

## FLOWS OF EXERGY IN A RECOVERY BOILER OF PULP AND PAPER INDUSTRY USING THE BLACK LIQUOR AS MAIN FUEL

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**Abstract.** This work presents a study of the exergy flows in a recovery boiler of pulp and paper industry using the black liquor as main fuel. The black liquor is generated during the wood digestion process with steam in digestors, and the compound obtained is constituted by organic and inorganic substances. The recovery boiler is at the same time a chemical reactor and a steam generator. As a chemical reactor, it has the function of producing smelt, with maximum efficiency of reduction of the original sodium sulfate held in the burnt black liquor, to sodium sulfide. As a steam generator, it has the function of producing steam for processing, taking advantage of the heat liberated in the combustion of the organic fraction of the black liquor. As the environmental point of view, it is necessary to maintain these equipments in operation, for its operational disposal is indispensable for the destruction of a significant portion of the residues generated in the process, with heat recovering. Thus, an exergetic analysis was made, considering the operational data of a recovery boiler that burning 780 t/day of black liquor and generates 140 t/h of steam. This boiler makes part of an utilities system of a paper and pulp industry, composite for five boilers. In this system, two boilers burn fuel oil, a boiler burning biomass (wood chips), and two recovery boilers burns black liquor, producing a total of 470 t/h of steam. For this exergetic analysis, its was considered the exergy of the condensed, of smelt, of black liquor and of electric power.

**Keywords:** exergy, pulp and paper industries, black liquor, recovery boiler, energy conservation.

### 1. INTRODUCTION

The steam consumption in a pulp and paper is considerable, due to the great amount of equipments and mainly paper machines (SBS, 2001). The scheme of production process stages of pulp and paper industry can be seen in the Fig. 1.

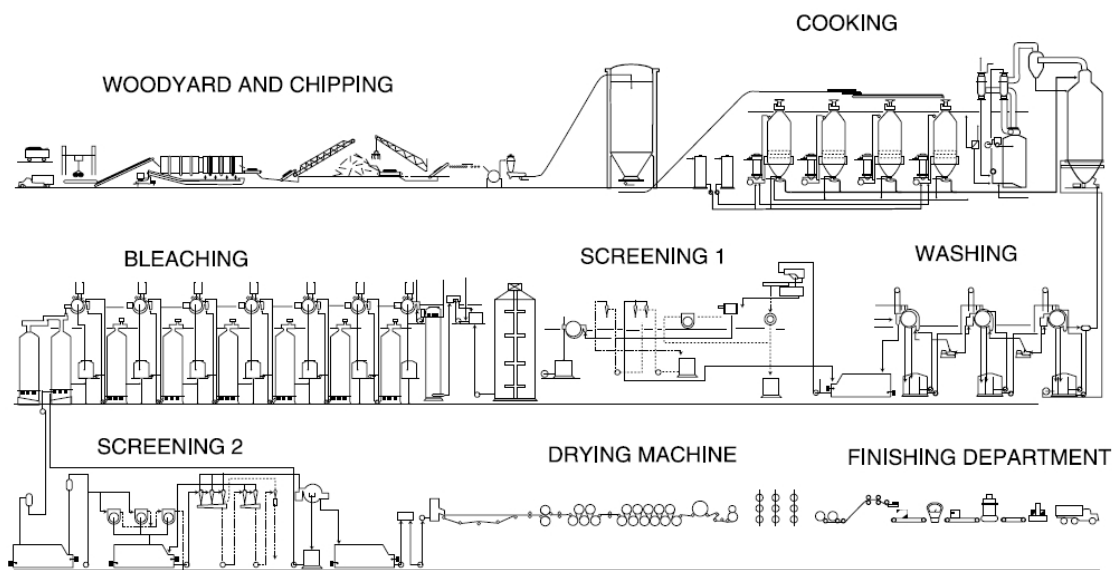


Figure 1 – Stages of production process in a pulp and paper industry (EPA, 2002).

The installation of steam generation of the plant analyzed, is formed by a group of five boilers what makes part of a utility system and some of them very importantly inside of the pulp and paper manufacturing. In this industrial installation in study, according to SPC (2002), the steam production is constituted by two auxiliary boilers, a biomass boiler and two chemical recovery boilers, in which the fuel is the black liquor. This work presents the study in a plant with a medium production of 470 t/h of steam, produced by five boilers. In this utility system, two boilers burn fuel oil, one boiler burn biomass (wood chips), and two recovery boilers burns black liquor, producing a total of 470 t/h of steam. The main control factors are the pressure and the steam temperature. The Fig. 2 shows a diagram this installation. This work will make an exergetic analysis of chemical recovery boiler that burn black liquor and produce 140 t/h of steam, in 50 bar and 400°C.

