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EXERGY ANALYSIS OF MECHANICAL VAPOR RECOMPRESSION SYSTEMS TO IMPROVE UTILITY CONSUMPTION AT A CAUSTIC SODA EVAPORATION PLANT

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Abstract. *Operating parameters for the evaporation plant at a caustic soda production unit that consumes, in nominal conditions, 60 t/h of 617 kPa saturated steam from a natural gas-fired boiler, are varied and their impact on the utility demands for the system are evaluated using a detailed physical model. Three alternative configurations using mechanical vapor recompression (MVR) to recover the enthalpy from the low-pressure steam rejected from the evaporator are proposed for the utility plant and evaluated using exergy analysis for different operating conditions. The first alternative, cooling the steam between compression stages with cooling water heat exchangers, reaches up to 94% reduction in steam consumption at the cost of up to 0.83 kWh of electrical power per kg of soda production. The second alternative, which uses de-superheaters to cool the steam and up to 1.15 kWh/kg*$_{NaOH}$ *electrical power, requires no additional steam from the boiler and produces a surplus of high-pressure steam that can be used in other processes. As a combination of the two previously presented configurations, the third one considers intercooling through the injection of liquid water instead of exchanging heat. A second production unit is considered as a sink for a fixed 10 t/h of steam in the same conditions, and the entire complex is considered in the exergy analysis, including both evaporation plants, the boiler, the MVR system, and the electricity input. Renewable and non-renewable exergy costs and exergy destruction rates were used to compare the configurations overall performances, and exergy destruction rates breakdown by equipment were used to evaluate opportunities for further improvement, showing that intercooling with water injection is the most efficient option, with a specific exergy destruction of 1.13 kWh/kg*$_{NaOH}$ *in nominal conditions, about 65% lower than the original configuration without MVR, and 25% lower than the other MVR scenarios.*

Keywords: *exergy, mechanical vapor recompression, caustic soda, evaporation, MVR*

1. INTRODUCTION

The production of caustic soda has long been of great importance in the chemical industry. The production process for this chemical, also known as chlor-alkali process, stems mainly from the electrolysis of brine (water and sodium chloride solutions) through three different processes, which are the diaphragm cell process, the mercury cell process, and the membrane cell process, all resulting ultimately in the production of caustic soda and chlorine gas as finished goods (US EPA, 1995), which are both important inputs to several industrial processes. Among other applications, caustic soda is mainly used in paper, soap, and alumina production and in petroleum processing, while chlorine gas is widely used in water treatment, and in the production of plastics, solvents, and medicine (Hong et al., 2014).

Electrolysing brine produces an aqueous solution of caustic soda and both chlorine and hydrogen gas, and for diaphragm-based cells there is also the presence of sodium chloride that has not been completely electrolysed. Since it is a very costly process to achieve commercial purity requirements for the hydrogen gas, the chlorine gas is separated from the gas mix (US EPA, 1995), and the remaining low purity hydrogen is mostly used as a fuel in steam generators in chlor-alkali plants, which usually find wide use for steam among their processes. On the other hand, the liquid product needs to undergo an evaporation process to achieve product specifications for the caustic soda of 50% NaOH and 1% NaCl in mass.

This production process is very energy-intensive, using electricity for the electrolysis portion, and heat, usually in the form of high-pressure steam exchanging heat with the aqueous solution, for the evaporation. According to Pfisterer and Meissner (1993), the total energy consumption usually ranges from 2.4 to 3.5 MW per ton of caustic soda. The lower end of the spectrum is associated with the use of membrane-based electrolytic cells, which are more efficient and are able to produce a more concentrated soda solution (33% in mass) with virtually no sodium chloride residue, while the upper end involves the use of diaphragm-based electrolytic cells, an older type of technology that can only achieve a product with around 10-12% caustic soda in mass, and 20% sodium chloride in mass. Naturally, the less concentrated intermediate product leads to a higher specific energy consumption (SEC) for the whole process, since there is an increased amount of steam per ton of caustic soda produced required to reach the commercial specification for the product.

