below focuses on the high temperature high pressure gasification process applied in DP1. [34]

6.2.2 Conversion of black liquor during high-temperature gasification

Similarly in the traditional recovery system (see section 4.3), black liquor in direct gasification is atomized and goes through drying, pyrolysis and char conversion stages, producing gas and smelt (see figure 20).

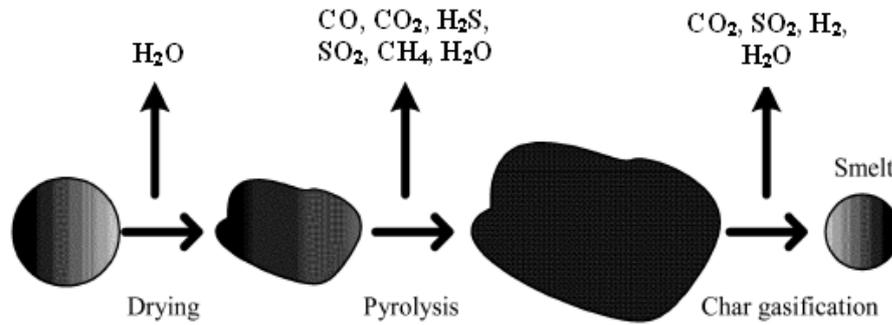


Figure 20. Conversion of black liquor during direct gasification [14, 41]

In line with the picture above, during the first stage of drying, black liquor droplets lose their moisture. Then the organic matter contained in black liquor is thermally degraded resulting in volatile gases and char formation. The remaining organic matter in solid char interacts with the gasifier agent and the result of this reaction is combustion gases and inorganic salt as smelt. [41]

One of the aims of direct gasification, as well as indirect is the production of a large amount of combustible gases (CO and H₂). There are two endothermic reactions providing the formation of these gases in Chemrec's gasifier (see Eqs. 12 and 13).

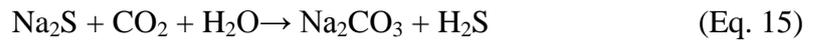


The heat required for the realization of these interactions is produced by the exothermic reaction of combustion of black liquor organic part:



During air-blown gasification, part of the sulfur compounds in the liquor equaling to 15 % is converted into hydrogen sulphide. When oxygen is a gasifier agent, this amount increases to approximately 55 %. It means that the degree of sulfur recovered in direct gasification is less than in the case of liquor steam reforming. [42]

Equation 15 shows the reaction of hydrogen sulphide formation [36].



Typical composition and heating values of sulfur cleaned synthesis gas generated during air and oxygen gasification are shown in table V [35].

Table V Typical composition and heating values of cleaned syngas produced by direct gasification technology [35]

| Characteristic of syngas | Air-blown gasification | Oxygen-blown gasification |
|--------------------------------------|------------------------|---------------------------|
| Hydrogen (H ₂), % | 10-15 | 30-35 |
| Carbon monoxide (CO), % | 8-12 | 28-32 |
| Carbon dioxide (CO ₂), % | 15-17 | 30-35 |
| Methane (CH ₄), % | 0,2-1 | 0,5-2 |
| Nitrogen (N ₂), % | 55-65 | 1-4 |
| Heating value, MJ/kg | 2.5-3.5 | 7-9.5 |

According to table 5, the gas leaving the gasifier where air plays the role of a gasifier agent mostly consists of nitrogen, which leads to a reduction in concentration of combustible gases (hydrogen and carbon monoxide) and as a result, the out coming gas is low energy. [38]

6.2.3 Description of direct black liquor gasification process and equipment

For high temperature and high pressure gasification, Chemrec uses an installation mainly comprising two parts: a gasifier and a gas cooler (see figure 21). Chemrec's gasifier is divided into an upper section, which is an entrained flow reactor, and a lower section that is a quench cooler.

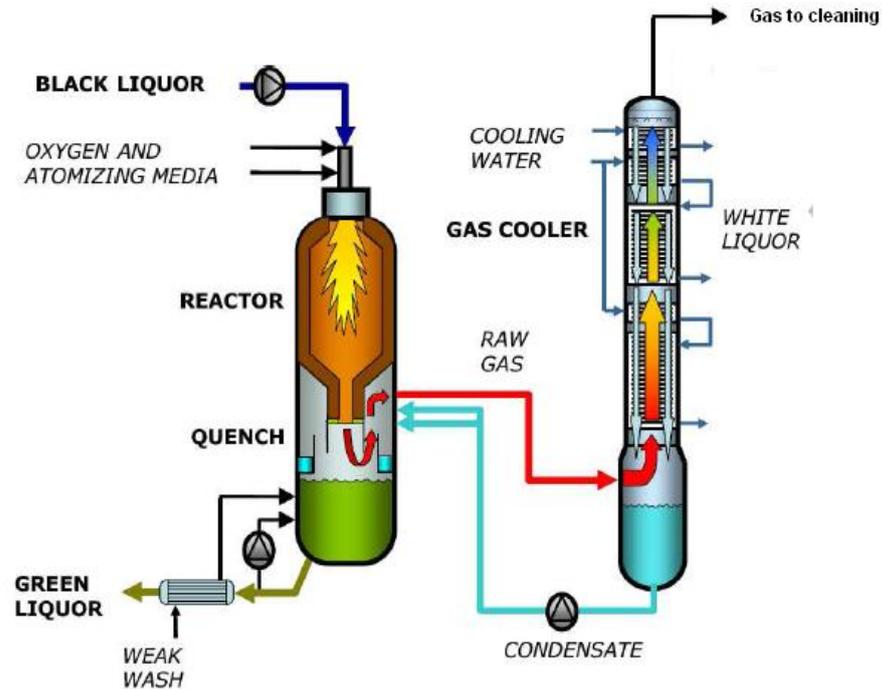


Figure 21. Chemrec's installation of black liquor gasification [40]

Black liquor is introduced into a spray nozzle along with steam required for its atomization. Droplets of liquor are gasified under the following operation conditions: the temperature is approximately 1000 °C and the pressure is approximately 30 bars. Oxygen is applied as a gasifier agent that is injected into the gasifier simultaneously with the liquor. The ratio of oxygen to liquor is an important because it defines the process temperature. The results of the reaction are a combustible gas chiefly consisting of H₂, CO, CO₂ and a smelt of inorganic salts. The retention time of droplets in the reactor needed to transform organic matter into gas is 5 to 10 seconds. The process conditions are very aggressive and therefore, in order to avoid the destruction of the reactor, cooling screens of water tubes located along the reactor walls can be applied. Usually a ceramic lining is used to protect the reactor. [43]

The products of the reaction are discharged through the reactor bottom into the quench vessel, which is the most complex section of the gasifier. The functions of this vessel, situated directly under the reactor, are: quick product cool down, effective separation of melted salts from the gas, green liquor formation and side reaction prevention. Side reactions result in poor green liquor quality, leading to an increase of causticization department load. Condensate from the gas cooler is sprayed into the quench vessel which results in the separation of smelt from the gas by gravity. The smelt drops to the bottom of vessel and green liquor is generated by adding weak liquor or water. The quench temperature is approximately 220 °C. [14]

The green liquor formed is sent to heat exchangers where it is chilled by means of heating the weak wash passing through the first exchanger and the condensate from the evaporating plant introduced in the second exchanger, to a temperature equal to 205 °C. Then the weak wash consisting of sodium hydroxide goes to the quench vessel and condensate is transported to the gas cooler. Green liquor having a temperature of approximately 90 °C is depressurized and cleaned of dissolved gases in order to be used for white liquor preparation. [30]

The produced gas leaving the gasifier is sent to the gas cooler, which is a pressurized cylindrical vessel divided into three or four parts for chilling. Chilling water coils are placed in the upper part of the cooler. In the upper level the flow of generated condensate goes down in the opposite direction to gas. The temperature at the bottom of the cooler equals the temperature in the quench. During gas cooling, medium and low pressure steam are produced in the upper three parts and lowest parts, respectively. The temperature of the cooling gas reaches 40 °C. Water vapors in the incoming syngas in an amount of approximately 70 % are condensed and undesirable particles are removed along with the water vapor from the gas, therefore the cooler performs a cleaning function. The condensate from the cooler is fed into the quench vessel. Since in cooled gas, the content of hydrogen sulfide is 1.4-2.5 % the syngas is transferred for the further treatment from sulfur compounds before being use for steam or electric energy production. [30, 43]

After chilling, the gas is transported to the gas cleaning system, whose primary function is the extraction of sulphurous gases, specifically H_2S , by absorption. Selectively absorbed H_2S is sent to the stripping installation from which exits as off-gas. [30]

Hydrogen sulfur can be sent to short time contactors where direct absorption is performed or to a Claus unit, where sulfur is recovered from it. In the first case, sulfur compounds are absorbed in white liquor (NaOH) passing in sequence through three time contactors. The content of hydrogen sulfide in the gas at the outlet of the unit is 0.1% of the incoming H_2S . This type of gas cleaning is used in the gasification plant in Piteå, Sweden. In the second case, elemental sulfur is generated through a heating process using a Claus burner, converting approximately half of the sulfur compounds in the incoming gas. After the gas has cooled, a further conversion process is carried out by three catalytic Claus reactors. In order to condense the sulfur produced, the gas is chilled between each reactor. Then the liquid sulfur is used for white liquor preparation. [30]

The main issue facing Chemrec's gasification process is the selection of material protecting the gasifier body from aggressive conditions. Also attention to the feed pump, burner and quench nozzle is required because of plugging and sealing problems. [43]

6.3 Comparison of low-temperature and high-temperature gasification processes

Demonstrations of low-temperature and high-temperature black liquor gasification showed that both of these processes can be used to replace conventional recovery systems and have the potential opportunity for improvement the last one. To understand which of these gasification methods is the most feasible in the pulp and paper industry, a comparison of methods is given below.

The results of numerous studies indicate that TRI's gasification has some significant benefits over Chemrec's process, such as:

- a high degree of alkali recovery (99 %) from the liquor leading to simplification in the gas cleaning system,
- a much lower operation temperature requires less energy consumption to run the reactor and less energy is lost during gas cooling,
- the creation of gasification conditions in the absence air or oxygen, which leads to a hydrogen-rich, medium-Btu product gas (low-Btu product gas in case of HTBLG process),
- a higher lifespan for the gasifier lining and also limited alkali silicates formation due to the recovery of alkali as dry solids,
- a higher sulfur/sodium split ratio, achieving a degree of sulfur recovery from syngas of over 90 % due to a lower operation temperature (50 % of sulfur/sodium split ratio in case of HTBLG). [34, 44, 45]

The complete segregation of sulphur compounds from alkali values during indirect gasification opens opportunities for polysulfide cooking. In contrast, it has the unfavourable effect of increasing the causticization system's load more so than in the case of direct gasification. Another shortcoming of low-temperature gasification is the problem of the equipment plugging caused by tars and the high molecular weight of sulfur compound generation. The main and crucial drawback in the case of the low-temperature gasification is a low rate of reaction resulting in incomplete carbon conversion and sulfur reduction or an increase in the size of equipment. The residual time in the steam reformer takes 50 hours. [45, 46]

Thus, based on the literature reviewed, it can be concluded that, in spite of the fact that low-temperature gasification surpasses high-temperature gasification in many areas, the latter is the most advanced and commercially feasible technology for replacing the traditional recovery system due to the high speed of the gasification process (residual time takes 5 seconds) and the desired quality of output products. Furthermore, for the cogeneration of gasification with a gas turbine pressurized system is more preferable

because the pressure of the fuel gas carried should be higher than in the combustion chamber of the gas turbine. [44]

Based on the assumption above a technology which is more capable of becoming a decent alternative to the existing recovery system at pulp mills and can increase the amount of electric energy generated from black liquor is the oxygen-blown gasification because it is more technically ready for use in the industry than the low-temperature alternative.

6.4 Black liquor gasification combined cycle

Increasing energy production is a crucial factor contributing to the implementation of the gasification process at a pulp mill. Energy efficiency is improved due to the integration of black liquor gasification technology with the treatment of syngas in gas and steam turbines. This integration is called the black liquor gasification combined cycle (BLGCC) [47]. Chemrec's BLGCC is considered as an advanced alternative replacement for the traditional system of chemical recovery with a recovery boiler performing the main role. Figure 22 illustrates the black liquor gasification combined cycle. [30]

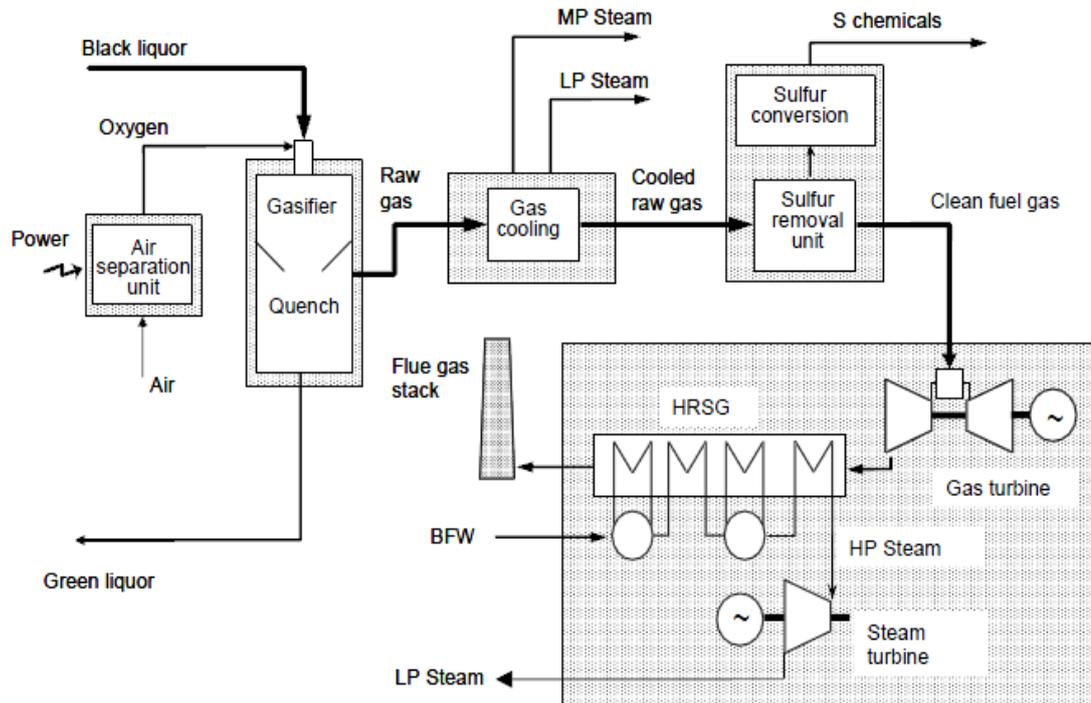


Figure 22. Chemrec black liquor gasification combined cycle [30]

The oxygen-blown, entrained-flow gasifier at high pressure and temperature is a key element in BLGCC. Several gasifiers can be used in a system that allows increase to its productivity if necessary. Generated syngas from the gasifier passes through stages of cooling and cleaning and then is preliminarily superheated and sent to the gas turbine where power is produced. The increment of power output of the gas turbine can be achieved due to the increasing mass flow of syngas through humidification in a saturator. In a heat recovery steam generator (HRSG), boiler feed water is converted into low-pressure, medium-pressure and high-pressure steam under the influence of energy of the expanded flue gas leaving the gas turbine. An additional amount of power is produced in a back-pressure steam turbine, which is supplied by high-pressure steam running from the HRSG. Using high-pressure steam, which results in a high power-to-heat ratio, is possible with BLG technology due to the purity of exhaust gases entering the turbine, which in the traditional system of chemical recovery is a problem leading to turbine destruction. Steam used for mill processes is taken not only from the steam turbine but also from the HRSG and a significant portion of medium-pressure and low-pressure steam is generated directly in the gasification reactor. [25, 30, 48]

BLGCC can be installed in parallel with the existing recovery boiler in order to avoid time spent on its installation and testing. In the case of a positive result of the new system, the recovery boiler can be removed from the production line.