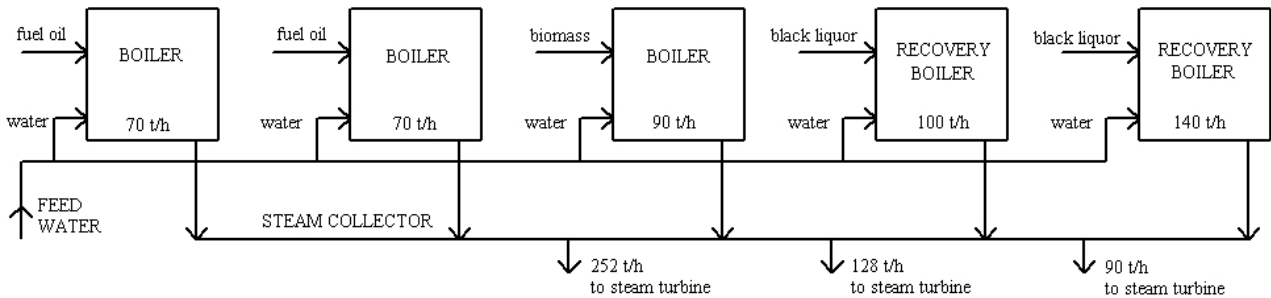


Figure 2 - Diagram of a steam production installation in a pulp and paper industry.

## 2. THERMAL SYSTEM OF STEAM

The biomass boiler and the chemical recovery boiler has great importance of the environmental point of view, because they use as fuels, residues generated in the process. These residues are: a) the biomass that is originating from the peel and chip of wood used in the cooking; b) the black liquor, that is resulting of the cooking process of wood in the digester. This cooking is made with steam and in a stage of the process they separate the fibers of the black liquor. The extracted liquor still goes by other processes before burning in the boiler.

The strong black liquor from the evaporators is burned in a recovery boiler. In this crucial step in the overall kraft chemical recovery process, organic solids are burned for energy and the process chemicals are removed from the mixture in molten form. Molten inorganic process chemicals (smelt) flow through the perforated floor of the boiler to water-cooled spouts and dissolving tanks for recovery in the recausticizing step. Energy generation from the recovery boiler is often insufficient for total plant needs, however, so facilities augment recovery boilers with fossil-fuel-fired and wood-waste-fired boilers (hogged fuel) to generate steam and often electricity.

Of the environmental point of view, it is necessary to maintain these equipments in operation, because its operational readiness is indispensable for the destruction of a significant portion of the residues generated in the process, with recovery of heat. The auxiliary boilers are important in the process, because they maintain the stability and the steam demand.

The water used in the process of steam generation is demineralized. The water is pumped by pumps of high pressure multi-stages. The pumped water is going to a collector, being distributed in the boilers. The boiler feed water is a combination of demineralized water and condensed that return, mainly, from the paper machines and evaporation plant.

This condensed, eventually, can be diverted for the station of effluents treatment by silica contamination, high alkalinity or presence of suspended solids.

The steam, in a pulp and paper industry is used mainly for the cooking of the wood in the digestors, in the process of chemical recovery of the soda used in the cooking and for drying of the paper in the machines, consuming, respectively, on average 13%, 25% and 38% of every generated steam.

### 2.1 Biomass Boiler

Besides of aid in the steam generation, the biomass boiler has an important function in the pulp and paper industry, in the economical and environmental subject, because it uses as main fuel the peel and the ship of the eucalyptus, residues of the raw material used in the cooking process in the digester (Gasa, 1994). The biomass boiler continual operation is important for the environment, because a very long stop to convey an accumulation of peel and that is harmful for the process. It also uses how it burns auxiliary two fuel oil burners to maintain the temperature of the constant steam.

The Fig. 3 presents a simplified flowchart of the operation of the biomass boiler, manufactured by Zanini, showing the currents that compose this operational subsystem (SPC, 2002).

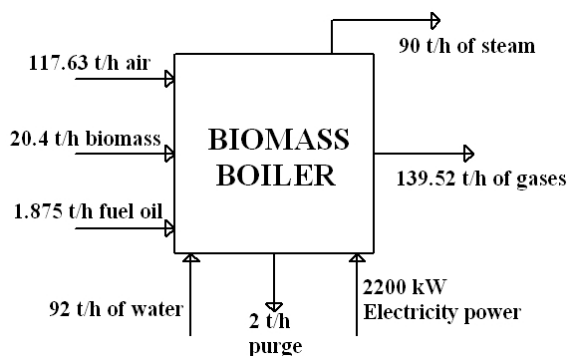


Figure 3 – Flowchart of biomass boiler.

