EXERGY ANALYSIS OF A MULTIPLE EFFECT EVAPORATION PLANT OF THE CHEMICAL KRAFT PULP EXTRACTION INDUSTRY

Haroldo Marinho dos Reis
Teaching Technician at SENAI "Theobaldo De Nigris", Pulp and Paper Department,
Rua Bresser, 2315, Mooca – 03162-030 São Paulo, SP, Brazil
celulosepapel114@sp.senai.br

Julio Cezar Ferreira Macedo
Specialist in Chemical Recovery - Fibria Celulose, Unit of Jacareí
Rodovia Gal. Euryale Jesus Zerbini, km 84, SP 66, Bairro São Silvestre, 12300 Jacareí, SP, Brazil.
julio.macedo@fibria.com.br

Rogério José da Silva
Federal University of Itajubá, Mechanical Engineering Institute,
Av. BPS, 1303, Pinheirinho, 37.500-903, Itajubá, MG, Brazil
rogeriojs@unifei.edu.br

Abstract – In the pulp extraction process from wood, the black liquor is an interesting product, because it is a very important source of energy for the pulp extraction industry. This liquor is a complex aqueous solution formed by organic and inorganic compounds and generated by wood chip cooking in an alkaline aqueous solution. Due to the cellulosic pulp washing process carried out to separate this liquor, the final solids concentration ranges from 10 to 20%. Water evaporation became necessary to increase the solids concentration contained in the black liquor, for a safe combustion in the chemical recovery boilers, also increasing its lower calorific value. The multiple effect evaporators are vessels operating with negative pressure values, reducing the use of energy in the water evaporation process, this energy being supplied by the superheated steam. The equipment in question consists of heat exchangers constructed of stainless steel plates, where the liquor flows on the plate outside, thus forming a film, while steam at 5 bar is injected into the plate inside. At the end of the evaporation process the black liquor is concentrated at 73% solids, in order to be used as fuel in the chemical recovery boilers. The exergetic analysis shows the efficiency of the process, according to the mass concepts and energetic balances of the first law of thermodynamics, as well as the use of entropy and its relationship with the environment through the analysis of the second law of thermodynamics. Through the analysis it is possible to identify, locate, evaluate and assign actual values to the losses, thus providing a more efficient use of energy. The flow of each evaporator was analyzed and the overall and local efficiency were measured. The results show that the losses of energy occur, so that we can reduce these losses, improving the efficiency of the system and reducing the cost of steam.

Keywords: *black liquor; evaporation; exergetic analysis; exergy, kraft process.*

1. INTRODUCTION

Black liquor is a product of utmost importance for the pulp extraction and paper manufacturing industry on the world scenario. Both in Brazil and worldwide the moment is of large investment in the sector due to the substantial increase in paper consumption. In 2010, Brazil occupied the 4th worldwide position in the ranking, with almost 14 million tons of extracted pulp, as well as the 9th position among the main paper manufacturers all over the world, with 9.8 million tons (BRACELPA , 2011).

Considering this growth scenario, the black liquor became the great responsible factor for the economic viability of the sector, supported by a highly improved technology, thus making the Brazilian companies highly competitive on the international market. Figure 1 shows the growth in the use of black liquor as fuel in Brazil, versus other types of fuel (BRACELPA, 2011).

The management of obtaining, storing and burning black liquor has become more and more improved, in order that the environmental questions are kept and sustained within the legal requisites stipulated by the environmental agencies.

The black liquor is used as fuel in the chemical recovery boilers with two purposes:

- To recover the chemical compounds used in wood cooking.
- To generate steam in its combustion.

Black liquor being a by-product in the pulp extracting process, its utilization as fuel provides a lower price of the steam used in generating electric power, and thus a highly competitive price of the end product (cellulosic pulp). At present, recovery boilers are being manufactured to be run at higher pressures, higher black liquor dry solids content, and higher solids burning capacity as well, making these companies self-sufficient in electric power generation.
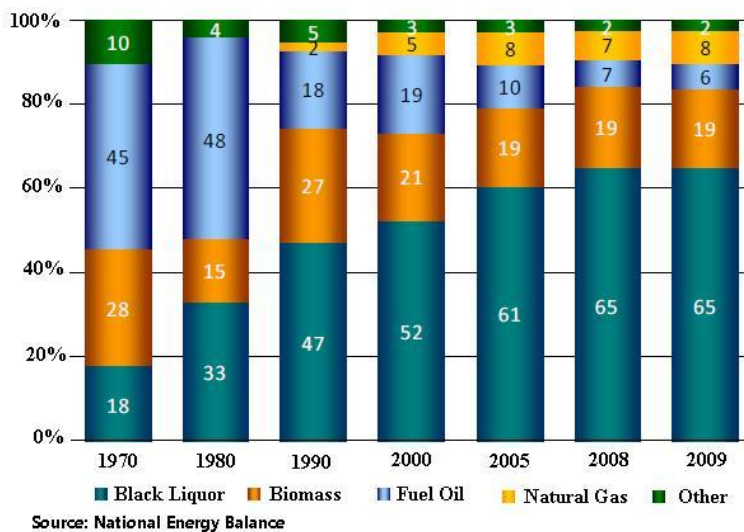
Fig. 1. Growth in consumption of black liquor in Brazil

