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EXERGETIC ANALYSIS OF A CHEMICAL RECOVERY BOILER IN THE PULP AND PAPER INDUSTRY

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Abstract. *The chemical recovery boiler is important in the pulp and paper industry for burning black liquor, allowing the recovery of inorganic chemical compounds and the production of steam for the generation of electricity and use in the process. In this paper, the operational data of a boiler has a capacity of 180 ton/h of superheated steam at 400 °C and 50 bar, and burns 1,400 tonnes of dry solids per day. A stoichiometric analysis is made from the burning of black liquor as biomass, taking into account the chemical reactions for the formation of smelt and gases. The exergetic analysis methodology of boiler is fundamentally based on the elemental composition of the black liquor. The generation of steam and smelt in the boiler has a rational exergetic efficiency of 24.2%. The composition of black liquor can vary from one industry to another, showing its impact on the recovery process of inorganic compounds and on the generation of steam. The combustion gases are released into the atmosphere in the order of 6,360 tons/day at 200 °C and can also be used, with* CO_2 *flow in the order of 1,480 ton/day, generated from the combustion of biomass.*

Keywords: *black liquor, chemical recovery, efficiency exergetics, pulp and paper*

1. INTRODUCTION

The pulp and paper industry uses long or short fiber wood as the primary source of raw materials. The production process essentially consists of obtaining the pulp of cellulose from wood, the Kraft process being the dominant methodology used, as it presents advantages of producing cellulose with high resistance, greater flexibility regarding different types of wood, availability of recovery of chemical reagents and steam and electricity generation (Baum, 2008; Reis, 2013; Passini, 2017). The generation of steam and electrical energy from the use of black liquor as fuel allows a reasonable portion of the electrical energy consumed at the plant to be generated in the cogeneration system, been able to achieve self-sufficiency in newer systems with a higher pressure. This implies lower electricity and thermal costs in an energy-intensive sector.

The Kraft process consists of using cooking liquor, a combination of two chemical reagents, sodium hydroxide (NaOH) and sodium sulphide (Na_2S), acting on wood in the form of chips, resulting in the dissolution of lignin and the release of fibers. These released fibers, the brown cellulose or brown mass that is washed later (Tran and Vakkilainnen, 2008; Carreiro, 2009). After the wood digestion or cooking process, about 50% of the mass of chips dissolves in liquid form (lignin), the so-called black liquor (Reis, 2013).

After leaving the wood cooking process, the black liquor containing about 80% water is destined to a series of evaporators, from where it comes out with a concentration of 70% to 80% dry solids and 30% to 20% of water. Then before being sent to the boiler furnace, you can add sodium sulphate (Na_2SO_4) to this liquor to supply the losses of inorganic ions retained in the pulp (Cardoso, 1998).

In the Kraft process, the recovery boiler allows the chemical compounds in the cooking liquor been recover during the burning of the black liquor. Within this process, the wood lignin contained in the black liquor is burned, generating heat that used in the generation of steam, used in a cogeneration system, for the generation of electrical energy in the backpressure steam turbines and later as process steam (Baum, 2008; Carreiro, 2009). In the chemical recovery boiler, the black liquor is pulverized so that there's the burning of the organic compounds, the release of heat for the generation of steam, and, at the same time, the recovery of the inorganic compounds presented in the black liquor.

In this sense, this paper aims to evaluate the exergetic efficiency of a chemical recovery boiler in the cellulose and paper industry based on its energy flows and the chemical composition of the burnt black liquor. This paper contributes with a methodology for the analysis of chemical recovery boilers, also applicable to other industrial components, aiming to evaluate their efficiency, avoid waste, and highlight the potentially available resources.

2. METHODOLOGY

When a thermodynamic analysis is made by the First Law of Thermodynamics, the results are not always satisfactory, as it evaluates the energy produced by a system and not which is utilized or harnessed (Passini, 2017). The Second Law of Thermodynamics inserts the concept of reversible and irreversible processes, and the reversible process consists of ideal systems, with no energy losses, that is, being able to return to its initial state, and irreversible processes are systems in which there are losses of energy during the process. From this, exergy may conceptualize as a property that quantifies the potential use of a given energy, in other words, it is possible to achieve better use of energy resources, reducing the destruction of exergy within a system. (Moran *et al.*, 2011).