The present work focuses on a triple effect evaporation unit that is used to concentrate the products from a diaphragm electrolytic cell in a production site in Brazil. The diaphragm cell delivers the feed (liquor) to the evaporation system, shown in fig. 1, which, at design conditions, consumes about 55 t/h of 6.2 bar saturated steam that is generated in a natural gas-fired boiler. However, due to a ban on the use of asbestos in the country, the design conditions can no longer be achieved by the electrolytic cell when operating with non-asbestos diaphragms, which lead to a direct reduction in the caustic soda concentration in the liquor that feeds the evaporator. As pointed by Olufemi (2011) and observed at the plant after substitution of the asbestos diaphragms, the non-asbestos cells deliver a less concentrated product, with a higher caustic soda yield and, consequently, a higher total mass flow rate. Thus, due to the liquor arriving at the evaporation system at these different conditions, but product specification remaining the same, the specific steam consumption increases, reducing expressively the total caustic soda yield. Because of the higher specific steam consumption associated with the increasing cost of natural gas and the ever present pressure to reduce carbon emissions, the company was prompted to seek alternative strategies to reduce the steam consumption from the fossil fuel-fired boiler.

Mady et al. (2018) proposed the use of mechanical vapor recompression (MVR) as an option to reduce the steam consumption in the evaporator, and in this work a modification of this configuration is proposed. As presented in the work by Le Cao Nhien et al.(2014), Hamed et al.(1996) and many other authors on the topic, vapor recompression, whether it is thermal or mechanical, usually has a positive influence on the performance of the evaporation, reducing greatly the plants steam consumptions. However, as pointed by Mady et al. (2018), the exergy destruction rate is lower with the use of MVR, it is higher relative to the total exergy input, which seems to suggest a lower thermodynamic efficiency, although only if the exergy cost of generating the electricity or the steam is not considered. What this work sets out to do is to explore the effects of the exergy destruction in the performance of the system and compare the configurations presented regarding efficiency, cost, and emissions. To this aim, the conditions of steam and electric energy generation will be pre-established for fair comparison.

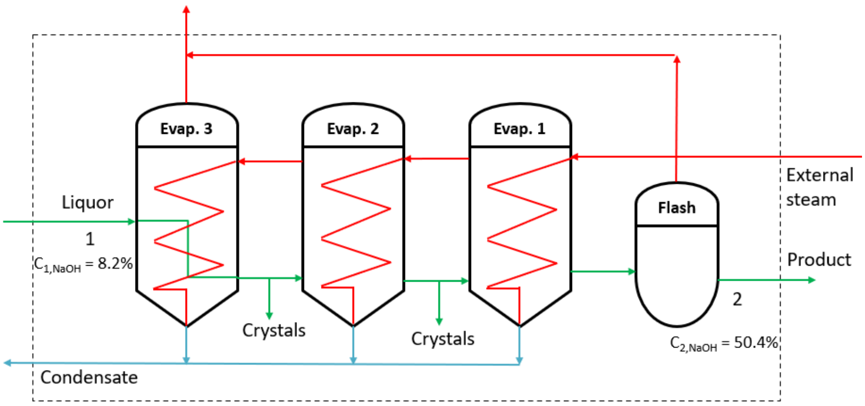

Figure 1: Triple effect evaporation system. Based on Mady et al. (2018).

2. METHODOLOGY

In a study initiated in 2014 by Mady et al. (2018) regarding the same plant, a mathematical model of the process was elaborated and implemented into the software EES, including the three evaporators and all heat exchange and separation processes involved from the third effect evaporator inlet to the finished product. This simulator is currently being updated and improved by the authors as a part of a new research project which produced, among other results, this text. The complete details of the modelling implemented in the original simulator can be found in the work by Mady et al. (2018), and the modified or newly implemented information will be elaborated here.

There are three different proposed configurations currently being analysed which will be compared with the original scenario, and seeking to compare the different configurations properly and fairly, a common set of assumptions needs to be established. Firstly, all the analysis is based around the systems operating in steady state. The product stream total mass flow will be kept at a fixed value, and so will its composition, with mass fractions of 0.504 for caustic soda, 0.01

for sodium chloride, and the remainder for water. Other key operating parameters such as the inlet soda concentration, the third effect pressure, and the vapor mass flow rate that is recompressed in the MVR system, will be varied and their effects in the performance of the system can be calculated by the detailed physical model used to simulate the plant.

Furthermore, considering real conditions of the production complex in question, another process will be considered running in parallel with the diaphragm cell evaporation presented. This other process consists of a smaller caustic soda production unit that uses a membrane-based electrolytic cell and consumes 10 t/h of steam in the same conditions as the diaphragm cell. Since some of the configurations proposed generate extra steam through water injection, it is interesting to consider the conditions of steam consumption in the entire complex. This will allow for a comparison between the configurations as all the steam in the complex was originally produced in the boiler, and thus the entire complex will benefit from the recovery of low pressure steam. The configurations will be compared using an exergy-based analysis, while also evaluating the environmental impacts through CO_2 emissions.