1.1. Kraft Pulping Process

The kraft process, developed in 1879 by C. F. Dahl in Germany, is at present the most employed chemical method for pulp extraction from wood. In this type of process, the solution used for chip cooking is mainly composed of sodium hydroxide and sodium sulphide.

The main characteristics of the process kraft in the extraction of cellulose paste of quality are evaluated by: the resistance mechanics and physical, the high degree of "whiteness" obtained in the pulp whitened, besides the efficient system of recovery of the chemical products. But its disadvantage is a low yield in pulp extraction, of approximately 50 to 55%, besides generating environmental problems caused by atmospheric emissions of pollutants, including the characteristic odour of sulphur and particulate material. These problems are being minimized by the use of additives in the chip cooking process, as well as by investments in more efficient pollutant treatment systems.

The pulp extraction process begins by introducing the debarked wood chips into a pressurized vessel called digester, to be cooked in the presence of an alkaline liquor called cooking liquor or white liquor, a solution composed of sodium hydroxide and sodium sulphide. The cooking temperature is controlled to keep between 150 and 170ºC during a given retention time allowing the degradation reaction of lignin, an amorphous polymer acting as interfibre binder, imparting firmness and rigidity to the woody structure (Gullichsen,1999).

The time/temperature ratio is associated with some variables, such as kind of wood, degree of delignification required, alkaline charge applied, among others. After cooking the chips are discharged into a depressurized tank, known as blow tank, where fibre separation occurs through pressure difference between digester and discharge tank, gases are released and defibration is carried out, thus obtaining the cellulosic pulp, called brownstock.

Then the pulp obtained is sent from the blow tank to the washing, screening, and oxygen delignification sector, where it is exhaustively washed to remove the chemicals solubilized during the cooking process. After the oxygen treatment, the function of which is the removal of further lignin, the pulp is sent to the bleaching sector. Then the pulp is screened in several stages, to remove solid contaminants like badly cooked chips, abrasive materials, plastics, among others.

During wood cooking there occurs the black liquor formation, a complex aqueous solution consisting of solubilized organic compounds (fractions of lignin, extractives, and fibres), as well as residual inorganic compounds from sodium salts (sodium carbonate, sodium sulphate, among others). This liquor is obtained by washing the brownstock in the digester, at washing, and at oxygen delignification, and is of paramount importance to the company, who makes the process economically viable by reusing it in the recovery cycle, besides reducing environmental impacts both directly and indirectly through its use (Gullichsen,1999).

1.2. Chemical Recovery in the Alkaline Pulping Processes

The black liquor formed in the process has a solids concentration ranging from 10 to 20% and consisting, on average, of organic (60%) and inorganic matter (40%). These values can vary, as they depend on factors like alkaline charge used, kind of wood, and degree of delignification of the wood. This liquor, known as weak black liquor, has its solids concentration increased to values above 60% to be able to be safely used as fuel in the chemical recovery boiler (Adams, 1997).

The recovery cycle begins with the multiple effect evaporation system, where the weak black liquor has its concentration raised to values between 60 and 85% solids by means of heat exchangers operating with a low-pressure system. After the evaporation process, the liquor, now called strong black liquor, is sent to the recovery boiler.

In the recovery boiler there occurs the combustion of the organic matter of the liquor, supplying the heat required for the reactions of conversion of organic sodium compounds into sodium carbonate, as well as sodium sulphate reduction to sodium sulphide. Thus, the inorganic matter contained in the liquor remains in the form of smelt inside the recovery boiler furnace. The smelt material mainly consists of sodium carbonate and sodium sulphide, with small amounts of impurities, such as unburnt carbon, iron salts, silica, calcium , aluminium, and iron sulphide. The smelt material is extracted from the boiler furnace to the dissolving tank (Venkatesh, 2001).