6.4.1 Gas turbine

To date, most pulp enterprises produce electric energy by using back-pressure steam turbines. The average amount of power generated from the steam leaving the recovery boiler generally varies from 1100 to 1300 kWh/ADt [10]. The power-to-heat ratio of a back-pressure steam turbine is relatively low. Under existing market conditions, as the price of electric energy derived from fossil fuels grows, increasing on site the power generation brings savings to pulp mills. [28]

An effective way to improve the generation of electrical and thermal energy is the use of a gas turbine. Gas turbines are divided into two categories: aero-derivative and industrial. The second type of turbine has a lower pressure and therefore a lower power output than the first one, but for the combined cycle of steam and power production the industrial gas turbine is more suitable since the temperature of outlet gases is sufficiently for steam production. [47]

The application of the gas turbine for the utilization of gas manufactured during black liquor gasification is perhaps in the presence of following items: existence of apt burners, corresponding limits of compressors and high-purity input gas. [28]

The burners of the gas turbine must be adapted to support the burning of black liquor fuel gases which have lower heating value in comparison with natural gas. A change in the design of the burners, as well as its testing, demands capital investment but in this case, the results of experiments on the burners applied in the treatment of biomass, coal or residual oil fuel gases can be used. Presently, burners which are suitable for

combustion gases with low and high heating value are produced by such companies as General Electric, ABB, Siemens, Nuovo Pignone and EGT. [28]

The cogeneration cycle used in gasification of other fuel indicates that improvement of power efficiency possible within the existing limits of compressor.

The high purity of entering gases is very important since the presence of alkali compounds is a cause of turbine corrosion and hence reduces its service life. Almost all parts of alkali in the black liquor are converted into smelt, as in the case of the recovery boiler, but some part is capable of being evaporated. The possibility of alkali evaporation is inversely proportional to pressure; therefore it is a low in oxygen-blown gasifier where the applied pressure is high. Furthermore, a good cleaning system applied to the whole gasification process has a positive effect on syngas purity. Even without further treatment, gas coming from the gas cooler satisfies the requirement of the gas turbine. [28]

A significant drawback of the gas turbine application is its fix capacity; it can not be tailor-made as in case of steam turbines. Moreover, the productivity of pulp mills is not constant and it has an effect on the work effectiveness of the gas turbine because of the mismatch between the amount of gas that can be processed in a gas turbine and the amount of entering gas. Figure 23 shows the change in the scheme of flows in the BLGCC depending on the size of the gas turbine. [49]

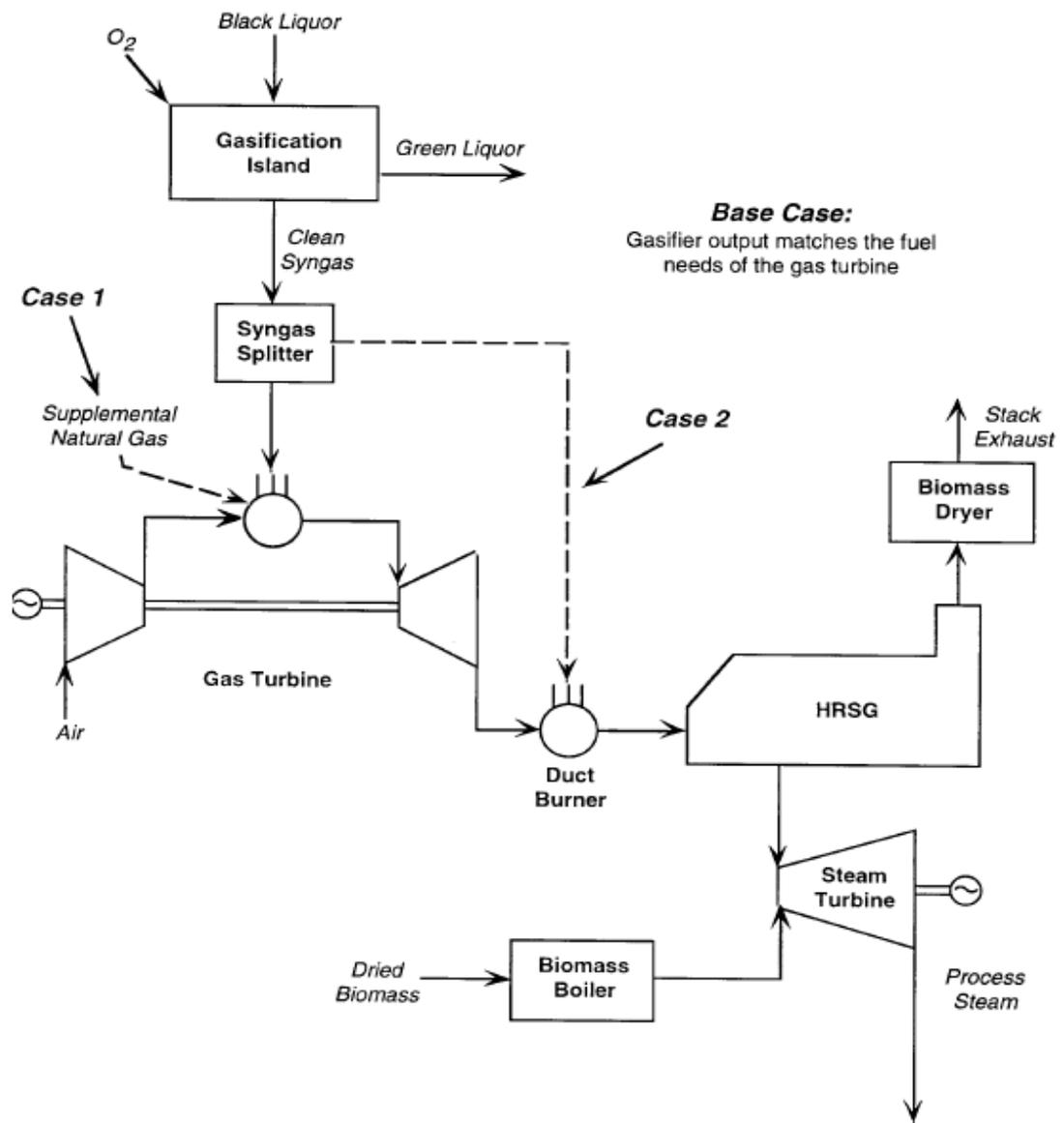


Figure 23. Change in BLGCC depending on the gas turbine size: 1) oversized, 2) undersized and 3) matched (base case) to the flow rate of black liquor [49]

According to the figure above, when the fuel requirement for the gas turbines is greater than the amount of incoming gas, the use of natural gas as a supplementary fuel is necessary. In the second case, when the amount of incoming gas is surplus, to be treated in the gas turbine, it is divided into two streams, one of which goes directly to the HRSG.

Figure 24 illustrates the impact of changes in the productivity of pulp mill on the amount of energy produced by the BLGCC and on overall system efficiency.

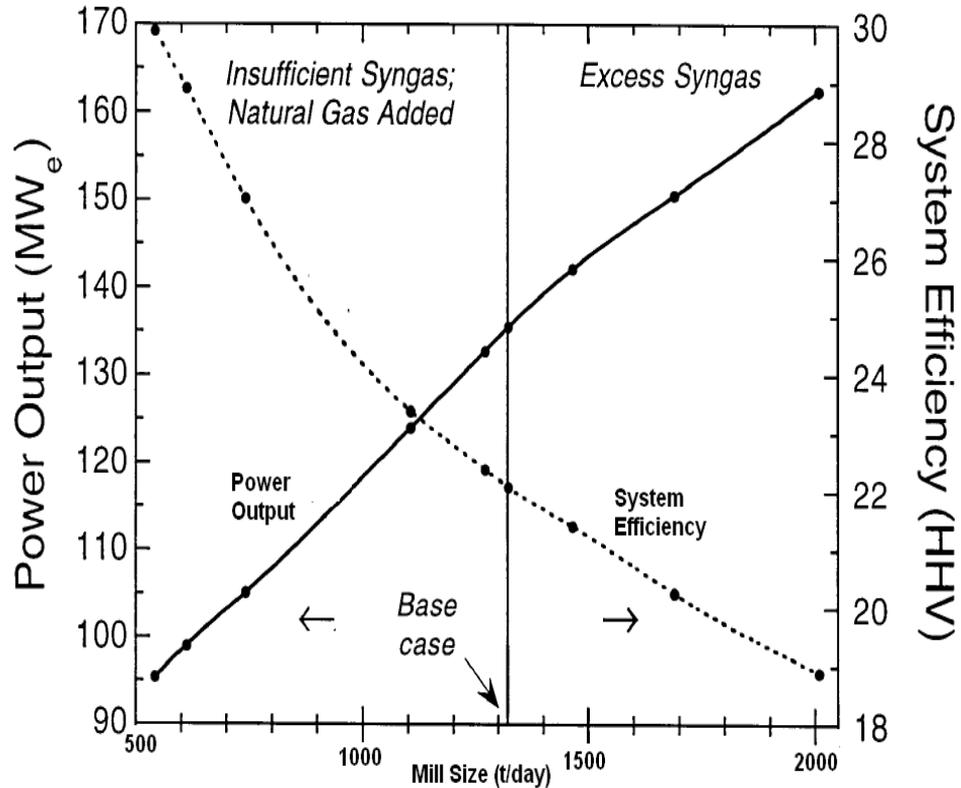


Figure 24. Power output and system efficiency of BLGCC as function of mill size [49]

In line with the figure, a decrease in pulp production leads to decrease of power output efficiency. This is a consequence of the fact that less steam is required for operating needs, and less biomass is used for its production, which also affects the power output manufactured by steam turbines. In addition, the amount of steam coming out from the gas turbine remains constant as the lack of syngas on its entrance is replaced with natural gas. This does not interfere with the process of black liquor gasification and improves the ratio of natural gas to synthetic resulting in an increase in overall system efficiency. The growing of pulp production on application of a fixed-size gas turbine leads to a reduction in overall system efficiency as the surplus of gas from the gasifier is only used in the steam turbine, but the total power output grows because the extended output from the steam turbine. [49]

Thus the increase or decrease of pulp mill productivity has a negative influence on the utilization of the combined cycle, because in the first case, all of gas produced could not be effectively used as it doesn't pass through the full combined cycle, while in the second case the use of additional fuel is requisite.

6.4.2 Comparison of energy generation of BLGCC and Tomlinson-based recovery system

Electric energy generation

The cold gas efficiency of the pressurized oxygen-blown gasifier is 70 %. In other words, this part of the heating value of black liquor can be regenerated as heating from out-coming syngas. [28]

The gas efficiency depends on temperature and content of the black liquor dry solids, so in order to get the maximum value of gas efficiency, the temperature at which the gasification process is carried out should be the lowest but sufficient for obtaining the required carbon conversion and the speed of sulfate recovery. [28]

In addition to the cold gas efficiency of the gasifier for predicting possible power outs during the gasification, the efficiency of combined cycle which includes a gas and a back-pressure steam turbine must be also taken into account. The combined cycle efficiency equals 42-47 %. [28]

Relying on the assumptions indicated above it was calculated that the possible amount of power produced by the oxygen-blown gasifier for the combined cycle described in appendix 4 (figure 1 and point 1) can reach 149.1-166.9 MW. More accurate data on the energy production by the gasifier in the BLGCC are obtained on the basis of calculations presented in appendix 4 (table I) and accounts for 117.6 MW or 2131.7 kWh/ADt. Therefore it can be accepted that the oxygen-blown gasifier is able to generate about 2100 kWh/ADt.

Extensive studies have been performed, in which power balances of different gasification types are compared with traditional recovery systems and whose results showed that an essential amount of energy can be generated by implementing the BLGCC.

Various information on the difference in energy production derived from the BLGCC and traditional recovery systems are shown in the literature sources. Table VI, derived from table II and appendix 4 (table D), illustrates that this difference depends on which type of recovery boiler is used for comparison.

Table VI Power production comparison of different types of recovery boiler and gasifier*

| | | Amount of power production per ton of pulp, kWh/t | Power produced from gasifier to energy produced from RB |
|------------|---|---|---|
| Type of RB | T = 450 °C P = 60 bars Dry solids = 75 % | 662.4 | 3.2 |
| | T = 480 °C P = 87.2 bars Dry solids = 80 % | 899.5 | 2.3 |
| | T = 520 °C P = 104.5 bars Dry solids = 85 % | 1257.3 | 1.6 |
| Gasifier | T=1000 °C P=25 bars Dry solids = 75 % | 2100 | |

* Author calculations based on sources [25, 26, 49]

In accordance to the table above, the oxygen-blown gasifier can generate three times more power than the tradition recovery boiler but less than two times of that generated by an advanced recovery boiler.

In order to evaluate the benefits of the gasifier technology before discussing Tomlinson's system from the point of view power recovery, it is necessary to consider not only power produced during the process but also the power consumption. Table VII shows the energy balance, including generation and consumption of electric

energy of a new recovery boiler system and Chemrec pressurized combined cycle taken from sources [27]. Such a recovery boiler, which has power capacity equal to 1700 kWh/t, is installed at Kymi Pulp Mill, Finland.