The base case considered for the sake of comparison, referred to as configuration (1), is the original scenario of the plant that includes the evaporation system associated with the diaphragm cell, as shown previously in Fig. 1, operating alongside the evaporator used in the membrane cell with its fixed steam consumption of 10 t/h ($\dot{m}_{membrane}$). In this case all the steam used as heat input to the evaporators is produced by a natural gas-fired boiler located on site. Figure 2-(a) shows the first energy optimizing configuration, called configuration (2) in this work, which was proposed by Mady et al. (2018) and in whose work the details of the design process can be found. It consists in implementing a mechanical vapor recompression (MVR) system with intercooling to recompress the low-pressure steam that is rejected from the evaporator at around 10 kPa. Two separate compressor trains are used due to the very high pressure ratio (over 60) between the reject steam and the required steam conditions to the first effect. Intercooling of the steam between compressor stages was proposed and is shown in detail in Fig. 3, where the steam is cooled to its saturation temperature or to the previous compression stage inlet temperature (whichever is higher), in order to increase compressor efficiency and keep the steam temperatures close to the design conditions for the heat exchangers in the evaporator.

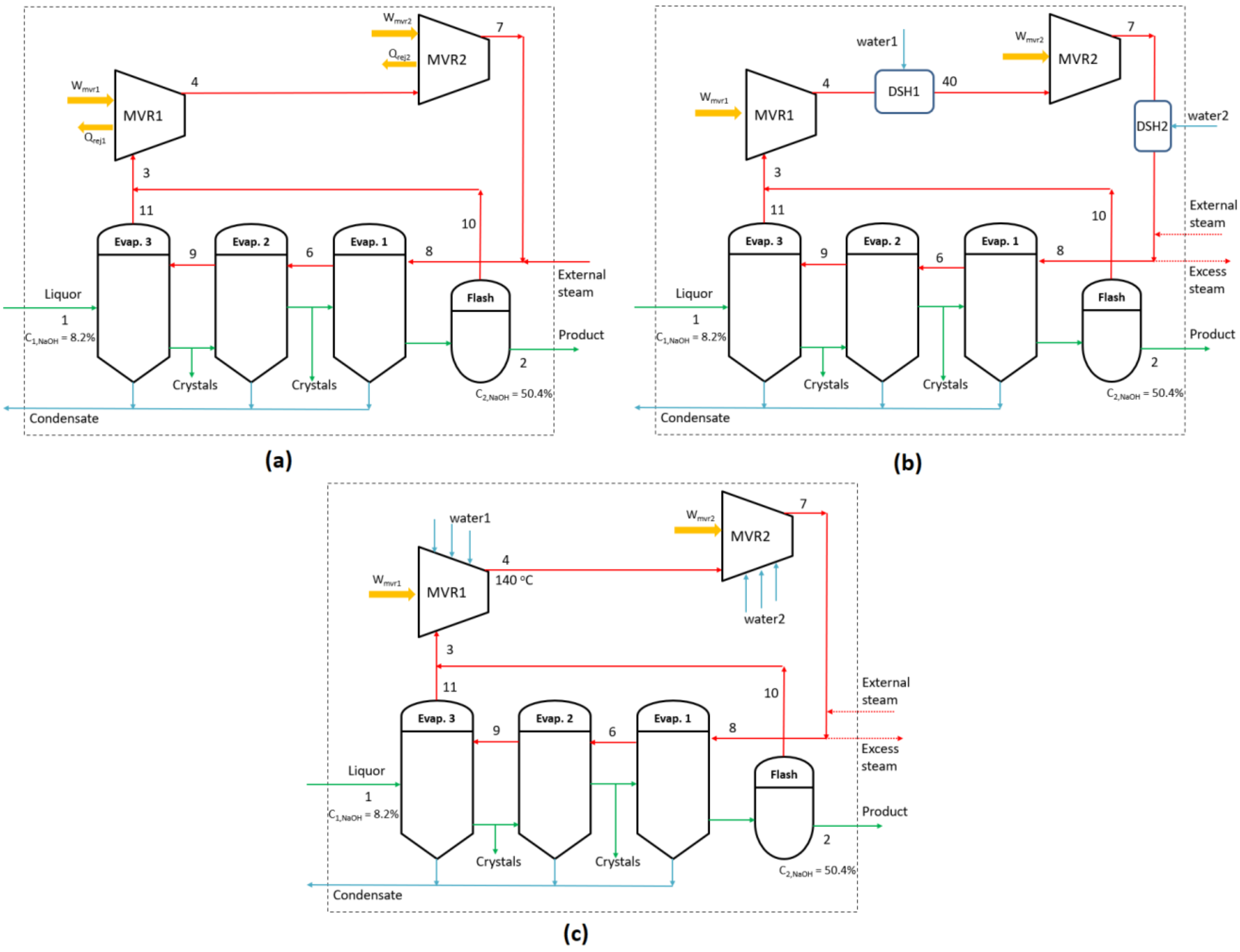

Figure 2: Diagrams of the configurations proposed with MVR. (a) MVR with intercooling by heat exchange, or configuration (2), based on Mady et al. (2018); (b) MVR with de-superheaters, or configuration (3), and (c) MVR with intercooling by water injection, or configuration (4).