## 2.2 Chemical Recovery Boiler

The chemical recovery boiler is, at the same time, a chemical reactor and a steam generator. As chemical reactor, has the function of producing smelt, with maxim efficiency of reduction of the sulfate of original sodium contained in the burned black liquor, the sodium sulfide. The composition of those smelt is: Na<sub>2</sub>S (sodium sulfide), Na<sub>2</sub>CO<sub>3</sub> (sodium carbonate), Na<sub>2</sub>SO<sub>4</sub> (sodium sulfate) and NaCl (sodium chloride).

As steam generator, has the function of producing steam for the process by heat liberated in the combustion of the organic fraction of the black liquor. This boiler uses as fuel the organic matter that corresponds approximately to 2/3 of the composition of the black liquor. The Fig. 4 shows a diagram of operational data this chemical recovery boiler.

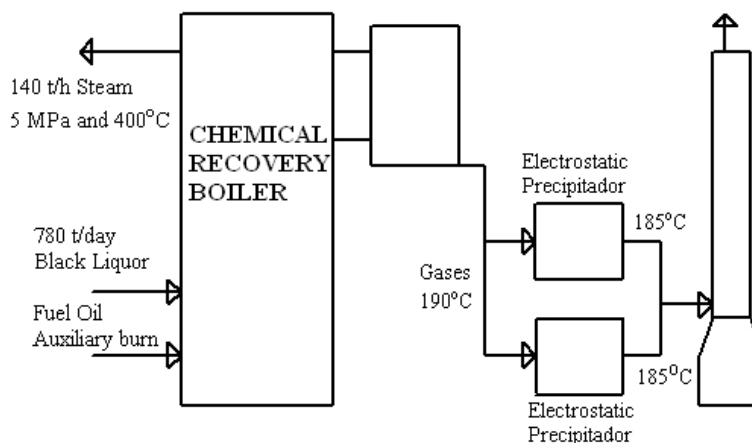


Figure 4 – Diagram of Chemical Recovery Boiler for 780 t/day of black liquor.

Environmental and energy factors conditioned the development of the technology of the chemical recovery boilers (CBC, 2002). The objective of the chemical recovery is to recover the reactants used in the cooking of the wood or other raw materials used in the cellulose production, and recovery of the energy liberated in the combustion of the dissolved organic components. Basically, the objective of the boiler is to recover in the Na (sodium) and S (sulfur) of the liquor of the digestors, searching the decomposition of the cooking liquor and the recovery of the energy values of the liquor in steam form (Schreiber, 2001). The singular characteristic of operation of the recovery boiler is the need to maintain a reduced atmosphere in the furnace in order to recover S, as well as Na<sub>2</sub>S.

In relation to the combustion, once in form of gases, the volatile ones formed during the dehydration, pyrolysis and gasification react quickly with oxygen to form CO<sub>2</sub> and H<sub>2</sub>O. Those reactions are extremely exothermic.

### 2.2.1 The Black liquor

The black liquor is a complex mixture of compound organic and inorganic. While some compositions originate directly from the wood or of the cooking liquor, many are formed by reactions chemistry in the cooking.

During the Kraft process, the lignin is extracted of the wood reacting with sodium hydroxide to form sodium compounds. In the internal conditions of the digester the whole Na<sub>2</sub>S through white liquor becomes sodium acid sulfite (NaHS) and sodium hydroxide (NaOH), as presented in the Equation 1.



During the cooking, the hemicelluloses and part of the cellulose degrade forming carboxylic organic acids. The fatty acids, called extractive acids, are present in the wood and they are extracted in the cooking. These acids form the soap in the black liquor. The soap content in the black liquor can vary from 1 to 7%. The soap is insoluble, with a limit of solubility of 0,5%. The efficiency of removal of soap of the liquor is approximately of 75% of the insoluble soap. The amount of soap in the burned black liquor is typically of 2% of the solids of these organic acids. The residual alkali present in the black liquor helps to avoid the effect stripping of H<sub>2</sub>S (sulfide gas), CH<sub>3</sub>SH (methyl mercaptan) during the evaporation and it helps to maintain the viscosity in an acceptable low level. The residual effective alkali usually has 10g/L Na<sub>2</sub>O with pH from 10 to 12 (Schreiber, 2001). The Fig. 5 presents the diagram of feeding of the black liquor in the chemical recovery boiler. The Table 1 presents the elementary composition of the black liquor, according to IPT (2001).