Table VII Power generation capability of Chemrec’s BLGCC and Tomlison-based system [27]

| | Power generation kWh/ADt | Power consumption kWh/ADt | Power sale kWh/ADt |
|--|-----------------------------|------------------------------|-----------------------|
| Pressurized gasification Chemrec type | 2100 | 1050 | 1050 |
| New pulp mill with RB | 1700 | 730 | 970 |

In line with table VII, Chemrec’s BLGCC has the ability to produce a significant amount of power, which exceeds the capability of today's Tomlinson-based recovery system by approximately 400 kWh/ADt. However, due to more power consumption in the combined cycle, only about 80 kWh/ADt can be generated as extra electric energy for sale as compared with the existing recovery system. It is a sufficient difference, for instance, in the case where the annual pulp capacity is 500 000 ADt and the cost of 1 MWh of power is 38 euros [51] the benefit from additional electric energy generation per ton of pulp would make 1.5 million euros annually.

Heat recovery

Owing to use of the gas turbine, in which incoming energy is rationally spent on power generation and to produce of significant amount of LP and MP steam in gas cooler, the steam cycle in BLG technology is small [28].

Based on the heat and mass balances of the BLGCC (see appendix 4, point II) the amount of the steam obtained from the gasification process was roughly calculated and it is 9.1 GJ/ADt, two times less than in Tomlinson-based system.

Thus production of steam by combined cycle does not meet pulp mill requirements where the steam demand stays on the higher level (see table VIII) and using of biomass boiler would be obligatory.

Table VIII Steam and electric energy demand of pulp mill [27]

| Pulp | GJ/t | kWh/t |
|------------------|----------|---------|
| Softwood | | |
| Unbleached | 7.5–10.6 | 400–490 |
| Unbleached dried | 10–13.9 | 520–630 |
| Bleached | 9–12 | 540–680 |
| Bleached dried | 11.5–15 | 660–800 |
| Hardwood | | |
| Unbleached | 7–10 | 390–500 |
| Unbleached dried | 9.5–13.2 | 500–650 |
| Bleached | 8.5–11 | 510–620 |
| Bleached dried | 10.9–14 | 630–760 |

Figure 25 illustrates that to reach the same process steam demand, the amount of biomass input in case of the BLGCC would be higher than in the Tomlinson-based system.

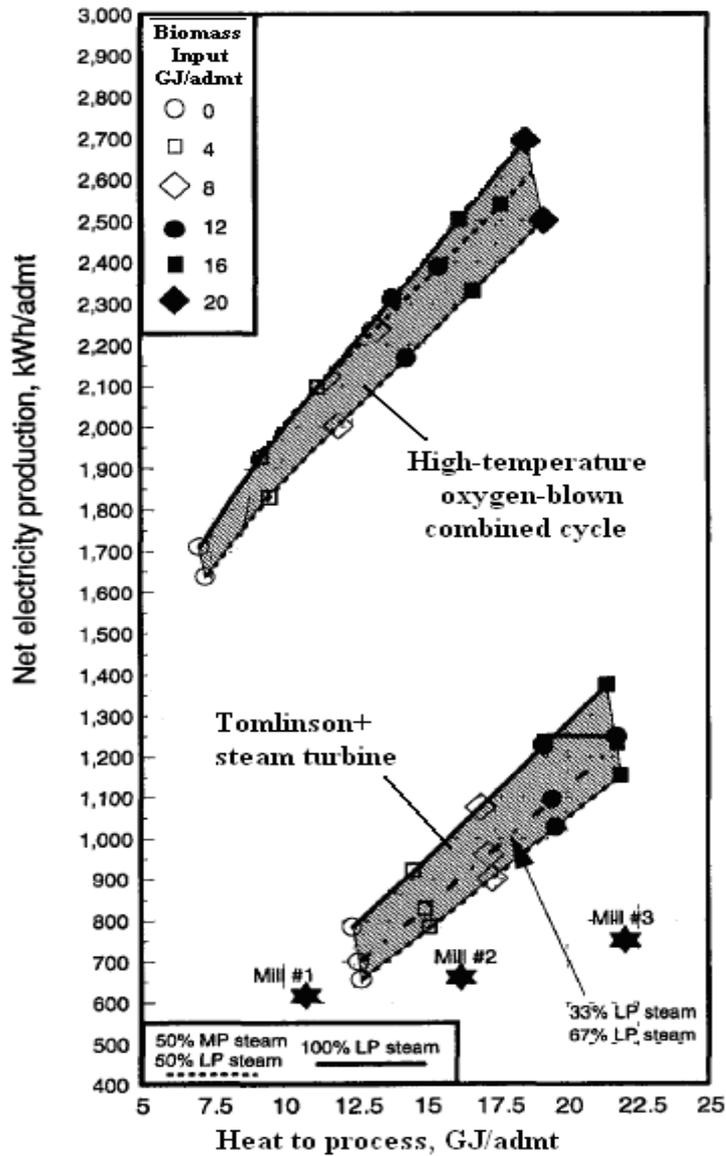


Figure 25. Summary performance of BLGCC and Tomlinson-based system [50]

In line with the figure above, the oxygen-blown gasification combined cycle can generate two to three times more electric energy than a system with an old recovery boiler on the condition the process steam consumption is at a higher level and at the bottom respectively [50].

The increase in the steam capacity of the combined cycle is possible due to pressure rising in the gasifier (see figure 10), because temperature of out-coming gas grows and it allows the efficient use of heat emitted during gas cooling for MP-and LP-steam recovery [28].

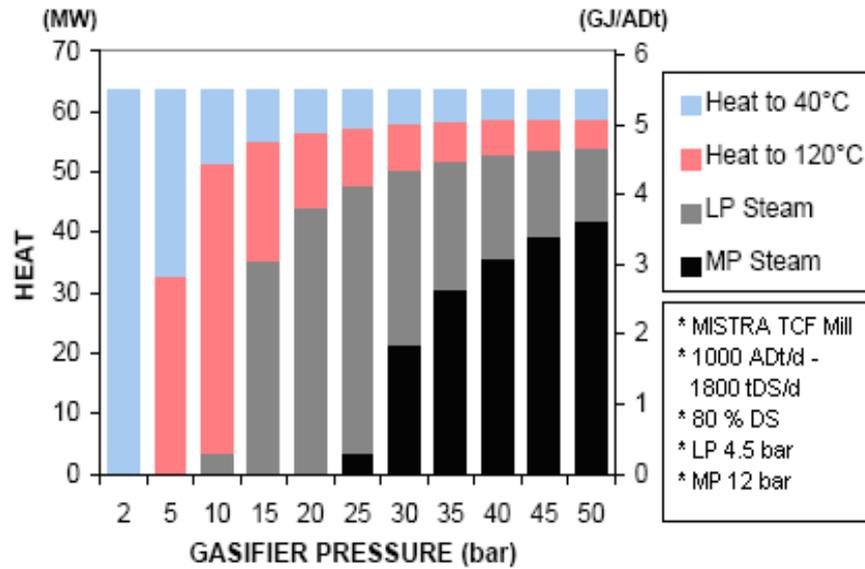


Figure 26. The impact of the pressure increasing on the heat recovery [28]

Besides the growth in pressure, which is restricted by the ability of the refractory to withstand an aggressive environment, an additional amount of heat recovered in the temperature range of 100-160 °C and below 100 °C can be used for preheating boiler feed water and for heating wash water used in bleaching plant [28].

To summarize the above mentioned the BLGCC increases power-to-heat ratio of the pulp mill. When producing more energy, the pulp mill suffers a loss of steam required for its processing needs and whether this is a negative consequence is determined by the price of steam and power production. In Russia the cost to generate 1 MWh of power is about 38 euros and steam is about 7-8 euros [51, 52]. The difference between the prices of these two types of energy in Finland is similar. Thus growing the power-to-heat ratio for pulp mills is the right direction to move in since it brings essential positive results from the economic point of view, which recalculates to an annual pulp production of several million euros.

6.4.3 The importance of the black liquor gasification process as power source

In order to evaluate the importance of the black liquor gasification process as an alternative method of electric energy production at existing pulp mill capacity, the place that this technology might take in the energy balance of countries such as Finland, whose fuel and energy resources are insignificant, and Russia, which has a vast reserve of primary energy sources, is considered below.

Finland is an energy-intensive country due to its developed industrial structure and its location in the north. However, the country has limited mineral reserves and as a result, great value is given to secondary energy resources and a considerable amount of energy is imported to satisfy the needs of industry. Table IX illustrates Finland's power production, divided by the source [53].

Table IX: Power production in Finland [53]

| Power source | Production, 2007 year | |
|--------------|-----------------------|------|
| | 10 ⁹ kWh | % |
| Wind | 0.3 | 0.3 |
| Oil | 0.4 | 0.4 |
| Waste | 0.5 | 0.6 |
| Peat | 5.8 | 6.7 |
| Coal | 8.5 | 9.8 |
| Bio fuel | 8.9 | 10.2 |
| Natural gas | 10.9 | 12.5 |
| Net imports | 12.8 | 14.7 |
| Hydro | 16.8 | 19.4 |
| Nuclear | 22.0 | 25.4 |
| Total | 86.9 | 100 |

As can be seen from the table above, the main power sources in Finland are: nuclear power, hydro and gas, respectively.

To compare black liquor gasification with other power sources it is necessary to calculate the amount of electric energy capacity achieved by this technology per year. According to appendix 5 (figure I) Finland produces 7.7 million tons of Kraft pulp per year. Taking into account that the BLGCC generates 2100 kWh per ton of pulp, the

annual power capacity of the country will be $16.2 \cdot 10^9$ kWh thus yielding only the performance of the nuclear and hydro power plant. One part of this recovered energy amount must be used primary for process needs in pulp mills, the rest being sold and equaling to $8.1 \cdot 10^9$ kWh/a (based on data table VII). Thus, the BLGCC can enter into a number of electric energy sources, which takes up the basic load to satisfy power demand in Finland.

Russia is a country with enormous natural resources including oil, gas and coal and this is a reason to focus energy sector on primary power sources. Thermal, hydro and nuclear power plants bring the main contribution to the power balance of the country (see table X) [55].

Table X Power production in Russia [55]

| Power sources | Production, 2005 year | |
|---|-----------------------|-----|
| | 10^9 kWh | % |
| Thermal | 610.0 | 64 |
| *Large hydro | 171.6 | 18 |
| Nuclear | 162.0 | 17 |
| *Other (biomass, small hydro, geothermal, wind) | 9.5 | 1 |
| Total | 953.1 | 100 |

* Renewable sources

In conformity with Russia's annual Kraft pulp production (see appendix 5, figure 2) which is $4.1 \cdot 10^6$ t/a, the amount of possible energy generation by gasification is $8.6 \cdot 10^9$ kWh/a, $4.3 \cdot 10^9$ kWh/a of which will be available for sale (based on table VII). Thus it can be assumed that BLG technology will not become a major power source in a balance of the Russian Federation but has an opportunity to increase share of green electricity.

Currently, the big attention is paid to environmental protection. Carbon dioxide emissions produced by incineration of fossil fuels (coal, oil and natural gas) lead to

greenhouse effect which is a reason of climate changing. Therefore it is important to increase the share of renewable sources in energy balance, especially, for such countries where fossil fuel is the major energy source.

Regardless of the role which the gasification process can adopt in the power balances of Finland and Russia or in other country for that matter, in view of the above specified data, the prices of electric energy generation and ecological regulations toughen it definitely brings a significant economic gain accounted for in the amount of several million euros.

6.4.4 Market of black liquor gasification implementation

The performance of the gasification system depends directly on the capacity of the pulp enterprise and the amount of black liquor produced.

As shown above, the manufacture of 2100 kWh/t electricity by a small gasifier with a gas turbine of 70 MWe requires the performance of pulp mills to be 1322 ADt/d or approximately 450 000 ADt/a. Increasing the power productivity by 3.5 times using of a commercial gasifier with a gas turbine of 250 MWe can be achieved if the pulp mill's capacity is increased by as much, which means in other words, approximately 1 600 000 t/a. On the assumption of this dependence, it is necessary to take into account the situation prevailing in the world of the pulp and paper industry. Table XI illustrates the capacity of chemical pulp mills and the amount of produced pulp in the world.

Table XI Pulp production in the world, 2000 [7]

| Capacity, t/a | World | |
|---------------------|-----------------|-------------|
| | Amount of mills | Capacity, % |
| 150 000 and less | 249 | 44.9 |
| 150 000-300 000 | 141 | 25.4 |
| 300 000-450 000 | 98 | 17.6 |
| 450 000 and more | 67 | 12.1 |
| Total | 555 | 100 |
| Total capacity, t/a | 120 000 000 | |

As the table shows, pulp mill production in the world lies within a wide range. The share of enterprises which exceed the capacity of 450 000 t/a is not insignificant and is continuously growing. Most of the smallest mills are located in China, while the largest belong to Brazil. [7]

According to source [58] during 2003, the productivity of pulp mills in Europe varied within the limits of 250 000 t/a to 700 000 t/a, with the biggest producers in Sweden and Finland. The precise data of Finnish pulp and paper mills illustrating that their average capacity is 450 000 -570 000 t/a are presented in table XII and appendix 6.

Table XII Capacity of Finnish chemical pulp mills during 2000 year [7]

| Capacity, t/a | Finland | |
|---------------------|-----------------|-------------|
| | Amount of mills | Capacity, % |
| 150 000 and less | 1 | 5.6 |
| 150 000-300 000 | 4 | 22.2 |
| 300 000-450 000 | 5 | 27.8 |
| 450 000 and more | 8 | 44.4 |
| Total | 18 | 100 |
| Total capacity, t/a | 6 900 000 | |

Considering Russia separately, the largest pulp and paper mills produce $500 \cdot 10^3$ - $1000 \cdot 10^3$ t/a, including pulp, which is used directly by paper machines, and market pulp (see table XIII) [59].

Table XIII. Pulp production in Russia [59]

| Pulp and Paper mills | Produced pulp, 2005 year | Market pulp, 2005 year |
|----------------------|--------------------------|------------------------|
| | Capacity, 10^3 t/a | |
| Arhangelsk | 826.6 | 227.9 |
| Kotlass | 999.4 | 351.1 |
| Syktyvkar | 545.0 | 9.4 |
| Ust-Ilimsk | 713.9 | 656.9 |
| Bratsk | 758.6 | 495.7 |

Thus the information represented above leads to the conclusion that the market for implementation of black liquor gasification as a recovery system with 2100 kWh/t of power capacity at existing pulp mills is wide enough, both in Finland and in Russia, and all over the world. The most suitable time for introducing gasification technology at the mill will be time when the lifetime of using recovery boiler expires [60].