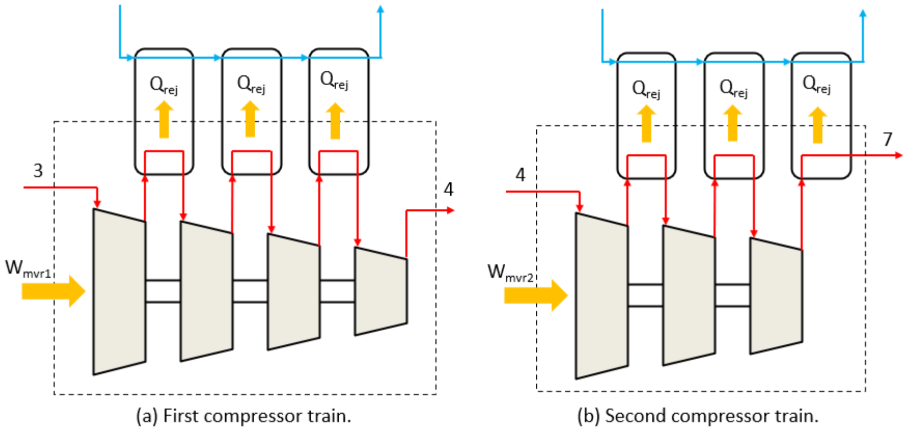

Figure 3: Detailing of the compression and intercooling system used in configuration (2). Based on Mady et al. (2018).

However, the authors observed that while this configuration is thermodynamically efficient, it may not be financially efficient due to the relatively low heat exchange coefficient associated with the superheated steam. This causes the required heat exchanger surface area to be somewhat large, which can substantially increase the capital costs. Considering this, the authors proposed configuration (3) which is based on the use of de-superheaters to cool the steam and is presented in Fig. 2-(b). Furthermore, configuration (4) is presented in Fig. 2-(c) as a combination of the previous two proposals, considering the intercooling to be achieved by means of water injection between the compression stages. In configuration (3), water at ambient conditions is injected in the flow exiting both the compression trains until the flow reaches saturation, while on configuration (4) this process is performed after every compression stage. The injection of liquid water into the superheated steam will keep the steam close to saturation while also generating more steam and eliminating the need for additional heat exchangers.

For all the MVR configurations, the total steam demand in the complex is given by the sum of the evaporation system steam requirement ($\dot{m}_8$), which is the flow rate for state 8 as shown in Fig. 2, and the membrane cell demand ($\dot{m}_{membrane}$). In the three MVR scenarios all the steam that leaves the third effect evaporator is recompressed and there will be excess steam if the flow rate after recompression and cooling by water injection is higher than the total steam demand in the plant. In this case, the excess steam is considered a co-product along with the caustic soda, and no external steam flow is needed. In case the steam flow rate after recompression and cooling does not exceed the total steam demand, there is no excess steam and thus the system will still require the use of an external source of steam. In all situations where supplementary production of steam is necessary, the same boiler considered in configuration (1) is considered for the steam generation. Since the steam requirement that is not met by the MVR system is generated in the boiler, the generation of steam by adding liquid water to the steam has potential to be more efficient and cause less emissions, and this will be discussed in later sections.

The general mass and energy balance equations are shown in Eqs. (1) and Eq. (2) for mixing and branching processes, considering no pressure drops or heat loss in pipes and ideal mixing and splitting, where the subscript "in" represents matter flowing into the control volume, and "out" represents flows going out of it, with $\dot{m}_i$ representing the mass flow rate for stream i, and h_i representing its specific enthalpy. Eqs. (3) and (4) present a sample of the mass and energy balances applied to DSH1 in configuration (3). This formulation is easily extendable to configuration (4) and is omitted here because of the large number of equations that arise as a consequence of multiple points of water injection. These equations specifically refer to the addition of water to the steam flow, which can also be used for current 7 in configuration (3) and for the intercooling in configuration (4), always considering cooling the flow back to saturation after compression. Equations (5) and (6) refer to the redirection of steam from the MVR system, where $\dot{m}_{excess\_steam}$ is zero if $\dot{m}_{MVR}$ is less than $\dot{m}_8$ and positive otherwise, and $\dot{m}_{external\_steam}$ is zero if $\dot{m}_{MVR}$ is greater than m_8 and positive otherwise.