Therefore, the evaluation of exergetic flows brings the results closer to what happens in a thermal system, allows the analysis of improvement and efficiency of the processes involved, and the comparison with the energy efficiency of the boiler.

The following is a calculation methodology for developing the exergetic analysis of the chemical recovery boiler.

2.1 Energy analysis

For this paper, the energy analysis will be done by assessing the energy efficiency of the chemical recovery boiler. According Passini (2017), the energy efficiency (η_E) of the chemical recovery boiler can be calculated from the Eq. (1).

$$\eta_E = \frac{E_{st}}{E_{BL}} \tag{1}$$

Being E_{st} the energy gained by the liquid water to the state of superheated steam that can be calculated from the Eq. (2), and E_{BL} the energy of the black liquor, which can be calculated from the Eq. (3).

$$E_{st} = \dot{m}_{st} \cdot (h_{st} - h_l) \tag{2}$$

$$E_{LP} = \dot{m}_{LP} \cdot PCI \tag{3}$$

Being $\dot{m}_{st}$ and $\dot{m}_{LP}$ the mass flow of steam and black liquor, h_v and h_l the specific enthalpy of superheated steam and liquid, successively, and PCI the lower calorific value of black liquor, which can be calculated from the Eq. (4), known as the Dulong Equation (Hosokai *et al*., 2016), for the elemental composition of a dry fuel.

$$PCI = 4{,}186 \cdot \left[8.140 \cdot C + 29.000 \cdot \left(H - \frac{O}{8}\right) + 2.220 \cdot S\right] \tag{4}$$

Being C the mass fraction of carbon, H the mass fraction of hydrogen, O the mass fraction of oxygen and S the mass fraction of sulphur.

2.2 Exergy analysis

The exergetic analysis seeks to point out the losses of a system, considering the irreversibility of the process, using the concepts of mass conservation and energy conservation, having as a principle the Second Law of Thermodynamics, which evaluates the irreversibility present in a thermal system, in the which exergy quantifies the work generated and qualifies its usefulness (Oliveira Junior, 2013; Passini, 2017).

For the calculation of the total exergy of a thermal system (B_{th}) that does not suffer the effects of kinetic and potential energies, they can be neglected (Kotas, 1985; Szargut *et al.*, 1988). Therefore, there's a definition of the exergy of interest in this paper, presented in Eq. (5).

$$B_{th} = B_{ph} + B_{ch} \tag{5}$$

Being B_{ph} physical exergy and B_{ch} chemical exergy.

For the application of thermodynamic analyses, it's necessary to define a system boundary or a control volume (CV). According to Moran *et al.* (2011), a CV is defined as a region bounded by a frontier in space, in which it's desired to study and that there's a mass or energy flow that crosses this imaginary boundary with the neighbourhood.

Figure 1 shows the CV of the chemical recovery boiler, with its respective exergy flows to be analysed.

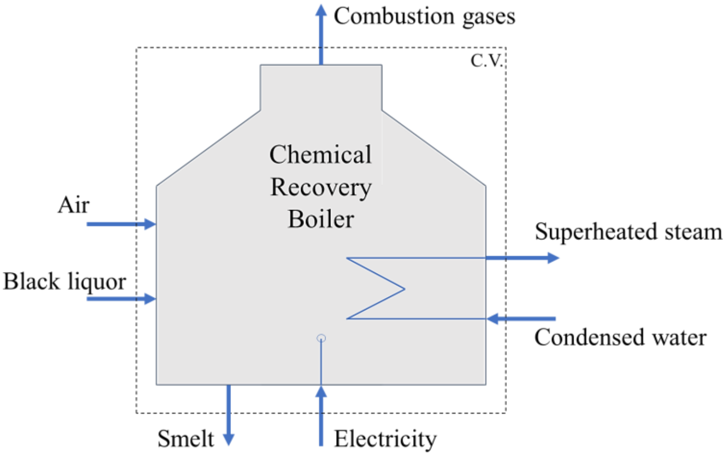

Figure 1. Definition of the control volume (CV) and exergetic flows for analysis in the chemical recovery boiler.