However if one considers BLG technology from the point of view of obtaining a large amount of electric energy which exceeds the specified amount by 3-3.5 times it will not be possible to implement this technology as a technology able to increase the capacity of existing pulp mills.

6.4.5 Obstacles of BLG implementation

Despite of fact that the gasification of black liquor is a promising technology for the pulp and paper industry, there are obstacles hindering its commercialization, the most significant of them include: the availability of funds for its realization, protection of

the gasifier from an aggressive environment, and also increased load on the causticizing department [27].

Financial risk

The most serious obstacles to the introduction of technological innovations are the necessity of great financial investments and the risk of not recuperating the capital investment made. The pulp and paper industry is a highly capital intensive industry and, unfortunately, insufficiently attractive to investors. [61]

The recovery system is the biggest and longest-term single investment at a pulp mill. Various cost data of existing recovery system and also the new system of black liquor gasification are presented in literature. Most of the published analysis revealed that the installed cost of a black liquor gasification combined-cycle will exceed the cost of an existing recovery system by two times approximately. According to source [49] the capital costs of a Tomlinson-based system calculated for pulp mills having the productivity of 1,580 dry short tons of unbleached pulp per day is 136.2 million USD and about 218 million USD for HTBLGCC. In addition to the high capital cost, it is expected that the operating and maintenance costs of gasification technology also will be higher than for traditional recovery. [48]

According to the cited data, it is obvious, that the gasification system demands significant capital investment. Experience of new technology implementation in the production line shows the mill owner's need of guarantees that a process can be successfully realized on an industrial scale before investing money into it. The trials of the BLG given the public is not enough, because the behaviors of this technology in the combined-cycle and problems which may arise remain unclear. Thus, it is too early to speak about gasification process on an industrial scale and about the widespread interest of pulp mills in its introduction before a demonstration of the gasification in combined-cycle.

First of all, it is clear that those countries for which renewable energy sources play a great role in their energy sector are ready to invest in the gasification of black liquor as a way to increase power capacity. For example, the interest shown to this process and associated risks in Finland are justified since it is a country where more than 10 % of energy is based on biomass and which is the leader of bioenergy production, having extensive knowledge in this field. If considering Russia, where the share of renewable energy sources used, excluding hydro power, is approximately 0.5 % and the amount of non-renewable sources is significant, the country will not accept active participation in the development of black liquor gasification technology without more serious reasons than increasing electric energy production. [61]

Protection of the gasifier

The aggressive environment created by high temperature and pressure, as well as the alkaline conditions is the cause of gasifier destruction. Therefore it is necessary to find a proper gasifier protection. There are two types of gasifier using different types of shell protection: refractory brick lining (see figure 27a.) and refractory coated coiled lining (see figure 27b.). [60]

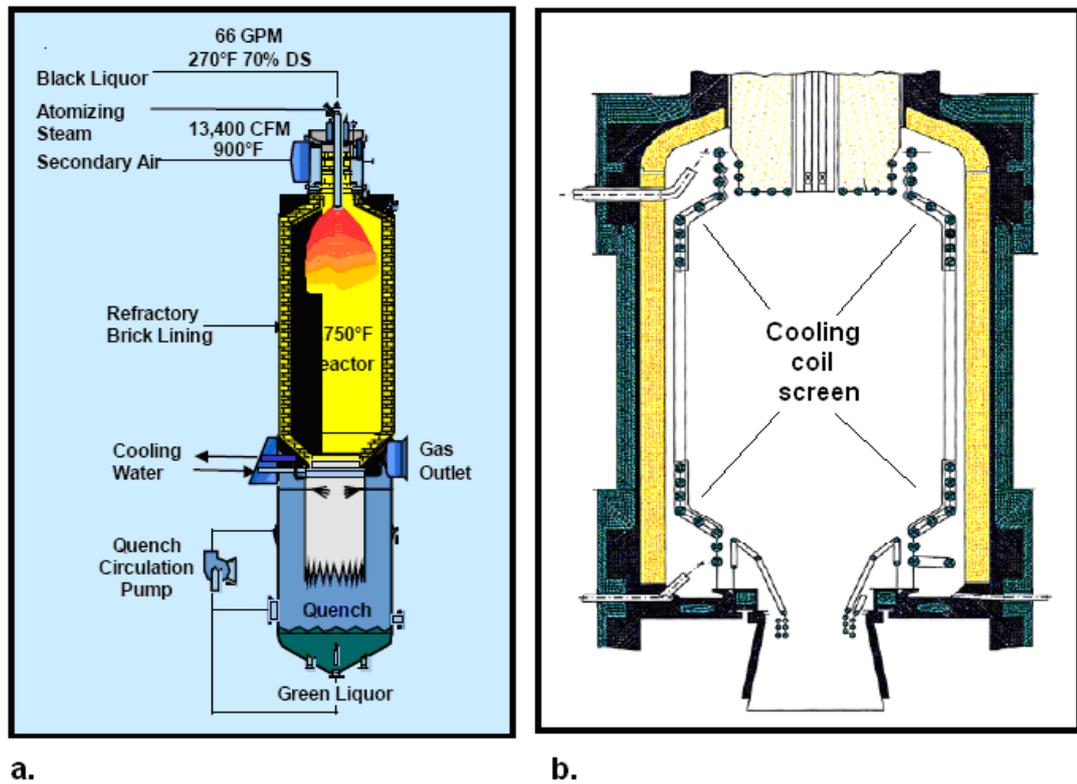


Figure 27. Two designs of HTHP gasifier [60]

The gasifier installed in Stoghall has the refractory brick lining, or the fusion-cast alumina refractory to be precisely, which is identical to one installed at New Bern's booster after its reconstruction (see figure 27a). After 1000 hours of work, the gasifier was shut down and the structure of refractory bricks was studied. The results showed that at the top of the bricks, the same products of reactions between the bricks and smelt as in case of the booster's refractory were found, characterized by the partial destruction of the lining. The service life of a gasifier with such a refractory lining is approximately one year. Further studies carried out on increasing the operation period of the gasifier showed that it is possible to extend this period to more than two if fusion-cast magnesia-alumina spinel refractory is used. In contrast, two essential shortcomings of fusion-cast based refractory are high costs and thermal shock sensitivity. [62-64]

The second type of HTHP gasifier has cooling coil screens representing refractory-coated helically-coiled metal tubes, in which the cold water, under pressure, is intended to cool refractory surface to below the melting point of smelt and to reduce the thermal shock to the gasifier's shell (see figure 28). [65]

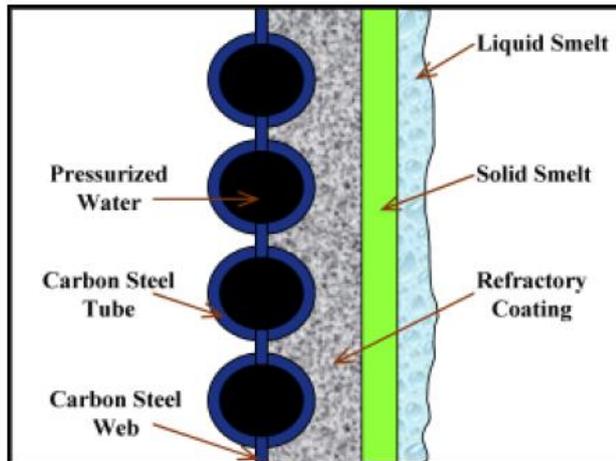


Figure 28. Illustration of cooling coil screens [65]

The material used as a protective layer of the tubes should have, besides good thermal conductivity and corrosion resistance, a coefficient of thermal expansion which allows it to stay in good contact with the tubes. Numerous tests were executed on a selection of coatings with high adhesion, surface quality and resistance to smelt. Specifically, alumina and magnesia cement, alumina ram mix, magnesia castable were put through trials. Among the mentioned types of coverings, magnesia castable returned better results. [65]

Protection from an aggressive environment is very important in the operation of a gasifier because it determines the lifetime and hence the feasibility of gasification as a technology as a whole. A material which provides high-quality and economic protection of the gasifier has not been found yet for both designs of the gasifier. Research in this area has resulted in a need for further study, and therefore a larger number of laboratory tests is necessary. [64]

Increasing load on the causticizing department

As mentioned in section 6.2, the gasification process of black liquor taking place in the gasifier has two output products: gas in which hydrogen sulfide is present, and smelt mainly composed of sodium carbonate. The natural separation of these two streams, sulfur and sodium, provides an opportunity to obtain white liquor in different compositions by altering their ratio to each other, and opens the possibility of using methods alternative to Kraft process to increase pulp yield per ton of wood. [66]

A negative consequence in the division of sulfur and sodium flows during black liquor gasification is causticization load increasing. In case of high-temperature gasification, the addition load is approximately 16 % higher in comparison with a traditional recovery system. This fact is explained by chemical reactions during these two processes. In the cycle with the recovery boiler, the product of black liquor combustion is smelt consisting mainly of Na_2S and Na_2CO_3 , while in the gasification technology, sulfur partially participates in formation hydrogen sulphide gas and free sodium reacts with carbon dioxide creating additional Na_2CO_3 in the green liquor. In line with equations 2 and 3, the increase of sodium carbonate, required in the recovery of one of the reagents of the cooking process (NaOH), provokes a greater feed of lime and fuel to the lime kiln or in other words grows the causticization load. [31]

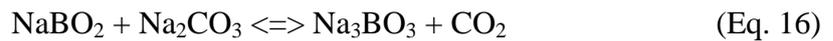
According to sources [31] and [67], the loading is not so high to install an additional causticizer and lime kiln, but in order to existing furnace satisfies to inquiries two options for solving this problems are considered: non-conventional causticization and oxygen-enrichment of the combustion air.

Initially the reasons for the development of non-conventional causticization methods were fuel costs and the high value of lime kiln. Further, the ability to reduce causticization load during gasification processes has raised interest. The concepts behind these alternative technologies include:

- the interaction of input amphoteric metal oxide (Me_xO_y) with sodium carbonate of black liquor and the formation of sodium salt ($\text{Na}_2\text{Me}_x\text{O}_{y+1}$) and carbon dioxide, and;

- dissolving formed smelt.

According to the solubility of the resulting products, the non-conventional causticization methods are classified into two categories: direct causticization, where besides aqueous sodium hydroxide, insoluble product is formed, and autocausticization, where all products are soluble. Direct causticization is preferable in the case of very high added load that is observed in low-temperature gasification. For high-temperature gasification, autocausticization is the most suitable, avoiding extra loading. Boron oxide B_2O_3 is the most promising among other metal oxides that can be applied to autocausticization. Simply put, this process can be represented by two equations, the first of which takes place in the gasifier and the second with sodium hydroxide formation in the dissolving tank:



Borate ($NaBO_2$) circulates through the pulping cycle and negatively influences pulp yield, so it is possible to use only partial autocausticization along with the existing causticization cycle. Another significant drawback is the high cost of chemicals used in this technology. [67]

The enrichment of combustion air by oxygen is the most attractive in terms of small improvements to the capacity of the lime kiln. The required amount of oxygen can be generated by an air separation unit, which is included in the pressurized gasification system. The size of that unit will need to be increased but its increase is less expensive than installing another kiln, even though the modernization of the existing kiln must be done. [31]

7 EXPERT' OPINIONS

While researching the black liquor gasification process, interviews of specialists in this field were carried out in order to find out their opinion of the most interesting questions with a view to reveal topics and answers to which are not clear. The experts were interviewed by email and personal meetings. The results can be found in appendix 7 (tables I-V). A summary of the specialists' views is below.

As can be seen from appendix 7 (table I) the most promising technology of black liquor gasification is a high-temperature gasification developed by Chemrec. The reason for the successful development of gasification in this direction is a high enough rate of carbon conversion to combustible gases. The inorganic substances leave the gasifier in the form of molten smelt thus the chemical recovery process is the same as in existing technology, is familiar and functions well.

In regards to low-temperature BLG, theoretically it can provide higher power production per ton of black liquor and, as expected investment cost will be lower than for HTBLG but in practice operation problems with runnability are a crucial. Conditions created under temperatures below the melting point of inorganic substances in black liquor do not permit the required degree of carbon conversion due to its low reaction rate. Increasing the temperature in this kind of technology leads to the melting of ash, which causes tar formations and reactor plugging.

The opinions of experts on the issue of energy generation by gasifier are divided. All of the interviewees think that increasing power production by two or three times is possible as compared to tradition recovery system, in which the heart of the process is an old recovery boiler. However, the possible electric energy augmentation is given different when an advanced recovery boiler is compared. Two of the experts claimed that it is possible to generate two times more power using Chemrec's gasifier. One of the specialists noted that the power capability of today's boilers is high enough, and as the result, the gasification technology has the benefit with 400 kWh/ADt extra total power, but which is lower than in two times.

Considering steam consumption, it is logical that the increase of electric energy leads to the situation when pulp mills have an insufficient amount of steam needed for the fiber line process. On the whole, the experts assume that enough of steam should be produced by the combined cycle for processing needs. Otherwise, the capacity of the biomass boiler must be increased but it does not have a negative impact due to the steady prices of steam and electric energy. In Finland the cost of power is four times higher than the cost of steam.

BLGCC technology as an alternative to the recovery system at Pulp and Paper plant is doubtful. In accordance with table V (appendix 7) there are no reasons to replace the recovery boiler by a gasifier. Advanced recovery boilers perform recovery functions of chemicals and energy at a high enough level. On the one hand, BLGCC has many advantages, such as augmented power recovery from the liquor, safety and environment friendliness, but on the other hand, there are still technical challenges related to gas turbine work. Thus, the replacement of the existing recovery system by combined cycle seems risky and unreasonable.

The current price situation in the market makes the production of motor fuels more beneficial than power generation. Gasification of black liquor opens opportunities for the generation of green motor fuels and Chemrec is working in this direction. The stage of development which they have reached now looks promising. Experts assume that BLG will be at mill scale in the future, producing biofuel for automotive use, but not in the combined cycle with a gas turbine for addition electric energy recovery.

In the judgment of specialists, the following factors impede the progress of the black liquor gasification as technology: conservatism of the pulp industry and lack of money. Also technical problems are slowing factors but their solution directly depends on the money input. Among the technical problems, the service life of the gasifier is unresolved. Presently, refractory materials providing long gasifier life have not been found. The most optimistic forecasts of experts indicate that the service life of the gasifier is 2-3 years; while in accordance to pessimistic forecasts it is some months. The absence of demonstrations of BLGCC or BLGMF, and high investment costs, are the

reasons for the reluctance of pulp mills to invest in these technologies. Thus, in these circumstances the specialists believe that BLG technology will be at mill scale no earlier than in 10 years.