Considering that the mass flow rates and conditions in and out of the evaporators, specifically states 3 and 8 in Fig. 2, are a given to the MVR system after being calculated by the simulator depending on the operating parameters, this set of equations completely solves the flows and conditions for the MVR system along with Eqs. (7) and (8) that allow for the calculation of the compression powers and the compressors outlet conditions considering an isentropic efficiency of 85% per compression stage. In Eq. (7), $h_{n,s}$ represents the enthalpy that current "n" would have if it had undergone an isentropic compression, and it represents an arbitrary compression stage from state 'n' to the next state "n+1". For the compression power per compression stage, Eq. (8) can be used, and the power of each compression train is given by the sum of the power required by its stages.

$$\sum \dot{m}_{in} = \sum \dot{m}_{out} \quad (1)$$

$$\sum \dot{m}_{in} h_{in} = \sum \dot{m}_{out} h_{out} \quad (2)$$

$$\dot{m}_4 + \dot{m}_{water1} = \dot{m}_{40} \quad (3)$$

$$\dot{m}_4 h_4 + \dot{m}_{water1} h_{water1} = \dot{m}_{40} h_{40} \quad (4)$$

$$\dot{m}_7 + \dot{m}_{water2} = \dot{m}_{MVR} = \dot{m}_8 + \dot{m}_{excess\_steam} - \dot{m}_{external\_steam} \quad (5)$$

$$h_8 = h_{excess\_steam} = h_{external\_steam} \quad (6)$$

$$h_{n+1,s} - h_n = (h_{n+1} - h_n)\eta_{mvr1} \quad (7)$$

$$\dot{W}_n = \dot{m}_n (h_{n+1} - h_n) \quad (8)$$

2.1. Exergy analysis

To make a proper comparison between the configurations, the inputs to the system (electricity and steam) need to be levelled. The authors opted to extend the control volume as shown in Fig. 4, including both the steam and electricity generation processes, and to apply an exergy-based analysis. Some basic definitions are necessary to proceed with the discussion. Exergy is a thermodynamic property that is defined as the maximum amount of work that can be extracted from a given form of energy and its surroundings, and it was defined as such because it is the most convenient standard for the quality of energy (Kotas, 1984), allowing for direct comparison between different forms of energy. In this work, the reference conditions considered for the temperature and pressure of the surroundings will be 25° C and 1 atm since the plants is located at sea level. The reference composition conditions for the surroundings, used to calculate chemical exergy, will be those proposed by Szargut et al. (1988).The destroyed exergy in a process is directly proportional to the entropy generated and represents the amount of useful work that is lost in said process, and thus can be used to compare processes in terms of thermodynamic efficiency. Based on the exergoeconomics methodology used by Lazzaretto and Tsatsaronis (2006), Flórez-Orrego at al. (2014) proposed the concepts of the Non-Renewable Unit Exergy Cost (c_{NR}), which is the amount of non-renewable exergy required to produce one unit of exergy of a certain product, and the Renewable Unit Exergy Cost (C_R), representing the amount of renewable exergy required for the same task. The Total Unit Exergy Cost (C_T) is the sum of these quantities, and these indicators will be used to bring the inputs external to the evaporator and MVR system (electricity and steam) to the same basis of comparison by using exergy. The differentiation between renewable and non-renewable exergy costs is important since non-renewable sources are much more punishing in terms of costs and environmental impact then their renewable counterparts.

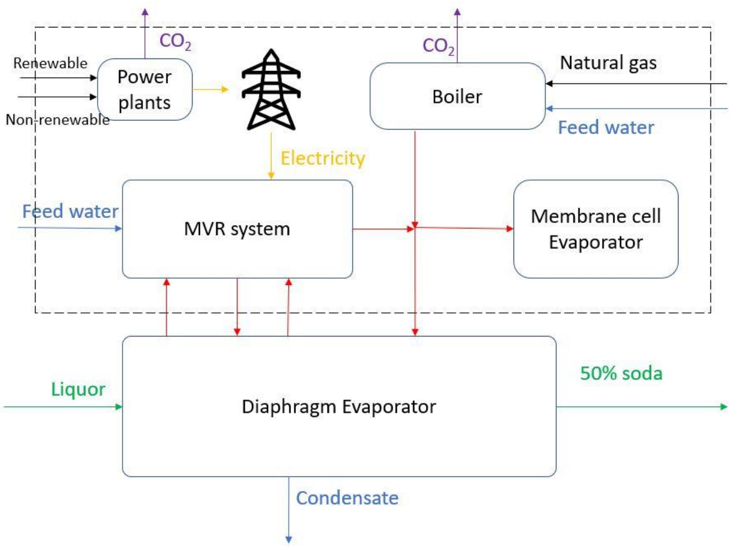

Figure 4: Extended control volume for the overall exergy analysis of the process.