2.2.1 Physical exergy

Physical exergy, also known as thermomechanical exergy, is related to temperature variation, defined as the maximum work that can be obtained when a given mass or energy flow is brought into equilibrium, with the environment, through processes reversible (Ortiz and Flórez-orrego, 2013).

According to Szargut (2005) physical enthalpy, entropy and exergy are calculated from the reference state (dead state) determined by temperature (T_0) and ambient pressure (p_0) without any change in the chemical composition of the substance considered, with that, the specific physical exergy (b_{ph}) can be obtained from Eq. (6).

$$b_{ph} = h - T_0 \cdot s \tag{6}$$

Being *h* the specific enthalpy and *s* is the specific entropy.

When one wants to know the variation of exergy in relation to the dead state, one can obtain the specific physical exergy (b_{ph}) from the Eq. (7), assessed at a given working temperature (T) up to the dead state temperature (T_0), in pressure p_0 (Szargut, 2005).

$$b_{ph} = (\Delta h - T_0 \cdot \Delta s) \tag{7}$$

Being Δh and Δs the enthalpy and specific entropy variations from T to T_0. These variations can be determined from Eq. (8) and (9), respectively, presented by Green and Perry (2008).

$$\Delta h = \int_{T_0}^{T} c_p(T) \cdot dT \tag{8}$$

$$\Delta s = \int_{T_0}^{T} \frac{c_p(T)}{T} \cdot dT \tag{9}$$

Being $c_p(T)$ the specific heat at a given temperature T.

Carvalho *et al.* (1997) presented two polynomials for calculating enthalpy and entropy variations from temperature variation and auxiliary coefficients “A”, “B”, “C” and “D”, being selected for each chemical element or compound, which also are presented in their work. Polynomials are presented by Eq. (10) and (11).

$$\Delta h = h_T - h_0 = 4{,}186 \cdot (A \cdot T + B \cdot 10^{-3} \cdot T^2 + C \cdot 10^{-5} \cdot T^{-1} + D) \tag{10}$$

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

Being T_0 the dead state temperature of 25.0 °C (298.15 K), T is the study temperature of the chemical compound, and “A”, “B”, “C” and “D” the tabulated coefficients for each chemical element or compound (Carvalho *et al.*, 1997).

For the calculation of the physical exergy of the gases, it is assumed that the gases approach the ideal gas conditions. The physical exergy of the gases is calculated from Eq. (12), as presented by Szargut (2005).

$$b_{ph} = \sum_i y_i \cdot \Delta h_i - T_0 \cdot \sum_i y_i \cdot \Delta s_i \tag{12}$$

Being y_i the molar fraction of compound i in a solution, which can be obtained from Eq. (13), Δh_i and Δs_i the variation of enthalpy and specific entropy of compound i at a given temperature T.

$$y_i = \frac{n_i}{n_T} \tag{13}$$

Being n_i the number of moles of compound i in a solution and n_T the total number of moles of a solution.

Therefore, the physical exergy of a chemical element or compound i ($\mathrm{B_{ph,\mathit{i}}}$) in a solution flow it can be calculated from Eq. (14).

$$\mathrm{B_{ph,\mathit{i}}} = \dot{n}_i \cdot \mathrm{b_{ph,i}} \tag{14}$$

Being $\dot{n}_i$ the molar flow and $\mathrm{b_{ph,i}}$ the physical exergy of a compound or chemical element i in a solution.

Finally, the total physical exergy of a solution can be obtained from Eq. (15).

$$\mathrm{B_{ph}} = \sum_i \mathrm{B_{ph,\mathit{i}}} \tag{15}$$

2.2.2 Chemical exergy

Kotas (1985) defined chemical exergy as the maximum amount of work produced until the thermodynamic balance reached in reactive, non-reactive processes, processes that involve heat transfer and when there is an exchange of compounds with the environment through reversible processes. Szargut (2005) presented that chemical exergy expresses the exergy content of the substance at ambient temperature and pressure through the difference in chemical potential between the two states, concerning the dead state (state of equilibrium in nature where the exergy of the system is zero).