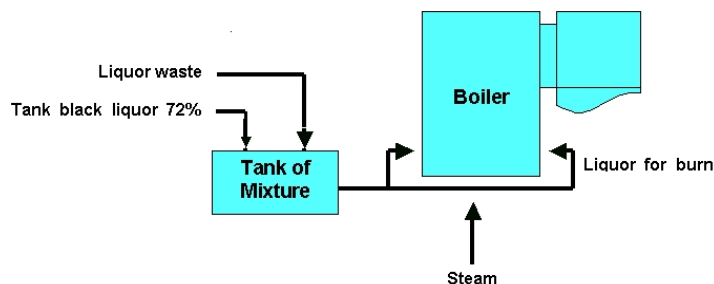


Figure 5 – Diagram of feeding of the black liquor in the chemical recovery boiler.

Table 1 - Elementary Composition of the solids of the inorganic black liquor in % weight.

Element	%	Element	%
Carbon	42.6	Sodium	18.3
Hydrogen	3.6	Oxygen	31.7
Sulfur	3.6	Inert	0.2

Source: IPT, 2001.

### 3. EXERGETIC ANALYSIS OF THE PROCESS

The exergy is the maximum available work that it can be obtained in a certain way of energy using the conditions of the atmosphere in its turn, as state referential (Kotas, 1985, apud Santana, 1998).

For an energy system that operates in different conditions to the reference temperature, it can be said that the exergy is the useful part of the energy, that is, the part of the energy that can be transformed in another form of energy.

According to Moran and Shapiro (2000), the specific exergy (exergy for mass unit) of a system can be expressed by the Equation 2.

$$b = (u - u_0) + p_0 \cdot (v - v_0) - T_0 \cdot (s - s_0) + \frac{C^2}{2} + gz + ex^{ch} \quad (2)$$

where,  $u$ ,  $v$ ,  $s$  are energy specific interns, volume and entropy, respectively, for a die state whose temperature is  $T_0$ ;  $u_0$ ,  $v_0$ , only, are the same specific properties in the conditions of thermodynamic balance with the middle,  $C^2/2$  is the specific kinetic energy,  $gz$  is the energy potential specific gravitacional and  $ex^{ch}$  is chemical exergy.

In many applications practices, there is the interest by associate exergy with continuous inflow or outflow in a control volume; in this case, for specific exergy can be calculated by the Equation 3:

$$b = (h - h_0) - T_0 \cdot (s - s_0) + \frac{C^2}{2} + gz + ex^{ch} \quad (3)$$

where,  $h$  is the enthalpy,  $s$  the entropy for a determinate temperature and pressure,  $h_0$  and  $s_0$  are enthalpy and entropy specific in the conditions of thermodynamic balance with the middle.

For energy systems, of mass flow, it is enough to just consider the portions regarding the thermodynamic balance with the middle, in other words, the exergy is given by the Equation 4, since there are not chemical reactions and nor the effects of the energies kinetics be considered and potential (Kotas, 1985).

$$B = m \cdot [(h - h_0) - T_0 \cdot (s - s_0)] \quad (4)$$

### 3.1 Exergy of a Substance

As the process involves such substances as steam of water, water liquidates, mixture of gases and liquid and solid fuels, it becomes necessary to evaluate its exergy, which she get applying the Equation 5.

$$B_g = n_g \cdot b^{\circ} M_g + (T_g - T_0) \cdot \sum_k n_{gk} \cdot C_p^{b_{gk}} \quad (5)$$

where, the first term corresponds to the portion of the chemical exergy and the second term, to the physical exergy. The values of  $C_p^{b_{gk}}$  used in the Equation 5 take into account the enthalpy variation and entropy in a die temperature interval for the different compound of gases (gk).

The chemical exergy of mixture ( $b^{\circ}_{Mg}$ ) is defined for Equation 6:

$$b^{\circ} M_g = \sum_k y_{gk} \cdot b^{\circ} g_k + R \cdot T_0 \cdot \sum_k (y_{gk} \cdot \ln y_{gk}) \quad (6)$$

where,  $y_{gk}$  is the molar fraction of gaseous compound; k represent the different gases; R the universal constante of the gases; and  $T_0$  the reference temperature.

The standard chemical exergy is defined by Szargut (1988), by Euqaton 7:

$$b^{\circ} g_k = \Delta G^{\circ} + \sum_{el} n_{el} \cdot b^{\circ} el \quad (7)$$

where, the subscript el represent the pure element used in calculus of chemical exergy standard; and n represent the number or quantity in kmol of this element.