The resulting solution, designated as green liquor (Na_2CO_3 and Na_2S), is pumped to the causticizing sector, where it will be initially filtered or decanted, in order to remove insoluble impurities, known as *dregs*, following , thereafter to the storage tank. Those impurities are washed and forwarded either to a sanitary landfill or used for other purposes, while the washing liquor generated is sent to dilute the smelt material in the recovery boiler dissolving tank.

There after the green liquor is treated as a concentrated calcium hydroxide suspension, transforming the sodium carbonate into sodium hydroxide. This reaction occurs in two stages: the first one happens in the slaker tank, where there occurs the calcium oxide hydration, generating the calcium hydroxide, that will be used in the second reaction stage, where it will convert the sodium carbonate into sodium hydroxide. After adding the lime to the slaker, the causticizing reaction proceeds in reactors (causticizers) for a period of time of about 90-120 minutes, after which the maximum conversion is obtained. The chemical reactions involved in causticizing are described in Eqs. (1-2), (Cornell, 2001):

$$CaO+H_2O \rightarrow Ca(OH)_2 \tag{1}$$

$$Ca(OH)_2+Na_2CO_3 \leftrightarrow 2NaOH+CaCO_3 \tag{2}$$

During the causticizing reaction, calcium carbonate precipitate, known as lime mud, is formed. From the reactors the cooking liquor obtained undergoes the precipitated carbonate mud separation process, by means of filtration or decantation. The filtered liquor, called white liquor, is sent to be used in chip cooking, while the calcium carbonate mud obtained is washed with heated water or recovered water, to remove cooking liquor residual. The liquor generated at mud washing (weak white liquor) is sent to the smelt dissolving tank of the recovery boiler (Cornell, 2001).

The calcium carbonate rich lime mud has its solids content increased to 60-80% before being sent to the rotary lime kiln.

In the kiln, heat is provided by burning either natural gas or fuel oil, and it should be enough for the lime mud calcination reaction to occur, according to Eq. (3),

$$CaCO_3 \rightarrow CaO + CO_2 \tag{3}$$

The recovered calcium oxide is stored in a silo and reused again for the causticizing reaction. As the calcium oxide recovery is not complete, but only about 85-95% (Pastor and Hortal, 1990), this difference is made up for by adding some quicklime acquired by the company.

The carbon dioxide generated at the lime mud calcination reaction can be used by companies producing precipitated calcium carbonate, set up at the pulp extraction plants, replacing the utilization of liquid carbon dioxide. The chemical cooking liquor recovery cycle is illustrated in simplified form in Fig. 2.

The purpose of this work was to study the exergetic analysis of a multiple effect black liquor evaporation plant of a pulp extracting company established in the State of São Paulo, in order to identify the exergetic efficiency of each stage of the process.

An analysis was carried out starting from the elementary composition of the black liquor studied, including a mass and energy balance, as well as the entropy balance for the Second Law of Thermodynamics for the flows resulting from each evaporator involved.

The control volumes studied refer to a black liquor concentration process, using water evaporation in vessels operating in depression. The liquor and evaporated gas flows operate in countercurrent, where the flows at the preceding evaporator outlet feed the subsequent evaporator, the gases are condensed and flow back into the cellulosic pulp washing system, while the concentrated black liquor flows out through the first evaporator, to be used as fuel in the chemical recovery boiler.