The standard chemical exergy ($\mathrm{b^{\circ}_{ch}}$), also called exergy of chemical or elemental compounds, can be obtained by means of exergy balance in the process of compound formation (Szargut, 2005), as shown by Eq. (16).

$$\mathrm{b^{\circ}_{ch}} = -\Delta_r G^{\circ} + \sum_k B^{\circ}_{ch,k} - \sum_j B^{\circ}_{ch,j} \tag{16}$$

Being: $-\Delta_r G^{\circ}$ the standard Gibbs free energy for the reaction, $\sum_k B^{\circ}_{ch,k}$ *and* $\sum_j B^{\circ}_{ch,j}$ the sum of the standard chemical exergy of the reagents and products, respectively

For this paper, the standard chemical exergy values are used (B°_{ch}) presented by Kotas (1985), in the form of tables for various chemical elements and compounds.

Specific chemical exergy ($\mathrm{b_{ch}}$) of ideal solutions or gases in which the chemical composition is known, can be calculated from Eq. (17), as presented by Szargut (2005).

$$\mathrm{b_{ch}} = \sum_i y_i \cdot b^{\circ}_{ch,i} + R \cdot \mathrm{T_0} \cdot \sum_i y_i \cdot \ln(y_i) \tag{17}$$

Being $b^{\circ}_{ch,i}$ the standard chemical exergy specific to an element or compound i in a solution.

Therefore, the chemical exergy of a chemical element or compound i ($\mathrm{B_{ch,\mathit{i}}}$) in a solution stream can be calculated from Eq. (18).

$$\mathrm{B_{ch,\mathit{i}}} = \dot{n}_i \cdot \mathrm{b_{ch,i}} \tag{18}$$

Finally, the total chemical exergy of a solution can be obtained from Eq. (19).

$$\mathrm{B_{ch}} = \sum_i \mathrm{B_{ch,\mathit{i}}} \tag{19}$$

2.2.3 Exergetic efficiency

For the exergetic analysis to be carried out in different areas and applications, the rational exergetic efficiency (η_B) must be modelled for each case separately, even if in industries of the same industrial branch, being necessary to know and evaluate the system so that it's obtained from the useful products and the necessary inputs for certain applications of interest.

Szargut *et al.* (1988) defined the rational exergetic efficiency (η_B) as the ratio between the exergy available and the exergy transferred in a given system, in which it can be defined as the relation of the product flows by the inputs in a given VC. For this paper, the evaluation made in the chemical recovery boiler considers overheated steam and smelt as products, and black liquor, the air injected into the furnace and the electrical power consumed by the boiler as inputs.

Therefore, the rational exergetic efficiency (η_B) can be calculated from Eq. (20).

$$\eta_B = \frac{B_{st}+B_s}{B_{BL}+B_{air}+W_{el}} \tag{20}$$

Being B_{st} the exergy gained by liquid water to the state of superheated steam, B_s the exergy of the smelt, B_{BL} the exergy of black liquor, B_{air} the exergy of the total air inserted in the boiler and W_{el} the electrical power consumed by the boiler.

2.3 Parameters for exergetic analysis of the chemical recovery boiler

For the exergetic analysis of this paper, a chemical recovery boiler is used, the type usually used in industries that operate from the process Kraft (Reis, 2013; Passini, 2017). Table 1 shows the parameters of the chemical recovery boiler for analysis in this paper.

Table 1. Details of the chemical recovery boiler.

Description		Value
Burnt black liquor (tss/d)		1,400
Concentration of dry solids in black liquor (%)		75
Black liquor temperature (°C)		110
Steam flow (t/h)		180
Steam temperature (°C)		400
Steam pressure (bar)		50
Feed water temperature (condensate) (°C)		140
Feed water pressure (bar)		80
Air inlet temperature (°C)	Primary air	175
	Secondary air	175
	Tertiary air	55
Output temperature of smelt (°C)		860
Combustion gas outlet temperature (°C)		200
Electricity consumed (kW)		2,440

Source: Reis (2013) and Passini (2017)

The composition of black liquor is one of the principal challenges for the energy analysis of a pulp and paper industry, as its composition may vary according to the production process, the raw material used, the concentration of chemical compounds used in cooking wood, among others.