Flórez-Orrego et al. (2014) thoroughly analysed the Brazilian electric energy matrix and applied the Total Unit Exergy Cost methodology to it. The analysis included all the main electricity generation routes and explored in detail all the stages of transportation and processing of the used resources, and also the construction, operation and decommissioning of the power plants. As a result, a comprehensive overview of the average exergy costs and emissions associated with the production of electric energy in Brazil was obtained. The detailed methodology can be found in the work by Flórez-Orrego et al. (2014), but the main results are presented in Table 1, adapted to the updated electric energy matrix in Brazil, taken from a report elaborated by Brazilian public energy research company, EPE (2019). The specific costs associated with each energy generation route were assumed to be unchanged since the publication in 2014, but the electric energy share by source changed substantially. The Brazilian mix weighted averaged exergy costs and specific CO_2 emission will be used in this work as a representation of the thermodynamic and environmental implications of the use of electric power from the grid. As shown in Fig. 4, the electricity used to power the MVR system is held accountable for the consumption of renewable and non-renewable resources, according to the mix shown in Table 1. The renewable ($\dot{B}_{Re}$) and non-renewable ($\dot{B}_{NRe}$) exergy transfer rates required to produce the total electric power ($\dot{W}_{Te}$) input to the MVR system, and the CO_2 emissions from this process, can be calculated with Eqs. (9), (10), and (11), respectively. Furthermore, the exergy destruction rate in the power generation process ($\dot{B}_{d,e}$) can be calculated by applying an exergy balance to it, shown in Eq. (12). Analogously, the exergy destruction rate in every process "i" ($\dot{B}_{d,i}$) can be calculated by applying Eq. (13), which is the generalized form of the balance, where $\dot{B}_{in}$ is the flow exergy going into the control volume, $\dot{B}_{out}$ is flow exergy out of it, $\dot{Q}_k$ is a heat exchange happening at T_k, and $\dot{W}_i$ is the work interaction between the system and its surroundings. This equation will be used to calculate the exergy destruction rate for the whole control volume presented in Fig. 4, and in each of the individual processes for a deepened analysis, such as the intercooling and compression stages in configuration (2), the compressors and de-superheaters in configurations (3) and (4), and the boiler for all the configurations.

Table 1: Total, renewable, and non-renewable exergy costs, and CO_2 emissions for electricity consumed in Brazil. Adapted from Flórez-Orrego et al. (2014).

Power plant	Share (%) 2014	Share (%) 2019	C_{NR} (kJ/kJ$_e$)	C_R (kJ/kJ$_e$)	C_T (kJ/kJ$_e$)	M_{CO2} (g/kJ$_e$)	C_R/C_{NR}
Coal-fired	1.4%	2.5%	3.1597	0.0322	3.1919	2.48E-01	0.010
Oil-fired	2.5%	1.5%	2.7986	0.0160	2.8146	2.00E-01	0.006
Natural gas-fired	4.4%	9.4%	2.4178	0.0118	2.4296	1.33E-01	0.005
Biomass	6.6%	8.9%	0.4022	6.8002	7.2024	2.66E-02	16.91
Nuclear power	2.7%	2.7%	3.0905	0.0515	3.1420	7.62E-03	0.02
Wind farms	0.5%	8.4%	0.0308	2.2245	2.2553	8.33E-04	72.22
Hydro	81.9%	66.7%	0.0027	1.2215	1.2242	1.20E-03	452.4
Brazilian mix (weighted average)		2014	0.3329	1.4631	1.7960	1.72E-02	4.39
		2019	0.4712	1.6069	2.0781	2.51E-02	3.41

$$\dot{B}_{Re} = c_R\, \dot{W}_{Te} \tag{9}$$

$$\dot{B}_{NRe} = c_{NR}\, \dot{W}_{Te} \tag{10}$$

$$\dot{m}_{CO2,e} = M_{CO2}\, \dot{W}_{Te} \tag{11}$$

$$\dot{B}_{Re} + \dot{B}_{NRe} = \dot{W}_{Te} + \dot{B}_{d,e} \tag{12}$$

$$\dot{B}_{in} - \dot{B}_{out} + \dot{Q}_k(1-T_0/T_k) - \dot{W}_i = \dot{B}_d \tag{13}$$