The generated gas condensation results from the heat transfer with water, at ambient temperature, in a surface condenser. The water heated in the condenser is forwarded to the cooling tower, where the energy contained in the hot water is dissipated to the atmosphere. Figure 3 shows the processes involved in black liquor evaporation.
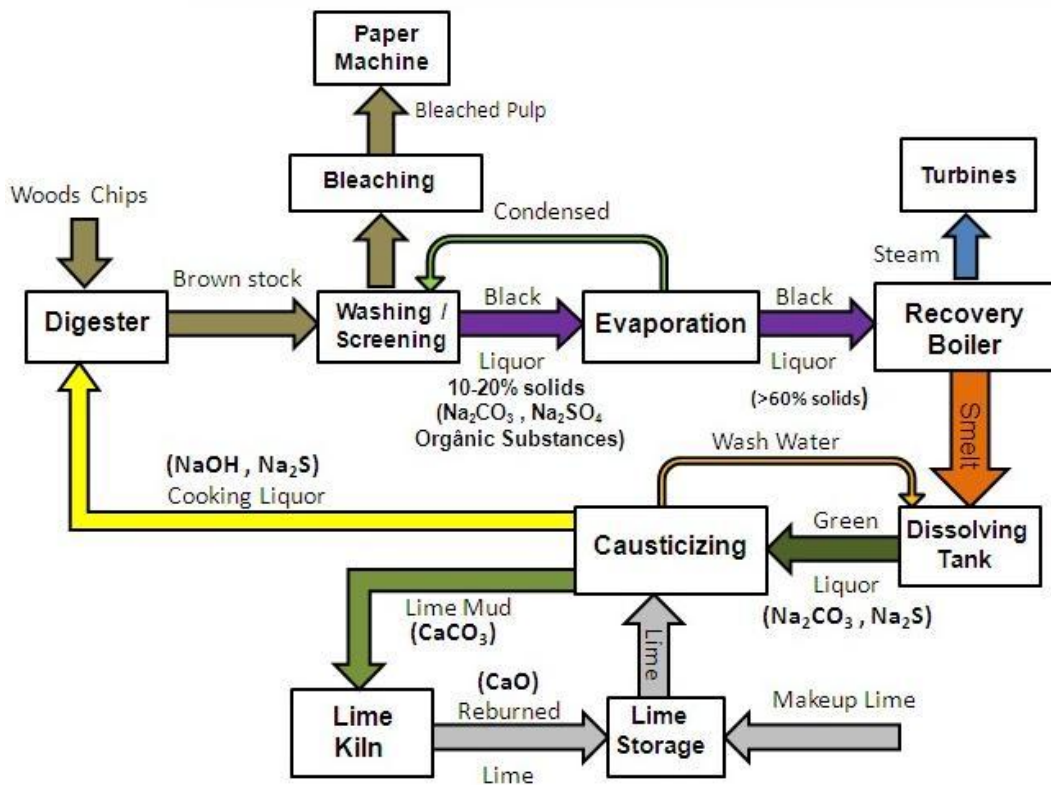
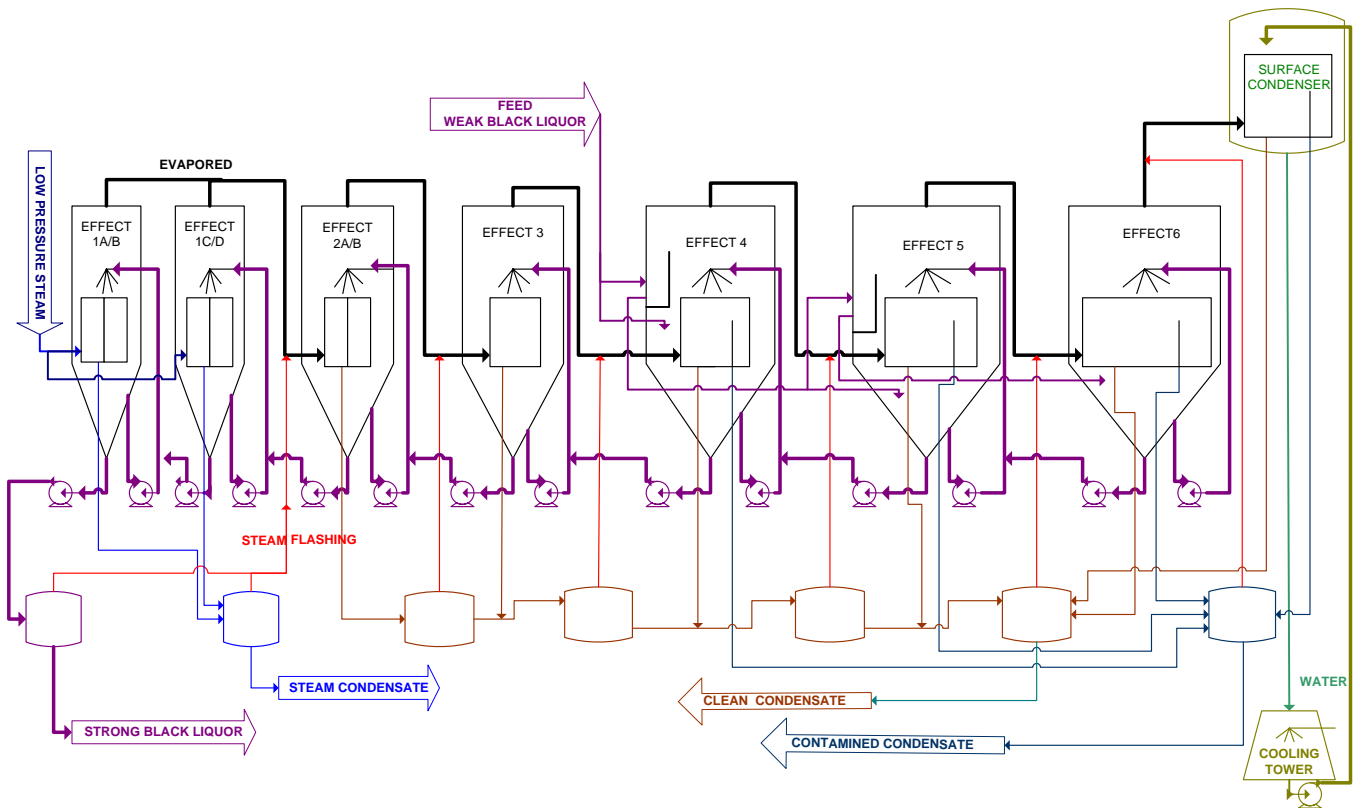Figure 2. Chemistry Recovery Cooking Liquor Preparation.