For the analysis of this paper, the elementary composition presented by Jalalian *et al.* (2018), was supplied by a French pulp and paper industry, as shown in Table 2. For comparison purposes, Table 3 also shows the composition of a Brazilian industry (Carreiro, 2009) and a typical range of black liquor composition (Reis, 2013). The black liquor used in this analysis has 70% dry solids by mass, has a bit of carbon (C) slightly lower than the average, and a bit of sulphur (S) above 4% in its composition when compared to other works as Fakhrai (2002), Carreiro (2009), Carlsson *et al.* (2010), Ahmad *et al.* (2018), Magdeldin and Järvinen (2020).

Table 2. Chemical composition of black liquor on a dry matter basis (DMB) and typical composition range.

Element	%DMB (%) Jalalian *et al.* (2018)	%DMB (%) Carreiro (2009)	%DMB range (%) Reis (2013)
C	32.39	33.8	34.0-39.0
H_2	3.28	3.4	3.0-5.0
S	4.05	2.9	3.0-7.0
O_2	37.17	36.0	33.0-38.0
Na	17.95	19.1	17.0-25.0
Cl	0.30	2.71	0.2-2.0
K	1.86	2.62	0.1-2.0
N_2	0.11	-	<2.0
Others	2.89	-	traits (Ca, Si, Fe, Al)

The coefficients "A", "B", "C" and "D" presented by Carvalho et al. (1997) are applied for the calculations of enthalpy and entropy specific to the elements of black liquor and other flows. For the calculation of chemical exergy, the standard chemical exergy (b°_{ch}) data of the elements, presented by Kotas (1985), are used. The black liquor is evaluated at a temperature of 110 °C (Passini, 2017).

Table 3 shows the coefficients “A”, “B”, “C” and “D” and the standard chemical exergy of the elements that make up the black liquor.

Table 3. Auxiliary coefficients for calculating enthalpy and specific entropy of black liquor elements and their respective standard chemical exergy.

Element	A	B	C	D	b°_{ch} (kJ/kmol)
$C_{(s)}$	4.03	0.57	2.04	-1,936.0	410,820
$H_{2\,(g)}$	6.52	0.39	-0.12	-1,938.0	238,490
$S_{(g)}$	5.26	-0.05	-0.36	-1,443.0	598,850
$O_{2\,(g)}$	7.16	0.50	0.40	-2,313.0	3,970
$Na_{(s)}$	4.02	4.52	0.00	-1,599.0	343,380
$Cl_{(g)}$	5.53	-0.08	0.23	-1,719.0	163,940
$K_{(l)}$	7.06	0.00	-0.70	-1,323.0	371,520
$N_{2\,(g)}$	6.83	0.45	0.12	-2,117.0	720
$H_2O_{(l)}$	18.04	0.00	0.00	-5,379	3,120

Source: Carvalho *et al.* (1997) e Kotas (1985)

The smelt is composed of the inorganic compounds present in the black liquor and other products of the chemical reactions that occur inside the chemical recovery boiler due to combustion. Its composition may vary according to the black liquor burned, being in most cases composed of sodium carbonate (Na_2CO_3), sodium sulphide (Na_2S) and sodium sulphate (Na_2SO_4) (Reis, 2013). For this paper, in addition to the compounds already presented, smelt contains potassium carbonate (K_2CO_3) and sodium chloride (NaCl), due to the presence of potassium (K) and chlorine (Cl) in the composition of the black liquor. Table 4 shows the coefficients and standard chemical exergy of the elements that make up the smelt

Table 4. Auxiliary coefficients for calculating the enthalpy and specific entropy of smelt elements and their respective standard chemical exergies.