In the case of the solids, the exergy of the mixture is given by Equation 8:

$$B_s = n_{ms} \cdot b^{\circ} M_g + \sum_k n_k \cdot [(h - h_0) - T_0 \cdot (s - s_0)]_k \quad (8)$$

where, in Equation 9, is defined the second term of Equation 8:

$$\sum_k n_k \cdot [(h - h_0) - T_0 \cdot (s - s_0)]_k = \sum_k n_{sk} \cdot \left[ \int_{T_0}^{T_s} C_{pk} \cdot dT - T_0 \cdot \int_{T_0}^{T_s} C_{pk} \cdot \frac{dT}{T} \right] \quad (9)$$

where,  $n_k$  - represent the kmol of each element present in the compound.

The values for exergy of the solids and gases can be calculated being taken into account the variation of the physical and chemical exergia of the solid and gaseous compositions. Like this, according to Kotas (1985) the values for exergy of the gases ( $B_g$ ) can be calculated by the Equation 4 and 6. The relative values to the specific heats of the compositions used in the calculations of the exergy of the gases and solids, they were obtained starting from the data reported by Carvalho et al. (1977) and Perry and Chilton (1980). Already the relative data the chemistry standard exergy was obtained of Szargut et al (1988).

The variation of the enthalpy and entropy of the chemical compositions in function of the temperature were calculated according to the Equations 10 and 11.

$$(h - h_0) = 4,186 \cdot (A \cdot T_s + B \cdot (1 \times 10^{-3} \cdot T_s) + C \cdot 1 \times 10^5 \cdot \frac{1}{T_s} + D) \quad (10)$$

$$(s - s_0) = 4,186 \cdot \left[ A \cdot \ln\left(\frac{T_s}{T_0}\right) + 2 \cdot B \cdot 1 \times 10^{-3} \cdot (T_s - T_0) + \frac{C}{2} \cdot 1 \cdot 10^5 \cdot \left(\frac{1}{T_s^2} - \frac{1}{T_0^2}\right) \right] \quad (11)$$

The constants A, B, C and D, used in the Equations 10 and 11, they were obtained of Carvalho et al (1977).

### 3.2 Rational Efficiency.

The efficiency of the systems can be evaluated using the concept of exergetic efficiency ( $\eta_e$ ), starting from an analysis of the flows of exergy of the solids, gases and liquids, considering the system and the subsystems.

According to Gallo (1998) the exergetic efficiency is the relationship between the variation of the wanted exergy and the consumption of necessary exergy to the process.

In this case represented by an installation of steam generation and electric power, that is, flow of gases, liquids and solids (fuels, electric power and steam), like this the rational efficiency can be defined in agreement with Kotas (1985), according to the Equation 12.

$$\Psi = (\text{Exergy transferred}) / \text{Exergy supplied} \quad (12)$$

where: Exergy transferred – exergy transferred to steam and smelt recovered exergy; Exergy supplied – exergy supplied by fuel and electric power. As not there are uses for the exhaustion gases, these will be scored.

### 3.3 Exergetic Analysis of the Chemical Recovery Boiler

The analyzed system, to proceed, it is a steam generator manufactured by CBC presenting capacity of steam production for 140 t/h. The chemical recovery boiler uses as fuel, black liquor and his consumption is approximately 780 to 800 t/24h of dry solids.

The Figure 6 presents a diagram of the mass balance for the combustion of the black liquor, identifying and quantifying the currents that participate of the burns this product of the pulp production.

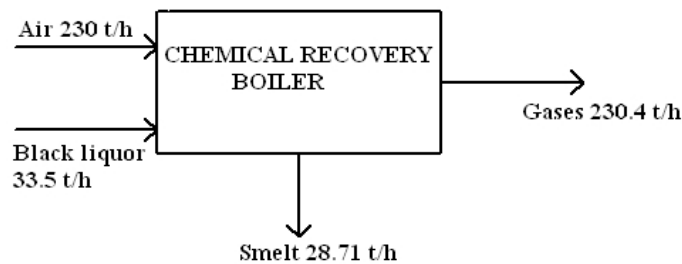


Figure 6 – Mass Balance of chemical recovery boiler in relation the burn of black liquor.

The exergetic calculation of the chemical recovery boiler presents the following steps (Silva, 2002):

- 1) calculation of the steam exergy;
- 2) calculation of the condensed exergy;
- 3) calculation of the black liquor exergy;
- 4) calculation of the smelted exergy;
- 5) calculation of the combustion gases exergy.

The presentation of the values of each one of the items considered for the calculation of the exergia of the boiler is made in sequence.