Figure 3 – Multiple effect evaporation flow diagram.

2. METHODOLOGY

The exergetic analysis is based on the concept of exergy i.e. the maximum capacity to obtain work when a system in unbalance with the environment is brought to balance with it. Can be in the form of: thermal exergy, mechanical exergy, and chemical exergy. To identify the irreversibilities and to determine the exergetic efficiency, the analysis by the second law of thermodynamics is used (Tsatsaronis, 1993). The exergy is a measure of the deviation from the condition of a system, when compared to the environment reference (T_0, p_o). Consequently, it is an attribute of the whole formed by the system and the environment reference. However, once the environment reference is specified, a value can be assigned to the exergy in terms of property values of the system and then the exergy can be considered to be a property of the system (Moran and Shapiro, 2002). The exergy can be divided into four components, according to Eq. (4).

$$B = B^{ph} + B^{ch} + B^{KN} + B^{PT} \qquad (4)$$

Where the kinetic (B^{KN}) and potential (B^{PT}) exergies do not present significant differences when compared to the physical (B^{ph}) and chemical (B^{ch}) exergies, so that they can be neglected in this case (Martinez, 2004; Moran, 2000). The term *physical exergy of a control volume* is obtained through the enthalpy and entropy variations from the real state, related to the environment reference ($P_0 = 1$ bar and $T_0 = 298.15$ K), according to Eq. (5) (Van Wylen, 2005).

$$B = (H - H_0) - T_0(S - S_0) \qquad (5)$$

The chemical exergy for liquids of complex chemical composition is given by Szargut et al. (1988), through its relationship with the lower heating value (LHV) of the material, Eq. (6).

$$B^{ch} = \beta.LHV \qquad (6)$$

where the LHV in MJ/kg is calculated from Vakkilainen (2000), according to Eq. (7).

$$LHV = (25.04\%C + 0.1769\%S - 2.582\%Na + 48.92\%H + 4.231) - 2.443\left[8.936\%H + \frac{(1 - \%X)}{\%X}\right] \qquad (7)$$

where %C, %S, %Na, %H, %X are the percentage concentrations of carbon, sulphur, sodium, hydrogen, and solids in the fuel, respectively.

The ratio of the chemical exergy to the LHV is demonstrated in Eq. (8) by term β, which for liquid fuels is given by Szargut (1988).

$$\beta = 1.0407 + 0.0154\frac{\%H}{\%C} + 0.0562\frac{\%O}{\%C} + 0.5904\frac{\%S}{\%C}\left(1 - 0.175\frac{\%H}{\%C}\right) \qquad (8)$$

The calculation for enthalpy and entropy variation is shown in Eq. (9 and 10), taking as reference Moran and Shapiro (2002).

$$\Delta h = \int_{T_0}^{T} c_p.dT \qquad (9)$$

$$\Delta s = \int_{T_0}^{T} \frac{c_p}{T}.dT \qquad (10)$$

The following equation by Masses et al. apud Vakkilainen (2000) estimates the black liquor specific heat capacity, according to Eq. (11),.

$$c_p = 4.216.(1 - X) + (1.675 + \frac{(3.31T)}{1000})X + (4.87 - \frac{20T}{1000}).(1 - X).X^3 \qquad (11)$$

Where

c_p = is the black liquor specific heat, kJ/kg°C;