Compound	A	B	C	D	b°_{ch} (kJ/kmol)
Na_2CO_3	27.13	7.81	4.78	-10,386.0	53,130
Na_2S	19.81	0.82	0.00	-5,979.0	930,340
Na_2SO_4	47.18	0.00	0.00	-10,190.0	35,000
K_2CO_3	-	-	-	-	22,200
NaCl	10.98	1.95	0.00	-3,447.0	90,110

Source: Carvalho *et al.* (1997) and Kotas (1985)

In this case, as there are no coefficients for K_2CO_3, for this compound the same method of calculating enthalpy and specific entropy of the black liquor elements is used, in this case for the elements potassium (K), carbon (C), and oxygen (O2) individually, at the smelt analysis temperature of 860 °C (Passini, 2017).

For the conditions of complete combustion of black liquor and that there is no significant drag of organic and inorganic compounds in the combustion gases, the elements present are carbon dioxide (CO_2), sulphur dioxide (SO_2), steam water (H_2O), free oxygen (O_2) e nitrogen (N_2).

Table 5 presents the coefficients and standard chemical exergy of the compounds present in the combustion gases and air, disregarding the compounds with the lowest composition, with the molar proportion of the air being 21% of O_2 and 79% of N_2. The enthalpy and entropy values of the water entering and leaving the chemical recovery boiler (condensate and superheated steam) are obtained from the tables of thermodynamic properties provided by Moran *et al.* (2011).

Table 5. Auxiliary coefficients for calculating the enthalpy and specific entropy of the elements of the gases produced.

Compound	A	B	C	D	b°_{ch} (kJ/kmol)
CO_2	10.57	1.05	2.06	-3,936.0	20,140.0
SO_2	11.04	0.94	1.84	-3,992.0	303,500.0
H_2O	7.30	1.23	0.00	-2,286.0	11,710.0
O_2	7.16	0.50	0.40	-2,313.0	84,493.0
$O_{2\,(air)}$	7.16	0.50	0.40	-2,313.0	3,970.0
N_2	6.83	0.45	0.12	-2,117.0	690.0

Source: Carvalho *et al.* (1997) and Kotas (1985)

With that, from the presented methodology, the calculations and analysis of the results found are presented below.

3. RESULTS AND DISCUSSIONS

Depending on the elemental composition of the black liquor shown in Table 3 (Jalalian *et al.*, 2018), a PCI of 9,754 kJ/kg is obtained by the Dulong Equation. From the chemical recovery boiler parameters shown in Table 1, there is a flow of 16.20 kg/s of dry solids and 4.86 kg/s of water, therefore, total flow of 21.06 kg/s or 1.31872 kmol/s of wet black liquor.

In the Kraft process under analysis, the black liquor leaves the evaporators and enters the chemical recovery boiler at about 110 °C, as shown in Table 1. Thus, calculations of physical exergy and chemical exergy are made, the values of which are shown in Table 6.

Table 6. Results of physical and chemical exergy of black liquor.

Element	$\dot{n}$ (kmol/s)	B_{ph} (kW)	B_{ch} (kW)
C	0.43736	52.87	179,678.3
H_2	0.26574	78.76	63,376.5
S	0.02051	4.85	12,281.1
O_2	0.18822	58.18	747.2
Na	0.12646	39.75	43,423.6
Cl	0.00137	0.31	224.8
K	0.00773	20.22	2,871.1
N_2	0.00127	0.38	0.9
H_2O	0.27006	207.99	842.6

From the flow of the liquor elements shown in Table 6, the stoichiometric combustion of the black liquor as air is made, based on the complete combustion of the organic compounds, in which the products are: smelt and combustion gases. For this stoichiometric balance, the following considerations are made:

- The black liquor has 35% inorganics on a dry matter basis (Reis, 2013);
- Initially, the smelt flow has an 80% $\mathrm{Na_2CO_3}$, 18% $\mathrm{Na_2S}$ and 2% $\mathrm{Na_2SO_4}$ on basic mass (Reis, 2013);
- Initially, the flow rate of the sodium element (Na) in the smelt is 69,3% $\mathrm{Na_2CO_3}$, 27,6% $\mathrm{Na_2S}$, 1,7% $\mathrm{Na_2SO_4}$ and 2,8% NaCl on a molar basis, according to the results presented by Carreiro (2009);
- The excess molar flow of the sodium element (Na) was added to that of $\mathrm{Na_2S}$, since all free sodium reacts with sulphur (S) and forms $\mathrm{Na_2S}$, considering that the molar flow of $\mathrm{Na_2CO_3}$ does not change during combustion (Passini, 2017);
- 7% excess air at room temperature (Tertiary Air).