8 CONCLUSIONS

The existing recovery system meets the current demands of the pulp mills and there are no substantial reasons for its replacement. Among the inherent shortcomings of the conventional chemical recovery system, the most important are relatively low power efficiency, gas emissions and the probability of smelt-water explosions.

The possibility of the power capacity increasing from black liquor is the impetus of new technologies development. Black liquor gasification technology at high pressure and temperature, developed by Chemrec, is the most promising and closest technology to implementation on an industrial scale. Compared to an advanced recovery boiler system, the Chemrec combined cycle, consisting of a gas and steam turbine, is able to produce 400 kWh of power more per ton of pulp, 80 kWh/ADt of which is extra electric energy for sale. However the mill's performance must be higher than 450 000 ADt/a in order to achieve such power efficiency from the gasified black liquor.

When producing more power, the pulp mill suffers from a loss of steam. At a plant with high steam requirements, the amount of steam generated by the gasification combined cycle can be insufficient. The price of 1 MWh of power is approximately four times higher than that of steam so increasing the power to heat ratio for the pulp mills is a profitable direction.

Having the electric energy capacity equal to 2100 kWh/ADt, half of which can be sold, the gasification combined cycle will bring additional economic benefits to pulp mills and moreover, will play the main role in power balance of countries like Finland, in which fossil fuel reserves are poor and pulp industry is full-blown.

Besides the electric energy production benefit, the feasibility of black liquor gasification is improved by environmental friendly and safety factors of the process, as well as the natural split of sulphur and sodium flows, giving the opportunity to apply polysulfide cooking for an increased pulp yield. Currently when pulp plants are trying to find ways to reduce costs per unit of product while ecological regulations

continuously toughen these advantages are the essential challenges to high capital cost which exceeds two times the cost of existing system.

Over the next ten years, favourable conditions for implementation of black liquor gasification will develop, since currently the amount of pulp plants having a capacity of more than 450 000 ADt/a is 12 % and will continue to grow. Furthermore, an urgent need to replace operating boilers is imminent because they are at the end of their operational lifecycle.

There are some technical problems with using the black liquor gasification combined cycle: the absence of an affordable and reliable refractory system which protects gasifier from severe conditions for more than a few years and achieving of sufficient purity of syngas required for gas turbine work. These issues demand further study directed towards their resolution and execution of new trials.

REFERENCES

1. Database of the Ministry of natural resources and ecology of the Russian Federation, <http://ecopages.ru/bulleten/view.html&page=1&id=81>, [accessed 10.03.2009].
2. Power in pulp and paper industry, http://www.krona.edu.ru/calendar/otchet/2008/02-04_06_08/tesis.pdf, [accessed 10.03.2009].
3. Novikova, A. I., The modified sulfate cooking process of pulp , St. Petersburg, Russia, 2006, 161p.
4. Ivanov, U. S., The modern ways of sulfate pulp cooking, St. Petersburg, Russia, 2005, 61p.
5. Nepenin U. N., The sulfate pulp production, 2nd edition, Forest Industry, Moscow, 1990, 601p.
6. Washington state air toxic sources and emission estimation methods, <http://www.ecy.wa.gov/programs/air/pdfs/pulpmil3.pdf>, [accessed 15.03.2009].
7. Henricson, K., An introduction to chemical pulping technology, Lecture notes, 2004.
8. Holmlund, K., Parviainen, K., Evaporation of black liquor, Chemical pulping, Papermaking Science and Technology, Book 6B, Gullichsen, J., Fogelholm, C. (Ed.), Fapet Oy, Helsinki, 1999, p 37-65.
9. Adams, T., Pulp and paper manufacture, Alkaline pulping, 3rd edition, Grace, T. & Malcolm, B., (Ed.), TAPPI, 1989, 637p.
10. Knowpulp database
11. Knowpap database
12. Fakhrai, R., Modelling of carry-over in recovery furnace, Licentiate thesis, Royal Institute of Technology, Department of Metallurgy, 1999.
13. Bogomolov, B. D., The conversion of sulfate and sulphite liquors, Forest industry, Moscow, 1989, p. 23-24.
14. Marklund, M., Recovery boiler: how does it work, http://www.etcpitea.se/blg/document/PBLG_or_RB.pdf, [accessed 29.03.2009].

15. Costa, A., Mathematical description of the kraft recovery boiler furnace, *Computers & Chemical Engineering*, 28(2004)5, p. 633-641.
16. Adams, T., *Kraft recovery boilers*, Adamson, T. (Ed.), Tappi, Atlanta, 1997, 381p.
17. Macek, A., Research on combustion of black-liquor drops, *Progress in Energy and Combustion Science*, 25(1999)3, p. 275-304.
18. Blasiak, W., Modeling of kraft recovery boilers, *Energy Conversion and Management*, 38(1997)10, p. 995-1005.
19. Kohan, A., *Boiler Operator's Guide*, 4th edition, <http://books.google.ru/books?id=tAQ-Gc2xvUC&pg=PA150&dq=flue+gases+from+black+liquor+boiler#PPP1,M1>, [accessed 12.04.2009].
20. Tran, H., Overview of factors affecting fouling in recovery boilers, *Colloquium on Black Liquor combustion and gasification*, Park city, May 12-16, 2003.
21. Vakkilainen, E., *Kraft recovery boilers, Principles and practice*, 2003.
22. Vakkilainen, E., *Evolution of recovery boiler design*, Jaakko Pöyry Oy, 2003.
23. Tran, H. & Vakkilainen, E. *Advances in the kraft chemicals recovery process*, <http://www.celuloseonline.com.br/imagembank/Docs/DocBank/Eventos/430/2TranOral.pdf>, [accessed 13.04.2009].
24. Vakkilainen, E., *Development of recovery boiler technology*, Jaakko Pöyry Oy, Vantaa, Finland, 2003.
25. Larson, E. D., McDonald, G., A cost-benefit assessment of BLGCC technology, *Tappi journal*, 83(2000)6, p. 1-16.
26. Consonni, S., Larson, E., Black liquor gasification combined cycles: mill integration issues, performance and emissions estimates, *Colloquium on black liquor combustion and gasification*, Salt Lake city, May 13-16, 2003.
27. Vakkilainen, E., *Advanced efficiency options—increasing electricity generating potential from pulp mills*, Jaakko Pöyry Oy, Vantaa, Finland.
28. Stigsson, L., & Berglin, N., *Black liquor gasification—towards improved pulp and energy yields*, 6th International Conference on New Available Technologies at SPCI'99, Stockholm, Sweden, June 1-4, 1999.

29. Whitty, K., Black liquor Gasification: development and commercialization upgrade, Institute for combustion and energy studies (ICES), The University of Utah, ACERC annual conference, Provo, Utah, February 17-18, 2005.
30. Ekbom, T., Technical and commercial feasibility study of black liquor gasification with methanol/ DME production as motor fuels for automotive uses BLGMF, Stockholm, Sweden, 2003, 126p.
31. Larson, E., Consonni, S., and Katofsky, R., A Cost-benefit assessment of biomass gasification power generation in the pulp and paper industry, Final report, Princenton University, 8 October, 2003.
32. Wisconsin biorefining development initiative, <http://www.wisbiorefine.org/proc/blackliquorgas.pdf>, [accessed 15.04.2009].
33. Whitty, K., The changing scope of black liquor gasification. University of Utah, Salt Lake City, 2009.
34. Kenaf Black Liquor Gasification Study, EPRI, Palo Alto, CA and Tennessee Valley Authority, Muscle Shoals, AL: 2006. 1014515.
35. Lindblom, M., & Chemrec AB., An overview of Chemrec process concepts, Presentation at the colloquium on black liquor combustion and gasification, Park City, Utah, May 13-16, 2003.
36. TRI biomass gasification technology-how it works, <http://www.tri-inc.net/pdfs/TRI%20How%20It%20Works%20Overview.pdf>, [accessed 16.04.2009].
37. DeCarrera, R., Engineering study for a full scale demonstration of steam reforming black liquor gasification at Georgia-Pacific's mill in Big Island, Virginia, final report, Georgia-Pacific, Department of Energy., 2002, 24p.
38. Wisconsin biorefining development initiative, <http://www.wisbiorefine.org/prod/fuelgas.pdf>, [accessed 15.04.2009].
39. Whitty, K., State of the art in black liquor gasification technology, IEA Annex XV Meeting, Piteå, Sweden, August 20-21, 2000.
40. Chemrec, <http://www.chemrec.se/>, [accessed 25.04.2009].
41. Richards, T., Theliander, H. & Wintoko, J., The kinetics of the gasification of black liquor, Final report, 2005, 33p.

42. Wessel, R., Salcudean, M., & Yuan, J., Computational modeling—a powerful tool for optimizing black liquor combustion and gasification processes, Colloquium on black liquor, May, Park city UT, 2003.
43. Lindblom, M., & Landälv, I., Chemrec’s atmospheric & pressurized BLG (black liquor gasification) technology—status and future plants, Stockholm, Sweden.
44. Berglin, N., & Berntsson, T., CHP in the pulp industry using black liquor gasification: thermodynamic analysis, *Applied Thermal Engineering* 18(1998), p. 947-961.
45. Dickinson, J.A., Verrill, C.L., & Kitto, J.B., Development and Evaluation of a Low-Temperature Gasification Process for Chemical Recovery from Kraft Black Liquor, International Chemical Recovery Conference, Tampa, Florida, U.S.A., June 1-4, 1998.
46. Lindström, E., Integration black liquor gasification with pulping—process simulation, economics and potential benefits, Dissertation, Raleigh, North California, 2007, 137p.
47. Nasholm, A, and Westermarck, M., Energy studies of different cogeneration systems for black liquor gasification, 38(1997)15-17, p1655-1663.
48. Larson, E., A Cost-Benefit Assessment of Gasification-Based Biorefining in the Kraft Pulp and Paper Industry, Final report, Princeton University, 21 December 2006.
49. Kreutz, T., Consonni, S., Larson, E., Performance and preliminary economics of black liquor gasification combined cycles for a range of Kraft pulp mill sizes. Tappi International Chemical Recovery Conference, Tampa, Florida, June 1-4, 1998.
50. Larson, E., Consonni, S., Performance of black liquor gasifier/gas turbine combined cycle cogeneration in the Kraft pulp and paper industry, 1997, p 1495-1512.
51. Power station and all about them, <http://pstation.ru/price.php>, [accessed 15.06.2009].
52. Energy tariffs on 2006, http://tarif-penza.ru/tariffs/heat/heat_2006, [accessed 15.06.2009].

53. Energy year 2008, Finnish Energy Industries, Press conference, Helsinki, January 22, 2009, <http://www.energia.fi/fi>, [accessed 20.06.2009]
54. Key to the Finnish forest industry, <http://www.forestindustries.fi/infokortit/key/documents/key2006.pdf>, [accessed 20.06.2009].
55. Merle-Béral, E., Russia renewable energy, Markets and Policies: Key trends, Paris, June 29, 2007
56. Akim, L., Russia, Advisory Committee on Paper and Wood Products, <http://www.google.fi/search?q=output+of+pulp%2C+paper+and+paperboard+in+the+russian+federation&ie=utf-8&oe=utf-8&aq=t&rls=org.mozilla>, [accessed 20.06.2009]
57. Kirsanov V., A., Cellulosa. Bumaga. Karton. Magazine #9-10/2003, http://www.cbk.ru/eng/cbk_mag.php?nom=30, [accessed 20.06.2009]
58. Ebeling, K., Integrated energy and fibre production by a sulphur-free and carbon dioxide neutral process, EFPRO, Budapest, 16-17 October, 2003.
59. Information network of support of inter-regional business cooperation, <http://www.marketcenter.ru/content/doc-2-8441.html>, [accessed 1.07.2009].
60. Finnish forest industries, <http://www.corporateregister.com/a10723/ffif06-env-fin.pdf>, [accessed 1.07.2009].
61. Vetrov, S. V., Problems of innovation implementation in Russia, <http://conf.bstu.ru/conf/docs/0033/0756.doc>, [accessed 5.07.2009].
62. Keiser, J. R., Corrosion issues in black liquor gasifier, Oak Ridge National Laboratory, Colloquium on Black liquor Combustion and Gasification, Salt Lake City, May 13-16, 2003.
63. Keiser, J. R., Improved materials for high-temperature black liquor gasification, Final technical report, June 2006, 39p.
64. The free library, <http://www.thefreelibrary.com/Changing+the+balance+of+power:+black+liquor+and+biomass+gasification%2F...-a0108598285>, [accessed, 5.07.2009].
65. Hemrick, J. G., Refractory testing and evaluation at oak ridge national laboratory for black liquor gasifier application, Oak Ridge National Laboratory, Oak Ridge, TN, Refractories Applications and News, 9(2004)6, 20p.

66. Jameel H., Pulping options with black liquor gasification, NC State University.
67. Arosenius, A., Mass and energy balances for black liquor gasification with borate autocausticization, Master Thesis, Lulea University of Technology, Chemical Engineering, Department of Chemical Engineering and Geosciences, 2007, 49p.