X = the dry solids concentration, kg dry solids/kg

T = the temperature of the black liquor, °C

For the black liquor inlet flows of 15% into the 4th and 5th effects, as well as the flows of the evaporated gases of the 6th effect, the exergy of the substances imparting odour to the black liquor is measured, which are as follows: methanol (CH$_4$O), hydrosulfuric acid (H$_2$S), methylmercaptan (CH$_4$S), and dimethylmercaptan (C$_2$H$_7$S). In the physical process of evaporation of the substances, only the physical exergy, utilizing the Eqs. (5), (9), and (10) was considered. The specific heat (cp) in kJ/kg.K for the substances is provided by Perry (1999), by means of Eqs. (12), (13), (14), and (15), respectively. Where, by integration of cp utilizing the Eqs. (9) and (10), was calculated the variation of enthalpy and entropy, for each substance. The temperatures inside the various effects of evaporation ranged from 150 °C to 57 °C, with a decrease in initial pressure of 5 bar at the entrance to the vacuum at the exit. The temperature and pressure were used in the calculations of exergy in several effects.

$$CH_4O \rightarrow c_p = 1.058 \times 10^{-5} - 3.6223 \times 10^2 T + 0.9379 T^2 \tag{12}$$
$$H_2S \rightarrow c_p = 7.15 + 3.32 \times 10^{-3} T \tag{13}$$
$$CH_4S \rightarrow c_p = 1.1530 \times 10^5 - 2.6323 \times 10^2 T + 0.60412 T^2 \tag{14}$$

$$C_2H_7S \rightarrow c_p = 1.4695 \times 10^5 - 3.8006 \times 10^2 T + 8.4787 \times 10^{-4} T^3 \tag{15}$$

According to Kotas (1985), the exergetic efficiency is the relationship between the variation of the exergy desired and the exergy required for the process, as shown in Eq. (16).

$$\psi = \frac{Exergy\ desired}{Exergy\ required} \tag{16}$$

3. Results

The exergetic efficiency was calculated for each control volume which the system shown in Fig. 4 consists of the exergies of the inlet and outlet flows were calculated, and the motor power itself was considered as inlet exergy. The overall exergetic efficiency was obtained after analyzing each individual equipment.

For the first effect, the exergies of steam inlet and condensate outlet of 5 bar, inlet of black liquor coming from the second effect, outlet of concentrated black liquor for burning in the chemical recovery boiler, and outlet of gases evaporated from the black liquor were calculated. The second and third effects differ from the first one in the fact of receiving the evaporated gases instead of the steam of 5 bar. The control volume for the first, second, and third effects is shown in Fig. 4.
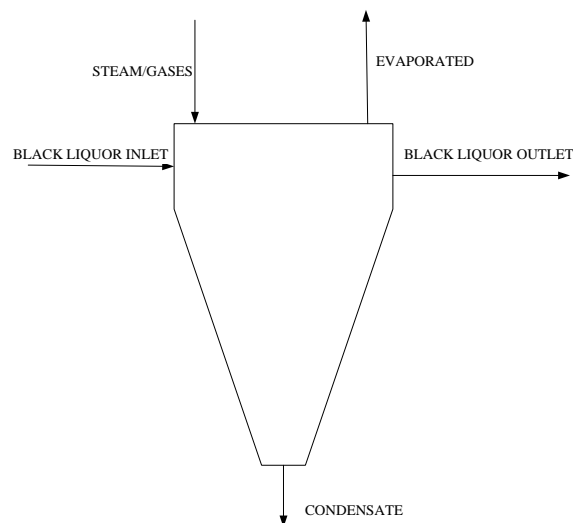

Figure 4 – Control volume for exergetic analysis of the first, second, and third effects

For the fourth effect, the exergies corresponding to the inlet of the gases evaporated coming from the third effect, the condensate outlet of these gases, the inlet of black liquor coming from the fifth effect, the black liquor outlet to the third effect, and the outlet of gases evaporated from the black liquor to the fifth effect were calculated. The fourth effect also receives the diluted black liquor coming from cellulosic pulp washing, which after heating it transfers to the fifth effect in countercurrent. The same configuration is obtained for the fifth effect. Figure 6 shows the liquor, gas, and condensate flows of the fourth and fifth effects.

In the sixth effect, the calculated exergies were those corresponding to the inlet of evaporated gases coming from the fifth effect, the condensate outlet corresponding to these gases, the inlet of black liquor coming from the fifth effect, the outlet of black liquor to the fifth effect, and the outlet of gases evaporated from the black liquor to the surface condenser. The sixth effect has the same configurations as shown in Fig. 5.
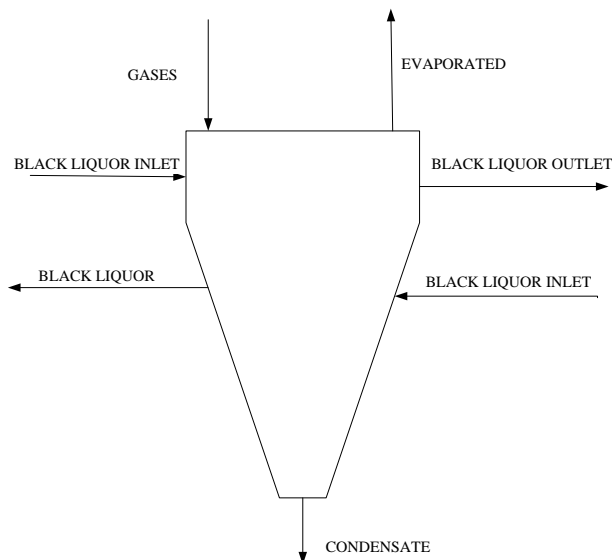