#### 3.3.1 Steam Exergy

With the data of the process ( $P = 50$  bar,  $T = 400$  °C and steam flow = 140 t/h), were obtained the enthalpies values and entropy that are applied in the Equation 4, being obtained the value of the exergy of the steam ( $B_{\text{steam}}$ ).

$$B_{\text{steam}} = 43,700 \text{ kW.}$$

#### 3.3.2 Condensed Exergy

With the data of the process ( $P = 80$  bar,  $T = 130$  °C and mass flow of condensed = 104 t/h), were obtained the enthalpy values and entropy, that are applied in the Equation 4, being obtained the value of the exergy of the condensed ( $B_{\text{condensed}}$ ).

$$B_{\text{condensed}} = 2,440 \text{ kW.}$$

### 3.3.3 Black Liquor Exergy

The chemical composition of the black liquor used in this installation is presented in the Table 2.

Table 2 – Chemical composition of black liquor.

Chemical composition of fuel		Chemical composition of Smelt
Organic (% weighth)	Inorganic (% weighth)	Smelt (% weighth)
C – 37	Cl – 0.4	Na <sub>2</sub> S – 9.37
H <sub>2</sub> – 3.3	K – 0.4	Na <sub>2</sub> SO <sub>4</sub> – 1.9
S – 4.2	Na – 1.87	NaCO <sub>3</sub> – 30
O <sub>2</sub> – 36		K <sub>2</sub> CO <sub>3</sub> – 2.12
		NaCl – 1.0

Source: IPT, 2000

Starting from the percentages presented in the Table 2 for the chemical composition of the fuel and of smelt, the percentual values were transformed for values molars per second, in way to allow the calculations of the exergy of the solids flow. The fuel used in the it burns has concentration of 72%. The Table 3 presents the molar flow (kmol/s) of the components of the black liquor, smelt and water.

Table 3 – Molar flow of dry solids of black liquor, smelt and water.

Molar flow of fuel		Molar flow of smelt
Organic [kmol/s]	Inorganic [kmol/s]	Smelt [kmol/s]
C – 0.2869	Cl – 0.001063	Na <sub>2</sub> S – 0.011779
H <sub>2</sub> – 0.1535	K – 0.0009593	Na <sub>2</sub> SO <sub>4</sub> – 0.001245
S – 0.01221	Na – 0.07565	Na <sub>2</sub> CO <sub>3</sub> – 0.026334
O <sub>2</sub> – 0.1046		K <sub>2</sub> CO <sub>3</sub> – 0.001429
H <sub>2</sub> O – 0.2010		NaCl – 0.0016043

Source: For smelt, the values were obtained according Terry (1988) of American Paper Institute.

However, it should be emphasize that, for not having the data of the compositions of organic and inorganic in his real form, but just the composition of the pure elements, obtained by Terry (1998), it was made the calculations considering the pure elements, not having therefore, conditions of esteeming the quantitative mistake, for this option.

The total flow of the burned black liquor is the sum of the mass flow of dry solids (ss) of the black liquor added to the mass flow of water. That water is still added in the evaporator increasing the concentration of 15% for 72%.

Applying a mass balance for the black liquor, it is obtained the mass flow in kg/s given by the Equation 13:

$$\dot{m}_{Lp}[72\%] = \left[ \frac{803.95 [\text{tss}/24\text{h}] \times 1000}{24 \times 3600} \right] = 9.305 \text{ kg/s} \quad (13)$$

With the result of the Equation 13, the Equation 14 can be applied to obtain the molar flow in kmol/s for each compound of the black liquor.

$$n_{Lp}(72\%) = \left[ \frac{\dot{m}_{Lp}}{M_i} \right] \times Y_i \quad (14)$$

where:  $M_i$  - Molecular mass of each compound, in kg/kmol;  $Y_i$  - Percentage in weighth of each compound of fuel;  $\dot{m}_{Lp}$  - Mass flow of black liquor, in kg/s of dry solids.

The result of the calculations obtained through the Equation 14, for the black liquor composition is presented in the Table 4, in way to allow the calculations of the exergy of the current of the solids. The water flow presented in the Table 4 refers the water added in the evaporation and envoy for burners.

The flow of black liquor used for it burn is from 800 t/day of dry solids, in temperature of 800°C. As in this case the black liquor is a solid fuel with a concentration of 72%, is applied for the exergetic calculation of the mixture, the Equation 15, complemented by the Equation 16.

Table 4 –Molar flow of solids black liquor, smelt and water.