Having made the considerations, the following stoichiometric balance is obtained:

$$0.43736\,C + 0.26574\,H_2 + 0.02051\,S + 0.01882\,O_2 + 0.12646\,Na + 0.00137\,Cl + 0.00773\,K + 0.00127\,N + 0.27006\,H_2O + 0.43848\,O_2 + 1.63114\,N_2 \rightarrow 0.04383\,Na_2CO_3 + 0.01765\,Na_2S + 0.00106\,Na_2SO_4 + 0.00386\,K_2CO_3 + 0.00137\,NaCl + 0.38967\,CO_2 + 0.00180\,SO_2 + 0.53580\,H_2O + 0.03069\,O_2 + 1.63178\,N_2$$

From the results obtained, there is a flow rate of 8.19 kg/s or 0.06778 kmol/s of smelt and 73.58 kg/s or 2.58974 kmol/s of combustion gases. Therefore, after obtaining the molar flow values of the smelt, the values of physical exergy and chemical exergy at 860 °C are calculated, whose values are shown in Table 7.

Table 7. Results of calculations of physical and chemical exergy of smelt.

Compound	$\dot{n}$ (kmol/s)	B_{ph} (kW)	B_{ch} (kW)
Na_2CO_3	0.04383	3,094.7	2,328.8
Na_2S	0.01765	681.7	16,417.2
Na_2SO_4	0.00106	109.2	37.3
K_2CO_3	0.00386	174.2	85.8
NaCl	0.00137	35.3	123.6

Likewise, after obtaining the molar flow values of the combustion gases, the values of physical exergy and chemical exergy are calculated, the values of which are shown in Table 8.

Table 8. Results of calculations of physical and chemical exergy of the combustion gases.

Compound	$\dot{n}$ (kmol/s)	B_{ph} (kW)	B_{ch} (kW)
CO_2	0.38967	618.31	6,019.38
SO_2	0.00180	3.00	512.83
H_2O	0.53580	695.21	4,182.72
O_2	0.03069	35.17	2,256.11
N_2	1.63178	1,813.93	-741.41

For air, from the molar flow values, assuming that the primary air and the secondary air enter the boiler at 175 °C and the tertiary air enters 55 °C, with a ratio of 40%, 40%, and 20%, successively, of the total airflow on a mass basis (Passini, 2017). Therefore, the values of physical exergy and chemical exergy for the different temperatures are calculated, whose values are shown in Table 9.

Table 9. Results of calculations of physical and chemical exergy in the air.

Compound	$\dot{n}$ (kmol/s)	B_{ph} (kW)	B_{ch} (kW)
O_2 (175 °C)	0.3069	267.48	947.30
O_2 (55 °C)	0.1315	111.33	129.84
N_2 (175 °C)	1.1418	966.31	3,495.23
N_2 (55 °C)	0.4893	19.50	470.71

As previously mentioned, the enthalpy and specific entropy values of water (condensate and superheated steam) entering and leaving the chemical recovery boiler are obtained from the tables of thermodynamic properties presented by Moran *et al.* (2011). Table 10 presents the results obtained for the condensate and superheated steam.

Table 10. Properties of liquid and water steam entering and leaving the boiler**.**

Property	Condensed	Superheated steam	Reference state
Temperature (°C)	140.0	400.0	298.0
Pressure (bar)	80.0	50.0	1.0
Specific enthalpy (kJ/kg)	593.5	3,196.3	104.3
Specific entropy (kJ/kg·K)	1,730	6,648	0.365
Mass flow rate (kg/s)	50.0	50.0	-
Total exergy (kW)	4,126.3	60,989.5	-

After obtaining the values of enthalpy, mass flow or molar flow, physical exergy, and chemical exergy of the compounds present in the exergetic flows entering and leaving the chemical recovery boiler, the sum is obtained, also the energy and thermal exergy of the flows are obtained themselves. From the enthalpy values presented, there is water that enters as a liquid (condensed water) and exits as superheated steam from the chemical recovery boiler with an energy gain (E_{st}) of 130,140.1 kW. With the results obtained, it is clear that the energy of the black liquor (E_{BL}) added to the boiler is 205,474.6 kW.