APPENDICES

APPENDIX 1

1(2)

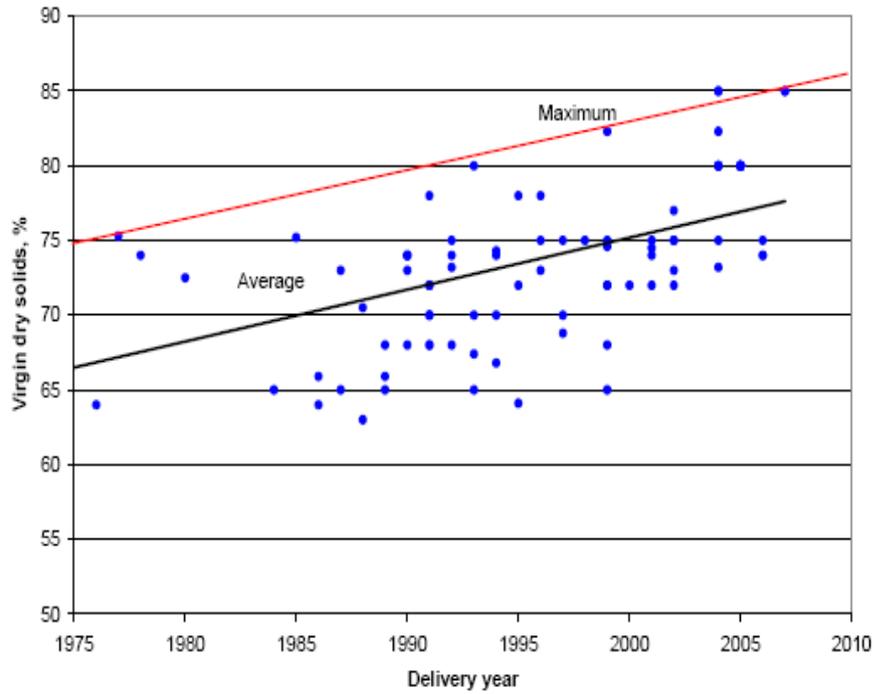


Figure 1. Change of dry solids concentration according to boiler start-up year [21]

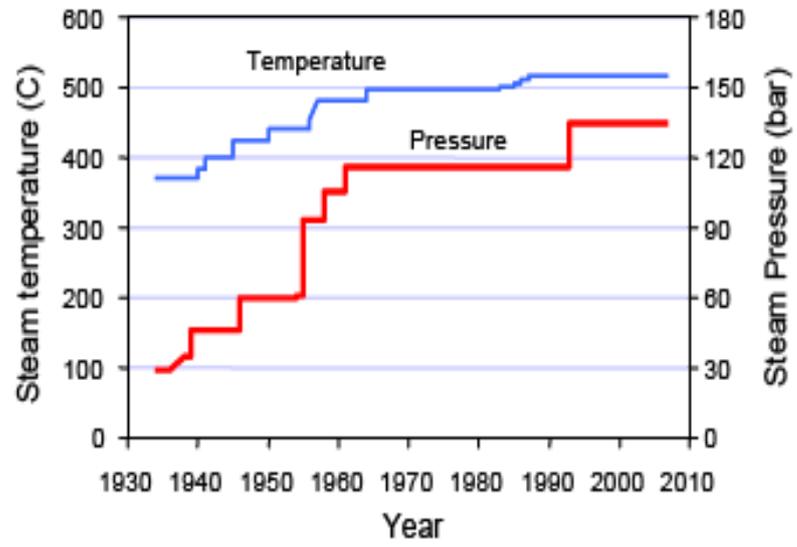


Figure 2. Change of main steam data according to boiler start-up year [23]

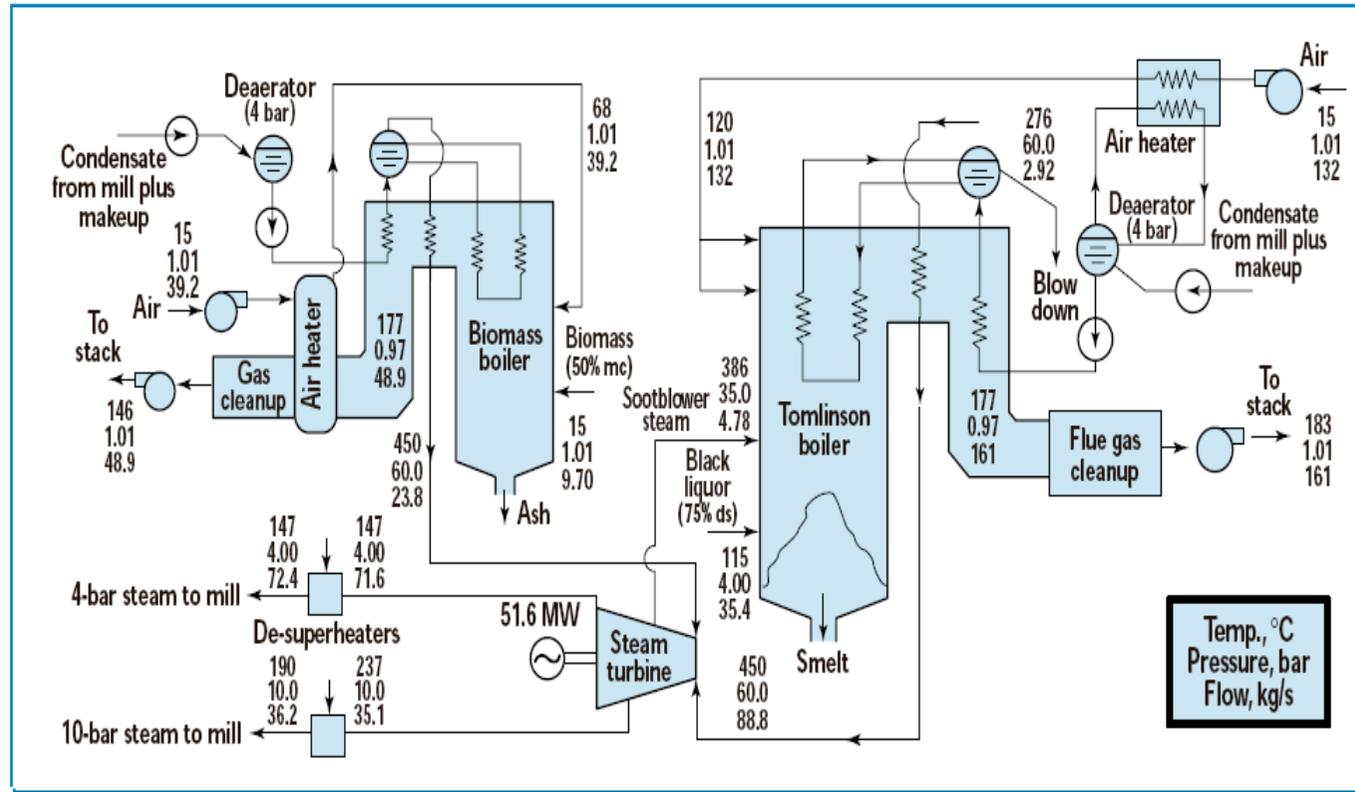


Figure 1. Heat and mass balance of Tomlinson-based recovery system. Pulp mill production is 1327 over-dry metric tons per day [25]

Table I Calculation of electric energy production within the system in figure 1, appendix 2

| 1 | 2 | 3 | 4 | 5 |
|--|----------------|---------------------|------------------|--------------------------------|
| | Flows, kg/s | Total flows,kg/s | Total power | Power by sources (4×2/3) |
| Recovery boiler T= 450 °C P=60 bar 75%, ds | 88.8 | 112.6 | 51.6MW or | 40.7 MW or 662.4 kWh/t |
| Bark Boiler | 23.8 | | 839.9 kWh/t* | 10.9 MW or 177.5 kWh/t |

- Total electric energy = 51.6 MW = 51.6 MJ/s = 4458240 MJ/d;

$$\frac{4458240}{1327} = 3359.6 \text{ MJ/ODt} \times 0.9 = 3023.7 \text{ MJ/ADt} = 839.9 \text{ kWh/t}$$

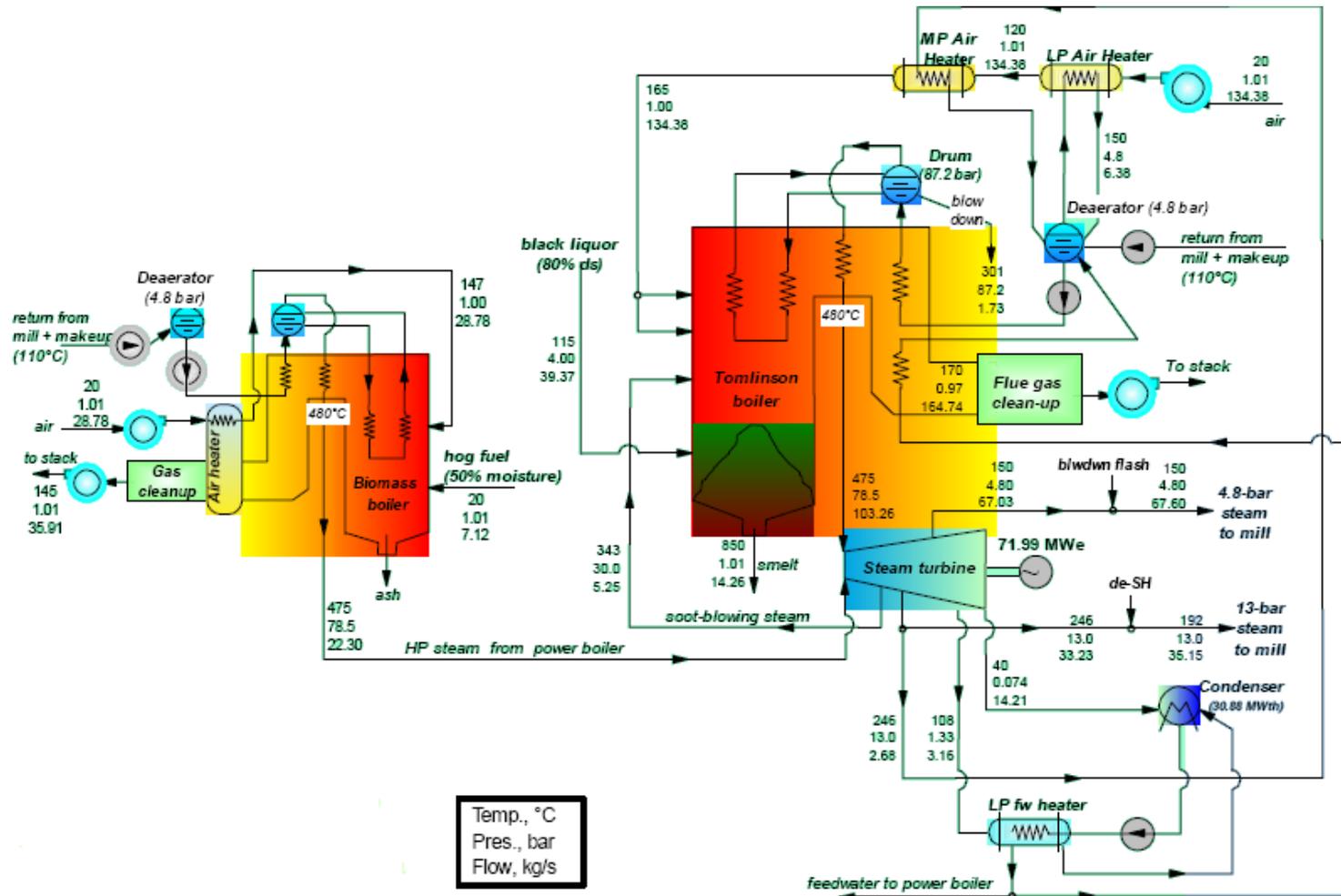


Figure 2. Heat and mass balance of Tomlinson-based recovery system. Pulp mill production is 1580 t/d [26]

Table II Calculation of electric energy production within the system in figure 2, appendix 2

| 1 | 2 | 3 | 4 | 5 |
|--|----------------|---------------------|-----------------|--------------------------------|
| | Flows, kg/s | Total flows,kg/s | Total power | Power by sources (4×2/3) |
| Recovery boiler T= 480 °C P=87.2 bar 80%, ds | 103.3 | 125.6 | 72 MW or | 59.2 MW or 899.5 kWh/t |
| Bark Boiler | 22.3 | | 1093.7 kWh/t* | 12.8 MW or 194.2 kWh/t |

- Total electric energy = 72 MW = 72 MJ/s = 6220800 MJ/d;

$$\frac{6220800}{1580} = 3937.2 \text{ MJ/t} = 1093.7 \text{ kWh/t}$$

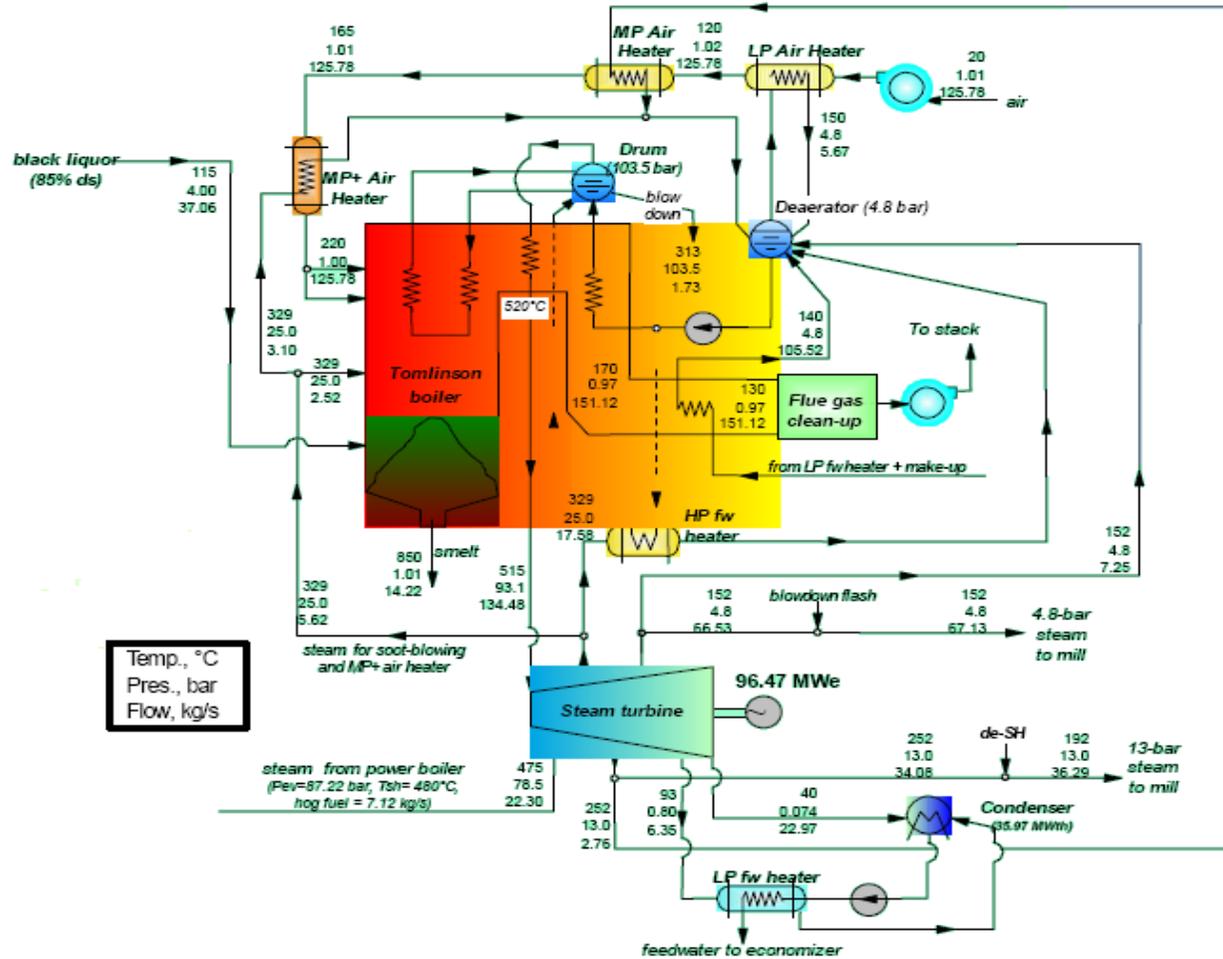


Figure 3. Heat and mass balance of Tomlinson-based recovery system. Pulp mill production is 1580 t/d [26]