Chemical composition of fuel.		Chemical composition of Smelt
Organic [ kmol/s ]	Inorganic [ kmol/s ]	Smelt [ kmol/s ]
C –0.2869	Cl – 0.001063	Na <sub>2</sub> S – 0.011779
H <sub>2</sub> – 0.1535	K- 0.0009563	Na <sub>2</sub> SO <sub>4</sub> – 0.001245
S – 0.01221	Na – 0.07565	Na <sub>2</sub> CO <sub>3</sub> – 0.026334
O <sub>2</sub> – 0.1046		NaCl – 0.0016043
H <sub>2</sub> O – 0.2010		

Source: Results of calculations.

$$B_s = n_{ms} \cdot b^\circ \text{Mg} + \sum n_k \cdot [(h - h_o) - T_o \cdot (s - s_o)]k \quad (15)$$

where, the second term is represented by Equation 16.

$$\sum n_k \cdot [(h - h_o) - T_o \cdot (s - s_o)]k = \sum n_{sk} \cdot \left[ \int_{T_o}^{T_s} C_{pk} \cdot dT - T_o \cdot \int_{T_o}^{T_s} C_{pk} \cdot \frac{dT}{T} \right] \quad (16)$$

With the Equations 15 and 16 and the data of the enthalpy and entropy to 800°C, it is calculated the value of exergy of the black liquor (Bln). The coefficients of the variation of Cp with temperature, for calculus of enthalpy and exergy, they were based on data of e Carvalho et al (1977), Perry and Chilton (1982) and Szargut et al. (1988) apud Silva (2002).

With the Equations 15 and 16 and enthalpy and entropy data to 800°C, it arrives to the value calculated of exergy of the black liquor (Bbl).

$$B_{bl} = 190,000 \text{ kW.}$$

### 3.3.4 Smelt Exergy

The calculation of exergy of the smelt is begin of the mass balance of black liquor, in the flow conditions and temperature of the black liquor mentioned in the previous item and considered the mass balance of their constituents, as presented in the Table 4. The coefficients for calculus of enthalpy and entropy are presented in Table 5.

Table 5 – Coefficients used in enthalpy and entropy calculation of the smelt and chemical standard (b°).

Compound	A	B	C	D	b° [kJ/kmol]
Na <sub>2</sub> S	19.81	0.82	--	-5,979	921,400
Na <sub>2</sub> SO <sub>4</sub>	47.18	--	--	-10,190	21,400
NaCl	16	--	--	260	14,300
Na <sub>2</sub> CO <sub>3</sub>	45	--	--	-13,100	41,500

Source: Carvalho et al. ( 1977 ), Perry and Chilton (1982), Szargut et al. (1988)

The data obtained like this are applied in the Equation 15, supplying the value of the exergy of those smelt (Bsm).

$$B_{sm} = 16,808 \text{ kW}$$

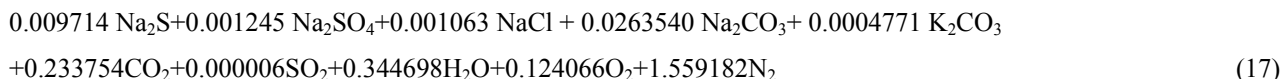
### 3.3.5 Exhaust Gases Combustion Exergy

The exergy values of the solids and gases can be calculated being taken into account the variation of the physical and chemical exergia of the solid and gaseous compounds. Like this, according to Kotas (1985) the exergy values for gases (Bg) can be calculated by Equations 4 and 5.



The boiler operates with an 6.5% excess O<sub>2</sub>, in dry base.

Through an applied mass balance to the solids and gases, whose values come in the Figure 3, were obtained the amounts of having melted (Smelt) that leave the furnace for the inferior part of the reactor and the exhaustion gases that leave for the stack, after they go by the electrostatic precipitador. To proceed, it was made a mass balance for the products of combustion. The Equation 17 represents the combustion equation of the obtained materials of the mass balance, the units are in kmol.



Applying the Equation 12, is obtained the mass flow of the gases ( $\dot{m}_g$ ) to the exit of the furnace.

$$\dot{m}_g = \sum (n_i) \cdot M_i + [(n)_{\text{O}_2} + (n)_{\text{N}_2}] \cdot M_{ar} \quad (18)$$

where:  $n_i, n$  - represent the flow molar of each composite contained in the combustion gas, in kmol/s;  $M_i$  - is the molar mass of each compound contained in the combustion gases, in kg/kmol;  $M_{ar}$  - is the molar mass of the air, in kg/kmol.

With the value of the flow molar of the gases according to the Equation 12 and with the application of the Equations 5 and 6, in which the properties were obtained in 473 K, that is the temperature considered for the exhausted gases, was calculated the value of the exergy of the gases ( $B_g$ ).

$$B_g = 10,739 \text{ kW.}$$

The results of the calculations, relative to the exergy of the flows that cross the volume of control of the boiler, are presented in the Figure 7, considering the five subdivisions of this, constituted by the boiler.