Table 6 presents the summary of thermal exergy calculated from the considerations detailed in this paper.

Table 6. Summaries of exergetic flows in the chemical recovery boiler**.**

Exergetic flow in the boiler	B_{th} (kW)
Black liquor	303,909.4
Smelt	17,664.4
Combustion gases	15,395.3
Air (primary, secondary and tertiary)	1,456.0
Condensate water (liquid)	4,126.3
Superheated steam	60,989.5
Electric energy	2,440.0

Figure 2 shows the CV of the chemical recovery boiler, with its respective exergetic flow values obtained in the analyses presented in this paper.

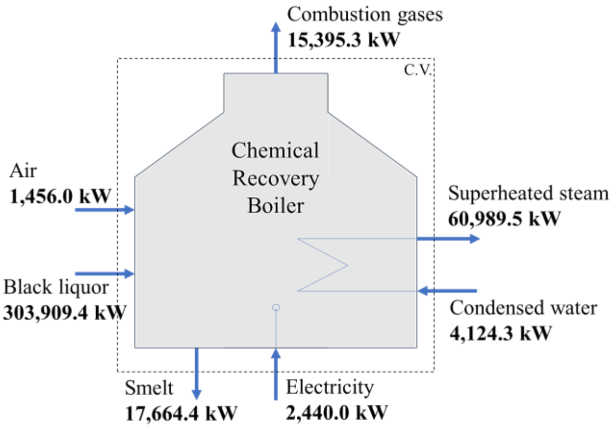

Figure 2. Definition of the results of the exergetic flows of the analysis in the chemical recovery boiler.

Finally, the efficiency of the chemical recovery boiler is calculated. Energy efficiency (η_E) obtained is about 63.3%, a value close to that reported by Carreiro (2009), which was 61.1% and within the range presented by Cardoso (1998), 50-70%. And rational exergetic efficiency (η_B) obtained in this paper is about 24.2%, above the value reported by Carreiro (2009), which was 21.3%.

For rational exergetic efficiency (η_B), combustion gases are not considered, as this flow is not used in the type of boiler analysed. The combustion gases leave the chemical recovery boiler at a temperature of 200 °C and a pressure of 1.8 bar. In more recent projects, the exergy of these gases is used through heat exchangers to preheat the condensed water that enters the boiler or to improve the preheating of the combustion air.

It can be noted that the main exergetic inlet flow is black liquor, as fuel, and the main exergetic outflow is superheated steam, as a product of the use of black liquor.

4. CONCLUSIONS

The results obtained meet expectations based on values presented in other works that analyse the Kraft process. The exergetic analysis of the chemical recovery boiler may vary from one industry to the other, mainly due to the characteristics of the black liquor burned from the wood cooking methodology and pre-combustion treatment of the liquor. The composition of black liquor and its concentration can vary depending on different factors, such as region, the raw material (a type of wood), type of digester, type of evaporator, and chemical compounds used in wood cooking. For this paper, when considering a black liquor with a lower concentration of carbon and a higher concentration of sulphur, it can be noted that the burning of organic compounds in a controlled manner from the injection of air in the correct measures is the principal emission mitigation methodology of gases with greater environmental impacts, such as CO, SO_2 and NOx. Combustion gases are exergetic resources with the possibility of greater utilization, and in newer boilers, this technology integrates the issue of costs and thermal utilization. Therefore, in industries, it is important to know the processes to apply the concepts of exergy, to minimize losses, preserve the environment, and increase the efficiency of the processes. Finally, it can be seen that the recovery of inorganic chemicals, the generation of steam and electricity makes the operation of the pulp and paper industries environmentally and economically viable, and relevant to today's markets.

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