Table III Calculation of electric energy production within the system in figure 3, appendix 2

| 1 | 2 | 3 | 4 | 5 |
|---|----------------|---------------------|-------------------|--------------------------------|
| | Flows, kg/s | Total flows,kg/s | Total power | Power by sources (4×2/3) |
| Recovery boiler T= 520 °C P=104.5 bar 85%, ds | 134.5 | 156.8 | 96.5 MW or | 82.8 MW or 1257.3 kWh/t |
| Bark Boiler | 22.3 | | 1465.8 kWh/t* | 13.7 MW or 208.5 kWh/t |

* Total electric energy = 96.5 MW = 96.5 MJ/s = 8337600 MJ/d;

$$\frac{8337600}{1580} = 5277 \text{ MJ/t} = 1465.8 \text{ kWh/t}$$

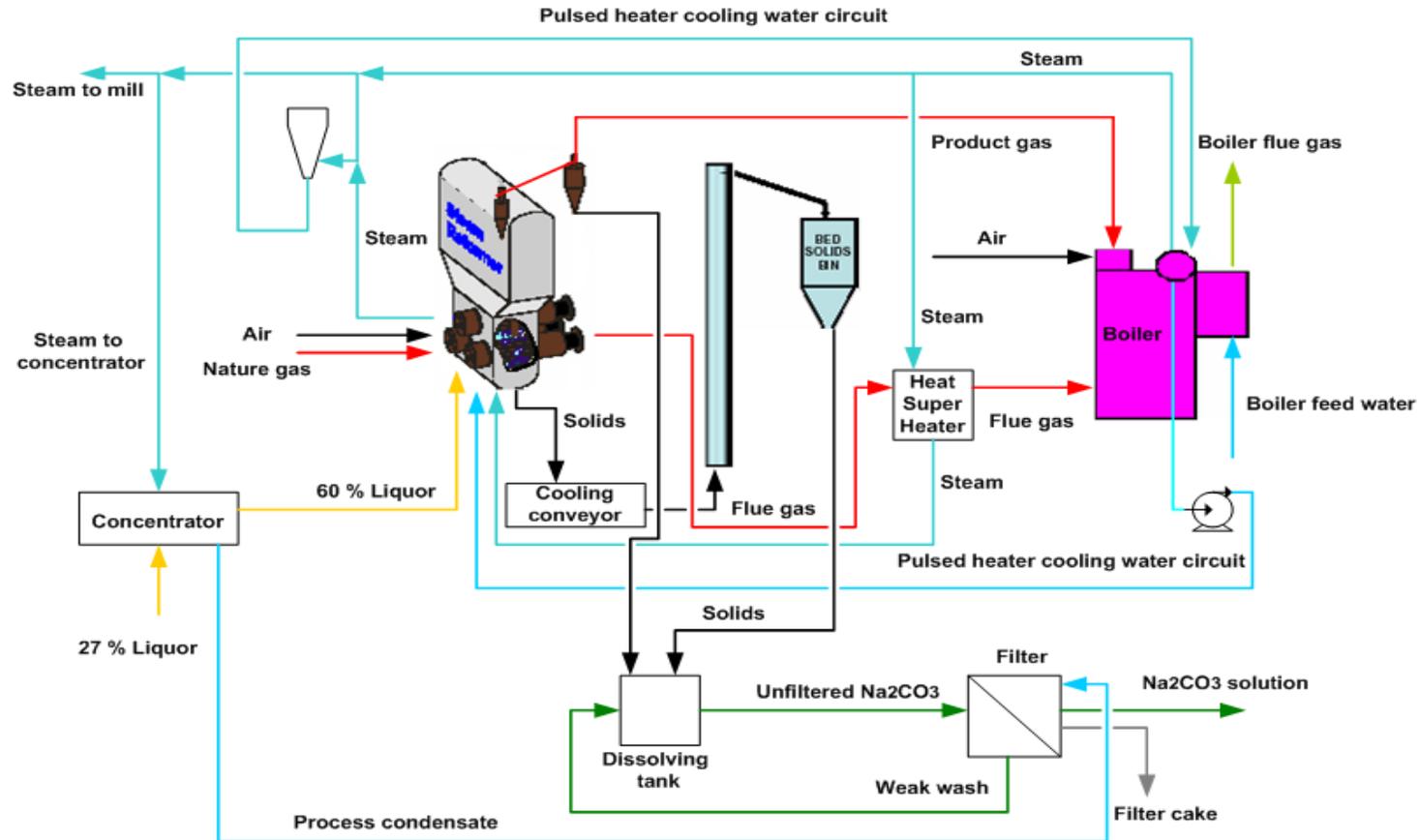


Figure 2. Demonstration of TRI's low-temperature gasification process, Norampac Paper Mill in Trenton, Ontario [34]

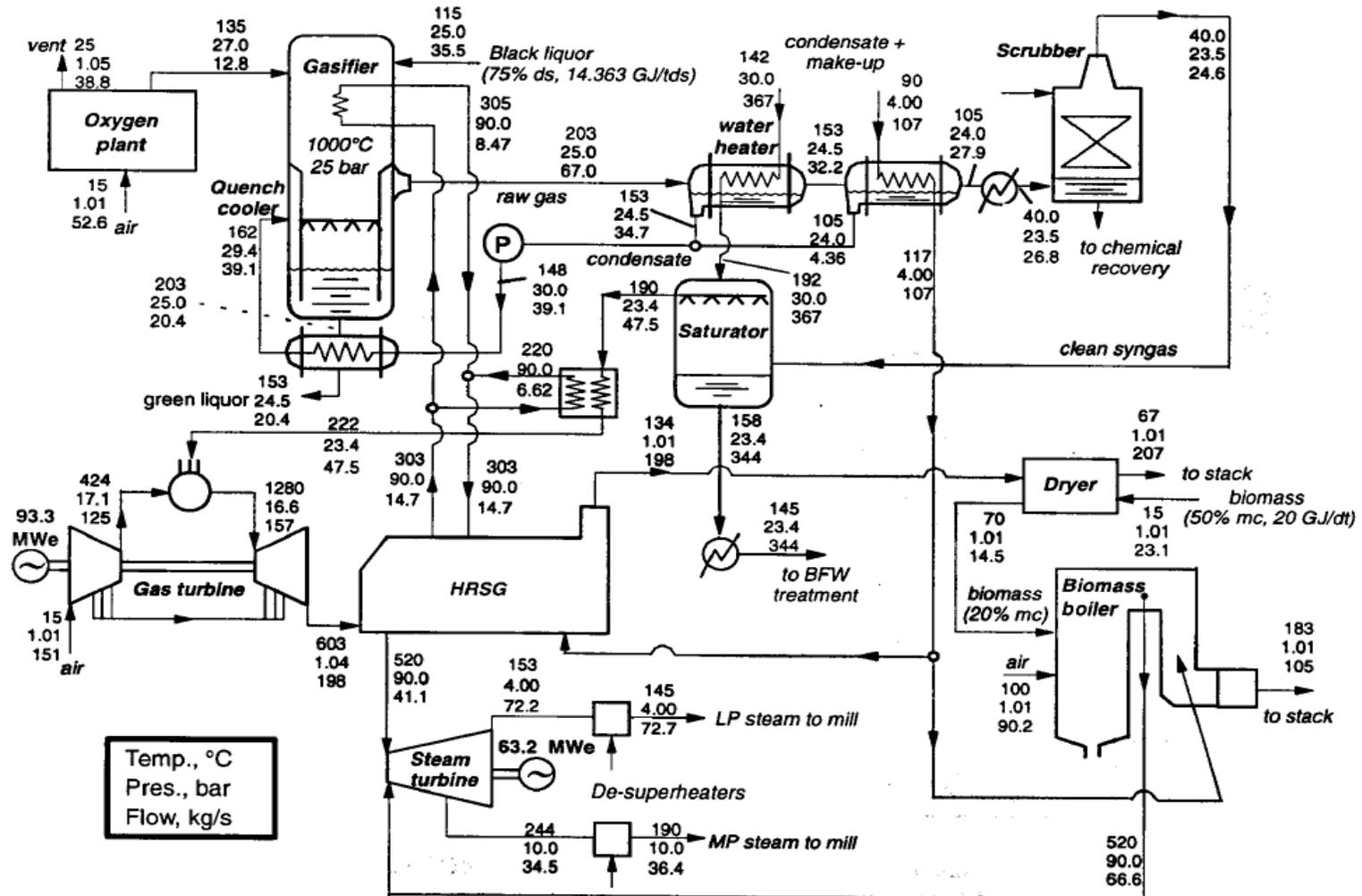


Figure 1. Heat and mass balance of oxygen-blown BLGCC. Pulp mill production is 1322 air-dry metric tons per day. Black liquor rate is 3067 tds/d [49]

APPENDIX 4

2(4)

- I. Calculation of power (E) produced by gasifier in the combined cycle described in appendix 4, figure 1 based on the cold gas efficiency of BLGCC (70 %) and efficiency of combined cycle (0.42-0.47):

$$E_1 = 14.4 \text{ GJ/tds} \times 0.7 \times 0.42 = 4.2 \text{ GJ/tds} = 1166.7 \text{ kWh/tds};$$

$$E_1 = \frac{1166.7 \times 3067}{24} = 149.1 \text{ MW}$$

$$E_2 = 14.4 \text{ GJ/tds} \times 0.7 \times 0.47 = 4.7 \text{ GJ/tds} = 1305.6 \text{ kWh/tds};$$

$$E_2 = \frac{1305.6 \times 3067}{24} = 166.9 \text{ MW}$$

Table I Calculation of electric energy production within the system in figure 1, appendix 4

| 1 | 2 | 3 | 4 | 5 |
|--|----------------|----------------------|--------------------------------|--------------------------------|
| | Flows, kg/s | Total flows, kg/s | Total power | Power by sources (4×2/3) |
| Gas turbine | | | | |
| Gasifier | | | 93.3 MW Or 1693.8 kWh/t* | |
| Steam turbine | | | | |
| Gasifier T=1000 °C P=25 bar 75%, ds | 41.1 | 107.7 | 63.2 MW or | 24.3 MW or 437.9 kWh/t |
| Bark Boiler | 66.6 | | 1147.4 kWh/t** | 38.9 MW or 709.5 kWh/t |

*Electric energy from gas turbine:

$$93.3 \text{ MW} = 93.3 \text{ MJ/s} = 8061120 \text{ MJ/d};$$

$$\frac{8061120}{1322} = 6097.7 \text{ MJ/ADt} = 1693.8 \text{ kWh/ADt}$$

APPENDIX 4

3(4)

**Total power from steam turbine:

$$63.2 \text{ MW} = 63.2 \text{ MJ/s} = 5460480 \text{ MJ/d};$$

$$\frac{5460480}{1322} = 4130.5 \text{ MJ/ADt} = 1147.4 \text{ kWh/ADt}$$

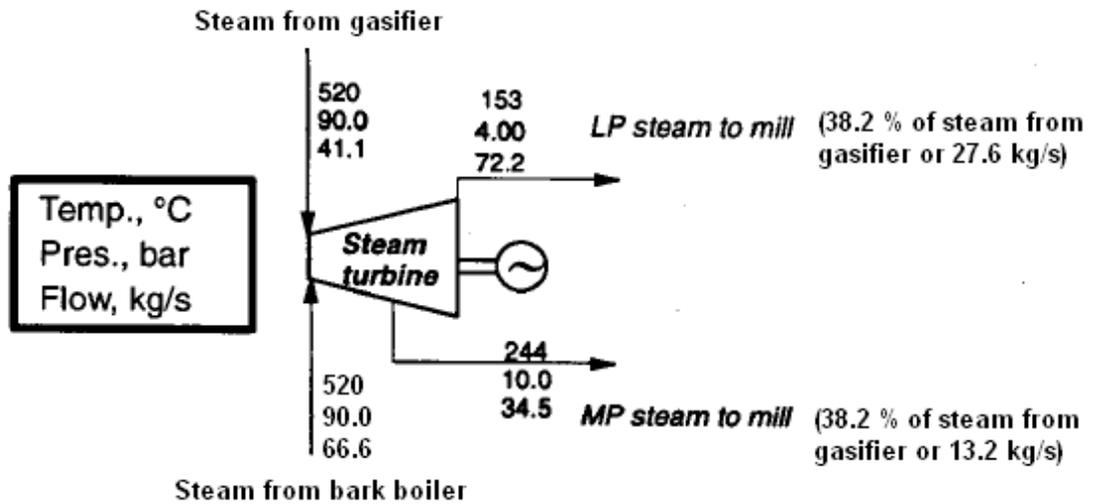
***Total power produced by gasifier in the system (kWh/t):