The same methodology will be applied to the steam used in the evaporation processes, but considering that it is generated in a natural gas-fired boiler located on site, the renewable exergy cost will be zero since all the exergy input to produce the steam is non-renewable. According to Che et al. (2004), an usual flue gas exhaust temperature of 180 °C in a natural gas-fired boiler results in a boiler energy efficiency (η_{boiler}) of 89,9%, which will be the value used as reference in this study. Thus, the exergy input rate to the boiler ($\dot{B}_{boiler}$) can be computed from Eqs. (14) and (15) using the fuel exergy (b_{fuel}), and the desired enthalpy increase for the steam produced in the boiler, from the environment conditions (h_0) to the input to the evaporators ($h_{external\_steam}$). From the natural gas composition from Campos basin as reported by Lora and Nascimento (2004) it was possible to calculate the values of 47.33 MJ/kg for the fuel lower heating value (LHV), 75.3% for the fuel carbon content in mass (I_f), and 1.032 for φ, which is the ratio between the chemical exergy and the lower heating value for the natural gas (Szargut, 1988). The exergy cost associated with natural gas extraction and primary separation (c_{gas_prod}) is also accounted for, with a value of 1.034 kJ of non-renewable exergy per kJ of natural gas exergy as calculated by Nakashima et al. (2004). With this information the exergy cost balance can be performed for the steam generation process in the boiler and is shown in Eq. (16). The total exergy consumption of the steam generation process is given by $\dot{B}_{steam\_gen}$, while c_{steam_gen} represents the accumulated unit exergy cost of the steam generation process. $\dot{B}_{boiler}$ is the natural gas exergy, which was produced in the gas production step at an exergy cost of c_{gas_prod} and acts as an exergy input to the boiler with the goal of producing steam. Alternatively, c_{fw} and $\dot{B}_{fw}$ represent the feedwater unit exergy cost and the feedwater exergy that flows into the boiler, but since the feedwater is considered to be at ambient conditions, it's specific exergy is very small when compared to the large chemical exergy carried by the natural gas, and thus this term is not considered in the calculation. Moreover, Eq. (17) will be used to calculate the direct CO_2 emissions ($\dot{m}_{CO2\_boiler}$) by the boiler in [g CO_2/s], where MM_{CO2} and MM_C are CO_2 and atomic carbon molecular weights, respectively.

$$\eta_{boiler} = \dot{m}_{external\_steam} \, (h_{external\_steam} - h_0)/\dot{m}_{fuel} \, LHV \quad (14)$$

$$\dot{B}_{boiler} = \dot{m}_{fuel} \, b_{fuel} \quad (15)$$

$$c_{steam\_gen} \, \dot{B}_{steam\_gen} = c_{gas\_prod} \dot{B}_{boiler} + c_{fw} \dot{B}_{fw} \quad (16)$$

$$\dot{m}_{CO2\_boiler} = \dot{m}_{fuel} \, I_f \, (MM_{CO2}/MM_C) \quad (17)$$

Finally, it is customary in the caustic soda production field to express key performance indicators on a per unit of pure caustic soda produced ($\dot{m}_{NaOH}$) basis, and thus the exergy costs from the electricity and steam generation, and their carbon emissions, will be combined and expressed as such. Equation (18) shows the calculation method for the specific CO_2 emission (SE_{CO2}), while Eqs. (19) and (20) present, respectively, the method for determining the specific renewable exergy consumption (SC_R) and specific non-renewable exergy consumption (SC_{NR}). Naturally, the specific total exergy consumption (SC_{exergy}), which will be the main tool for evaluating the overall thermodynamic performance in each case, is the given by the sum of SC_R and SC_{NR}.

$$SE_{CO2} = (\dot{m}_{CO2\_boiler} + \dot{m}_{CO2,e})/\dot{m}_{NaOH} \quad (18)$$

$$SC_R = \dot{B}_{Re}/\dot{m}_{NaOH} \quad (19)$$

$$SC_{NR} = (\dot{B}_{steam\_gen} + \dot{B}_{NRe})/\dot{m}_{NaOH} \quad (20)$$

3. RESULTS AND DISCUSSION

3.1. Utility requirements

The detailed physical model was run while varying key operating parameters, notably the inlet liquor soda concentration ($c_{soda,1}$) and the third effect pressure (p_{11}), while keeping the total soda production rate fixed. The main utility requirements are presented in Fig. 5, which shows the sensitivity of the evaporator system steam requirement (m_8) and low-pressure steam production (m_3) to the mentioned parameters.