Figure 5 – Control volume for the exergetic analysis of the fourth and fifth effects.

The surface condenser receives the gases coming from the sixth effect, condensing them by means of water coming in from the cooling tower, according to Fig. 6.
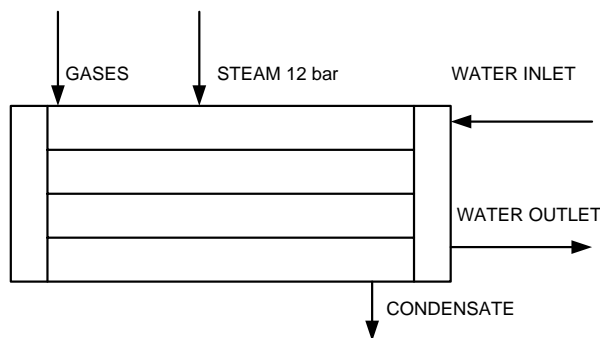

Figure 6 – Control volume for exergetic analysis of the surface condenser.

The black liquor elementary composition on dry basis is provided by Vakkilainen (2000), as shown in Tab. 1.

Table 1 – Black liquor elementary composition.

	C	H	O	S	Na	K	Cl	N	Inert
Elementary Composition (%)	34.8	3.3	35.5	4.1	19.1	1.8	0.7	0.2	0.5

According to Eq. (1), (2), and (3), the exergies of the inlet and outlet flows were calculated for each control volume regarding Fig. 3. The exergy values concerning the surface condenser and the cooling tower were considered as corresponding to only one system. The dry solids concentration values are shown in Tab. 2, in each black liquor flow.

The exergy calculated for the evaporated gases refers to the amount of water extracted from the black liquor in each flow analyzed in the control volume.

In evaporators 4 and 5 the black liquor flow system occurs in countercurrent, in order to recover a larger amount of energy, and the liquor coming from cellulosic pulp washing feeds the 4th effect indirectly and is sent to the 5th effect, where the process occurs in a similar way to the previous one.

Table 3 shows the exergetic yields i.e. of the second law of thermodynamics, bringing the inlet and outlet flows into relationship according to Eq. (16).

Table 2 – Exergy values of the inlet and outlet flows of the control volumes, in kW.

	1st Evaporator	2nd Evaporator	3rd Evaporator	4th Evaporator	5th Evaporator	6th Evaporator	Surface condenser/ cooling tower
Steam/evaporate inlet	11737	11964	8803	7136	4095	5440	18017
Condensate outlet	1051	6265	4826	4038	2429	3333	340
Evaporate outlet	11964	8803	7136	4095	5440	18017	-
Black liquor inlet	213450	207115	201653	202105	198642	183739	-
Black liquor outlet	221194	213450	207115	201653	202105	198642	-
Black Liquor Circulation	-	-	-	179792	183739	-	-
% dry solids feed liquor (circulation)	-	-	-	15.0	16.2	16.6	-
% dry solids black liquor (inlet)	72	42.4	32	26.5	27.2	24.5	-
Steam/evaporate purge	1569	1508	1009	608	831	2178	-
Electric power (pump)	364	64	72	150	150	100	1050
Water inlet	-	-	-	-	-	-	340
Water outlet	-	-	-	-	-	-	442

Table 3- Exergetic efficiency

	1st Evaporator	2nd Evaporator	3rd Evaporator	4th Evaporator	5th Evaporator	6th Evaporator	Surface condenser/ cooling tower
Exergetic Efficiency (%)	23.99	16.68	16.40	61.16	44.58	42.37	10.51

Glassmann's diagram was worked out, showing the occurrence of irreversibilities within the control volumes studied. Figure 7 shows the data regarding the exergy values calculated in kW.

4. CONCLUSION

According to Kotas (1985), the exergetic efficiency of the control volumes forming the evaporation system, given by Eq. (16), indicates that the highest losses occur in the surface condenser/cooling tower, as well as in the evaporators which the second and third effects are composed of. In the case of the surface condenser/cooling tower, there is a direct loss of energy to the environment, without this energy being reused.