$$1693.8 + 437.9 = 2131.7 \text{ kWh/ADt}$$

**** Total power produced by gasifier in the system (MW):

$$93.3 + 24.3 = 117.6 \text{ MW}$$

II. Calculation of steam recovery from the gasifier in the combined cycle described in appendix 4, figure 1



1. MP steam to mill from the gasifier

$$MP = 13.2 \text{ kg/s} \times 3600 \times 24 = 1140480 \text{ kg/d;}$$

$$MP = \frac{1140480}{1322} = 862.7 \text{ kg/ADt}$$

The enthalpy of the steam at 520 °C and 90 bar is accepted equal 3410 kJ/kg

$$MP = 862.7 \text{ kg/ADt} \times 3410 \text{ kJ/kg} = 2.9 \text{ GJ/ADt}$$

2. LP steam to mill from the gasifier

$$LP = 27.6 \text{ kg/s} \times 3600 \times 24 = 2384640 \text{ kg/d;}$$

$$LP = \frac{2384640}{1322} = 1803.8 \text{ kg/ADt}$$

The enthalpy of the steam at 520 °C and 90 bar is accepted equal 3410 kJ/kg

$$LP = 1803.8 \text{ kg/ADt} \times 3410 \text{ kJ/kg} = 6.2 \text{ GJ/ADt}$$

Total steam to mill from the gasifier is 9.1 GJ/ADt

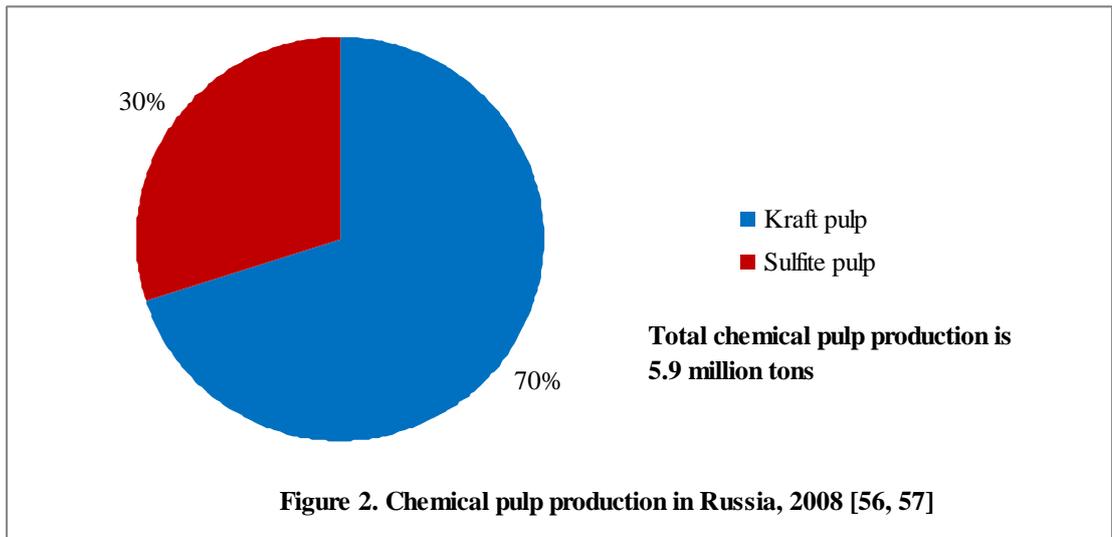
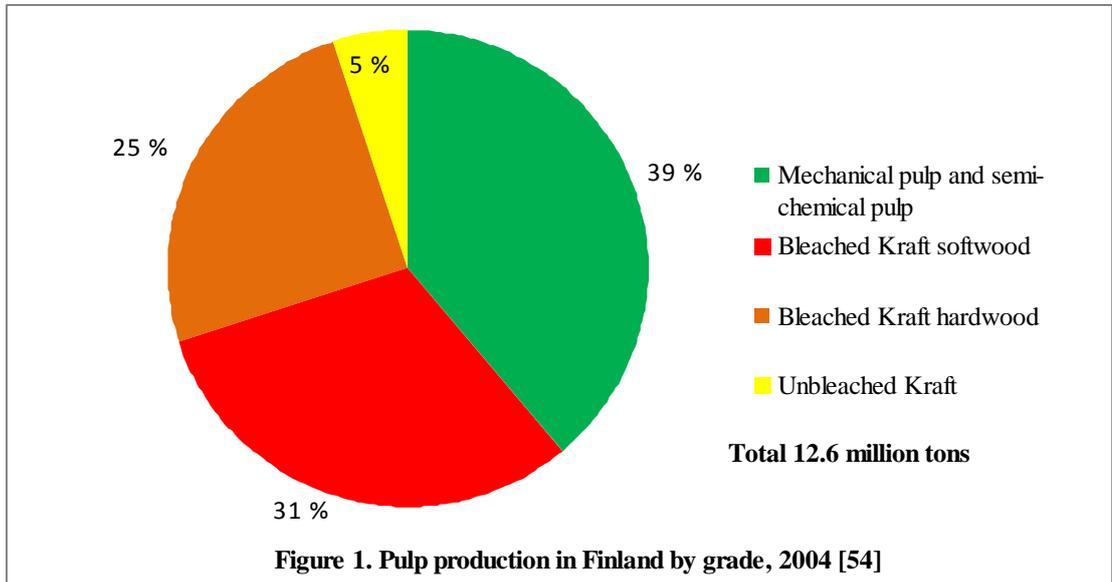


Table I Finnish Pulp and Paper Industry, 2006 [58]

| Pulp and Paper Mills | Pulp (t/a) | Paper/board (t/a) |
|---------------------------|------------|-------------------|
| Loparex Oy | | 50 000 |
| Tervakoski Oy | | 102 000 |
| Georgia-Pacific Nordic Oy | 39 000 | 83 000 |
| Kauttua paper mill | | 79 000 |
| Joutseno BCTMP | 258 000 | |
| Kangas | | 263 000 |
| Kaskinen BCTMP | 239 000 | |
| Kemiart Liners | | 325 000 |
| Kirkniemi | 226 000 | 659 000 |
| Lielähti | 99 000 | |
| Kyro | 87 000 | 208 000 |
| Simpele | 79 000 | 190 000 |
| Tako Board | | 237 000 |
| Äänekoski Board | | 177 000 |
| Nekoski Paper | | 172 000 |
| Mäntä mill | 51 000 | 128 000 |
| Joutseno | 571 000 | |
| Kaskinen | 413 000 | |
| Kemi | 533 000 | |
| Rauma | 532 000 | |
| Äänekoski | 471 000 | |
| Myllykoski Paper Oy | 240 000 | 502 000 |
| Pankakoski | 29 000 | 69 000 |
| Savon Sellu | 224 000 | 254 000 |
| Karhula Board | | 67 000 |

Continuation of Table I

| Pulp and Paper Mills | Pulp (t/a) | Paper/board (t/a) |
|-----------------------|------------|-------------------|
| Anjalankoski | 442 000 | 661 000 |
| Corenso United Oy Ltd | 97 000 | 105 000 |
| Enocell Oy | 655 000 | |
| Heinola Fluting | 272 000 | 275 000 |
| Imatra | 1 092 000 | 1 146 000 |
| Kemijärvi | 227 000 | |
| Keräyskuitu Oy | 22 000 | |
| Kotka | 260 000 | 300 000 |
| Oulu | 323 000 | 957 000 |
| Summa | 370 000 | 400 000 |
| Varkaus | 545 000 | 674 000 |
| Veitsiluoto | 481 000 | 879 000 |
| Stromsdal | 26 000 | 58 000 |
| Sunila | 362 000 | |
| Jämsänkoski | 499 000 | 764 000 |
| Kaipola | 440 000 | 642 000 |
| Kajaani | 455 000 | 588 000 |
| Kaukas | 613 000 | 499 000 |
| Kymi | 500 000 | 803 000 |
| Pietarsaari | 747 000 | 189 000 |
| Rauma | 551 000 | 1 105 000 |
| Tervasaari | 234 000 | 427 000 |
| Voikkaa | 58 000 | 147 000 |

Table I Comparison of low-temperature and high-temperature black liquor gasification

| <i>If one compares low-temperature (LT) and high-temperature (HT) BLG what type of these technologies is the best?</i> | |
|--|--|
| Interviewees | Answers |
| Esa Vakkilainen | <p>There are two problems with LT BLG: one is to get fast enough carbon conversion you need to get enough reaction rate and for achieving this you need to get temperature up otherwise the reaction rate is slow and gasification requires a big unit. Drawback of getting temperature up in LTBLG is temperature starts higher than ash melting temperature and then you have run problems.</p> <p>To me high-temperature black liquor gasification is only feasible options or feasible technology but of course it hasn't been proven, it is only opinion.</p> |
| Esa Hassinen | <p>If it is proved that in LTBLG chemical recovery works it will be very interesting system because there is expected more energy generation and lower investment cost compared to high temperature. In LTBLG inorganic materials are left in the gasifier as dry solids and it might be a challenge.</p> <p>Chemrec is rather similar to traditional recovery technology so chemical recovery from smelt should be work. However we don't know exactly what would be the runnability of the gasifier or how inner materials are able to resist rather high temperature; so this is one critical point in this technology.</p> |
| McKeough Paterson | High-temperature is the best because of unpromising experiences (operational problems) to date with low-temperature alternatives. |
| Niko DeMartini | In regards to your technology question of low temperature vs. high temperature, tars are the big problem for low temperature gasification. |
| Anja Klarin- Henricson | The high temperature system is the most probable and the most efficient one - only if the problems in the long time reliability of its refractory materials can be solved. |

Continuation of Table I

| <i>Is Chemrec a leader in the development of black liquor gasification?</i> | |
|---|--|
| Interviewees | Answers |
| Esa Vakkilainen | Yes, nowadays Chemrec is the leader in black-liquor gasification. Chemrec is the most closest to become the reliable technological one. |
| Esa Hassinen | It is difficult to say. |
| McKeough Paterson | Yes |
| Anja Klarin- Henricson | Chemrec and the Swedish P&P Industry generally have been investing already a couple of decades into the black liquor gasification. The Swedish industry has patience to run pilot tests for years without losing the hope for success. The Finns were running similar half-pilot tests in the late 1980's and early 1990's but they lost their interest after some years of laborious testing. |

Table II Power and steam generation by gasification technology

| <i>How many times does the amount of generated electric energy by using Chemrec BLGCC increase compared with traditional recovery system?</i> | |
|---|---|
| Interviewees | Answers |
| Esa Vakkilainen | The true is that you can get maybe more than about 2000 kWh/ADt with the gasifier, it is possible, but for example nowadays power efficiency of Kymi is 1700 kWh/ADt. Chemrec now turns to making biofuel, it is more profitable. |
| Esa Hassinen | It can be two times higher than typical recovery boiler produces. If compared with advanced boiler it is lower but it must be taken into account that you put much money for the last. |
| McKeough Paterson | The increase in power would be about 50 % compared to advanced recovery boiler and 80 % compared to today's standard recovery boiler. |
| <i>How many times does the amount of steam produced by Chemrec BLGCC system decrease compared with traditional recovery system and it is enough for processing needs?</i> | |
| Interviewees | Answers |
| Esa Vakkilainen | Heat production during gasification is enough for all process needs no problem with it. The changes in heat recovery are not big. But in case of integrated mill where paper machine somewhere you need of additional heating in both RB and gasifier. And in case of gasifier is more auxiliaries are needed, but price for steam production is approximately is 10-12 euro per MWh and price of electric energy is about 40-45 MWh, so it is beneficial doing changes to increasing electric energy yield. |
| Esa Hassinen | It can be a lack of steam but it is not a problem because pulp mill usually has an extra power plant, challenge can be increasing load at it. Anyway increasing power generation is a profitable direction. |
| McKeough Paterson | In a stand-alone pulp mill, the amount of steam produced by the BLGCC plant and the bark-fired boiler maybe about enough to satisfy the mill demand. |

Table III Gasifier technical problems

| <i>What is the service life of gasifier?</i> | |
|--|---|
| Interviewees | Answers |
| Esa Vakkilainen | To me I believe it can run during year and then when pulp mill stops as usually the gasifier can be checked and may be doing some repairing. But probably after 2.5-3 years gasifier should be shutdown for rebuilding refractory and it maybe takes 2-3 weeks. |
| Esa Hassinen | This is an interesting question. Corrosion problem is the challenge. It can be run 2 years and then change material. |
| McKeough Paterson | Service life not yet proved. No such lining available. I understand that, even with Chemrec's most resistant material, the lining will have to be replaced regularly – at best maybe once every 2 or 3 years. |
| Anja Klarin-Henricson | The refractory which has been promising is based on fused cast alumina or magnesia or ZAC, but the problem of those dense materials is their total lack of temperature shocks. In practice they break very easily. Porous refractory materials will react with sodium vapour and thus, they will easily break because of the volume increase when sodium reacts with the inner surfaces of refractory material. The maximum life time for the present BL gasifiers has been only some months. One cannot build a gasifier for a half year only. |

Table IV The main obstacles of black liquor gasification technology

| <i>What are the main obstacles of implementation of gasification system into pulp and paper industry?</i> | |
|---|--|
| Interviewees | Answers |
| Esa Vakkilainen | The biggest reason why people don't buy gasifier because there is not existing plant that runs and people cant go to this and say that it is really work. In chemical industry to get product working it is need 3 times money more the investment. So approximately 750 million euros should be put in the development of black liquor gasification, but nobody has this money. Several plants should pay money for development this technology. |
| Esa Hassinen | Investment cost/pay back time (how fast we are able to pay back investment cost). Material corrosion is a challenge because it effects on the investment cost. Runnability, it should be run steady because in another way it provokes fiber line stopping and loosing money as a result. |
| McKeough Paterson | Uncertainty about availability is probably the main issue. The pulp mill wants high availability what means no unscheduled stoppage due to problems in the recovery cycle. Economic competitiveness is already at a reasonable level and will improve as the value of green electricity increases. |
| Anja Klarin-Henricson | The main obstacle in implementation is the great conservatism of P & P Industry in general. Moreover, it is an industry with a very straight forward development tradition. The solutions have to be solved in a couple of years and any process which is extremely tedious will be neglected. This is valid at least in the Finnish P & P Industry. The Swedish industry has a very long tradition to do industrial development work and thus it is the only hope in finding a commercial break through in BL gasification sooner or later. The commercial full scale solution will be after 2015 or even after 2020. |

Table V Feasibility of black liquor gasification technology

| <i>What do you think about feasibility of black liquor gasification process in Pulp and Paper industry as alternative recovery system? Does it have a future as alternative recovery system in Pulp and Paper industry?</i> | |
|---|--|
| Interviewees | Answers |
| Esa Vakkilainen | Black liquor gasification is near to be used but not to do recovery cycle. It is promising to applied BLG for destroying black liquor and produce suitable gas for DME production. In principle it should work but it will be any engineering obstacles or not is a question. |
| Esa Hassinen | If the investment cost can be lower the feasibility is rather good. It is possible to replace the recovery boiler if you have an extra power plant for cover the lack of steam. So only the drawback is an investment and lifecycle. The feasibility increases due to lower NOx and sulfur emissions, safety and polysulphide opportunities. BLG will be in the future at pulp mill but maybe after ten years. |
| McKeough Paterson | It has potential if the outstanding technical issues can be resolved without major negative impacts on the costs of the process. At present energy prices, the BLG developing for higher electricity output seems questionable. Production of motor fuels is potentially a more economic option. |
| Keijo Salmenoja | My personal opinion is that there is no economical basis to replace traditional recovery system with gasification. But I do not think that black liquor gasification will never enter the markets. It will, but not as an IGCC system with a gas turbine. There are too many technical obstacles. However, if we could do something else than just recover the chemicals, then it might make sense. Otherwise not. |