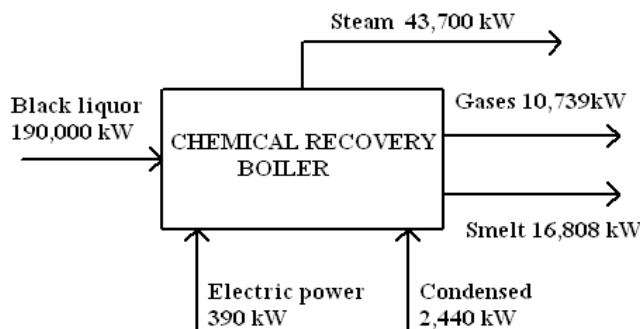


Figure 7 – Exergy of gases, solids, steam, condensed and electric power.

### 3.3.6 – Exergetic Efficiency

Starting from the values presented in the Figure 7, the Rational Efficiency ( $\psi$ ) can be calculated, according with the Equation 12, for the considered boiler. The values for the First Law Efficiency and the Rational Efficiency, are presented in the Table 6. The exergy of exhaustion gases are not considered in calculation of Rational Efficiency, because not have application for its in system utility.

$$\psi = \frac{(B_{steam} - B_{condensed}) + B_{sm}}{B_{bl} + B_{EE}} = \frac{(43700 - 2440) + 16808}{190000 + 390}$$

Table 6 – Results of Calculation of the First Law Efficiency and Rational Efficiency for the Recovery Boiler.

System	First Law Efficiency	Rational Efficiency
Recovery Boiler	$\eta_e = 74.8 \%$	$\Psi = 30.5 \%$

#### 4. CONCLUSION

The steam consumption in the pulp and paper industry production is considerable, representing a factor of great economical importance. The improvement of the raw material generates residues, that they are used as fuel in the biomass boiler and the recovery of chemical products of the black liquor, with the use of the recovery boiler, not only they contribute to the improvement of the environmental factors as, also, they contribute to the improvement of the global balance of the energy system. The exergetic analysis of the chemical recovery boiler shows that great part of the exergetic flow, which enters in the control volume, is destroyed in the chemical reaction and in the obtaining of steam of water. This destruction is related with the black liquor, because it is known that the main function is to recover the chemical products, producing steam for the reaction of the organic material, solubilized during the process of pulp production. The recovery boiler of black liquor are equipments that should constantly be monitored and always updated technologically, seeking better incomes in terms of combustion systems and operational control of the chemical reactions that happen in the boiler.

#### 5. REFERENCES

- Carvalho, J. R. L. et al, 1997, "Dados Termodinâmicos para Metalurgistas", Universidade Federal de Minas Gerais, Belo Horizonte.
- CBC – Companhia Brasileira de Caldeiras – Indústria Pesada S. A., 2000, Manual de Operação de Caldeiras de Recuperação Química.
- EPA – Environmental Protection Agency, 2002, "Profile of the Pulp and Paper Industry", Office of Enforcement and Compliance Assurance, U.S. Environmental Protection Agency, Washington, Dc.
- Gallo, Valdir, 1998, "Avaliação da Entropia pela Segunda Lei da Termodinâmica", Notas de Aula, Universidade Estadual de Campinas – UNICAMP.
- Gasa, G, 1994, "Biomassa", Gurgel Araújo Indústria e Comércio S.A.
- IPT – Instituto de Pesquisas Tecnologia – Universidade de São Paulo, 2001, "Celulose e Papel – Tecnologia de Fabricação de Pasta Celulósica", 2ª Edição, Volume I.
- Kotas, T. J., 1985, "The Exergy Method of Thermal Plant Analysis", Anchor Brendon Ltd, Essex, Great Britain.
- Moran, M. L. J., and Shapiro, H. N., 2000, "Fundamental of Engineering Thermodynamics", 4<sup>th</sup> Edition.
- Perry, R. H. and Chilton, C. H., 1980, Manual de Engenharia Química, 5ª Edição.
- Santana, J. A., 1998, "Código Computacional para Análise de Sistemas de Cogeração com Turbinas a Gás", Tese de Doutorado, Universidade de São Paulo.
- SBS – Suzano Bahia Sul, 2001, Sistema de Informações Operacionais de Celulose/Utilidades.
- Schreiber, G and M. Consultores Limitada, 2001, Curso de Segurança Operacional em Caldeiras de Recuperação Química.
- Silva, J., "Análise Termoeconômica do Processo de Geração de Vapor e Potência do Segmento de Papel e Celulose", 2002, Dissertação de Mestrado, Universidade Federal de Itajubá – UNIFEI.
- SPC – Suzano, Papel e Celulose, "História do Grupo Suzano", 20 Jan 2002, <http://www.suzano.com.br>.
- Szargut, J. et al, 1988, "Exergy Analysis and Thermal , Chemical and Metallurgical Process", Hemisphere Publishing Corporation, USA.