For the second and third effects, the exergetic efficiency is lower, due to the fact that the same vessels have no black liquor passage in countercurrent, as in the fourth, fifth, and sixth effects, resulting in lower energy recovery, which in turn affects the evaporator efficiency.
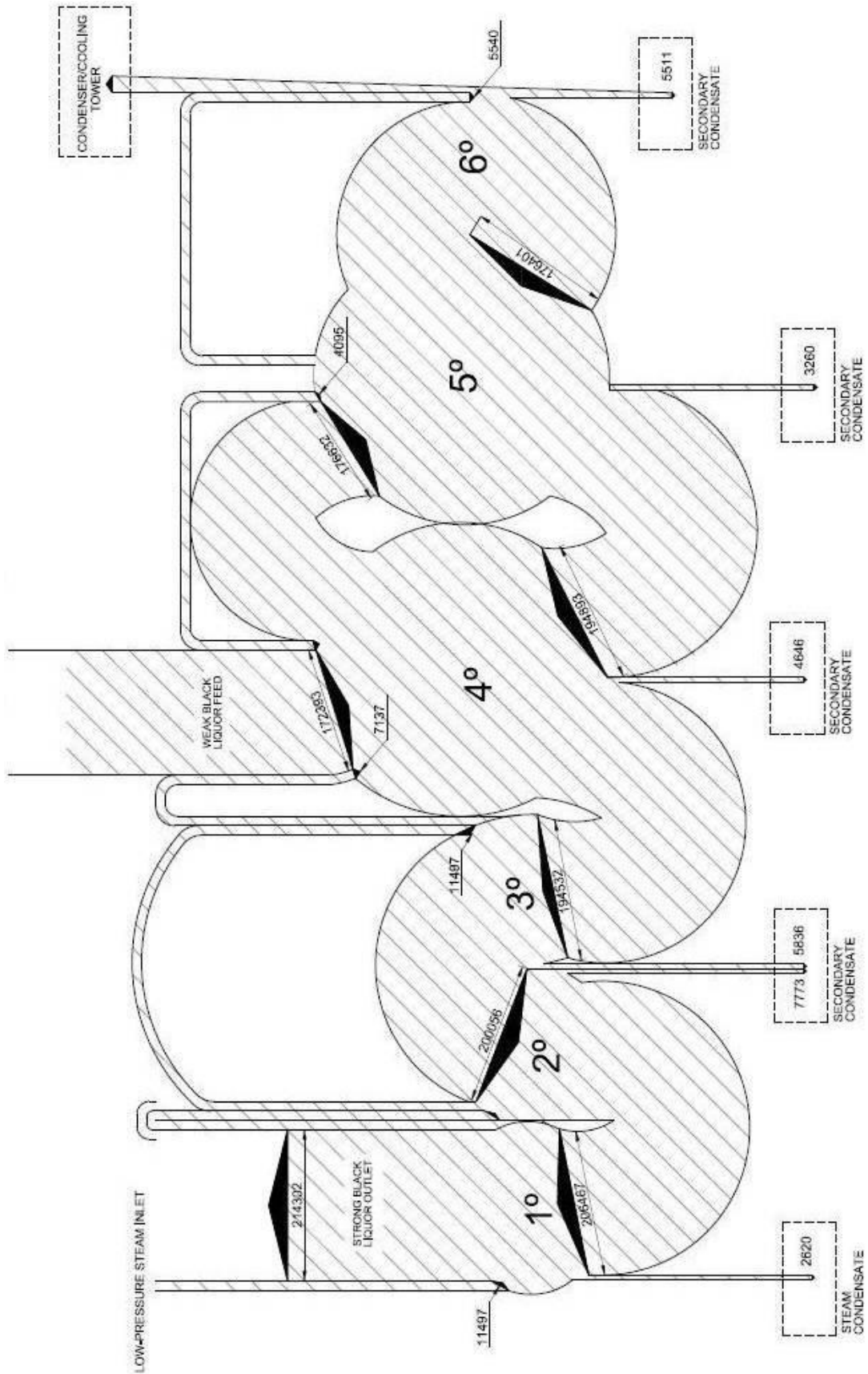
Figure 7 – Glassmann's graph of the black liquor evaporation plant.

The exergetic efficiency calculated for the complete black liquor evaporation system in the studied plant reached 74.88%, which reflects the relationship of the exergy involved to obtain the desired product – black liquor 72% – with the amount of supplied energy, coming from the steam of 5 bar.

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