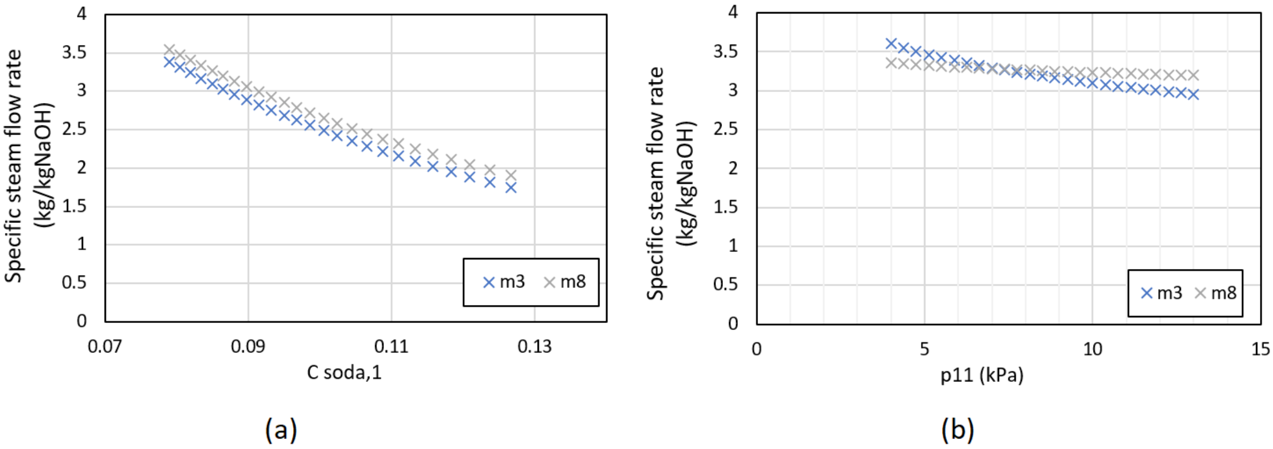

Figure 5: Steam mass flow rates flowing in and out of the diaphragm evaporation system as a function of (a) liquor inlet soda concentration, with p11 = 10.7 kPa; and (b) evaporator third effect pressure, with $c_{soda,1}$ = 8.5%.

The power supply to each compression train, the de-superheating water flow rates, and intercooling heat rejection rates as functions of the inlet liquor soda concentration are shown for the nominal conditions in Tab. 2 for each of the proposed configurations. As was shown in Fig. 5, the detailed physical model is capable of varying operating parameters and evaluate the impact of them on any indicators, as will be explored later in the exergy analysis section. The values of the indicators in Tab. 2 for non-nominal conditions are not shown explicitly here for the sake of simplicity.

Table 2: Power supply to MVR compressors, de-superheating water mass flow, and intercooling heat rejection rate, per unit of produced caustic soda, for each proposed configuration. Nominal conditions are $c_{soda,1}$ = 8.5% and p_{11} = 10.7kPa.

	Specific power consumption (kWh/kg_{NaOH})	De-superheating water specific mass flow (kg/kg_{NaOH})		Intercooling specific heat rejection (kWh/kg_{NaOH})	
		Water 1	Water 2	Qrej1	Qrej2
Config. (2)	0.764	0.355	0.887	0	0
Config. (3)	1.053	0	0	0.256	0.371
Config. (4)	0.84	0.38	0.599	0	0

The data presented shows the influence of key operating parameters over the diaphragm evaporation system, and how the demand for utilities changes in varying conditions. In evaluating Fig. 5 it is important to remember that m_3 is the low pressure rejected steam that is recompressed in configurations (2) through (4), and that m_8 is the mass flow rate required by the diaphragm evaporator, while there is still a requirement of a fixed 10 t/h of steam in the plant, demanded by the membrane cell and other sub-processes. It is possible to calculate the steam surplus that is created when water is added for de-superheating by inspecting the results in Tab. 2, and those results are shown separately in Fig. 6 since it is considered a co-product. As expected, in configurations (1) and (2) where there is no addition of water, there is no steam surplus. Conversely, in the other configurations some steam is available as a co-product if the compressed steam completely covers the steam demand of the plant. It is also interesting to show Fig. 7 which contains a T x s diagram tracking all the thermodynamic states achieved by the steam during compression. It is noteworthy that the path that the steam undergoes in configurations (2) and (4) is the same, with the difference between them lying only in the method of cooling, and that in all cases steam is made available for use as saturated steam at 617 kPa.

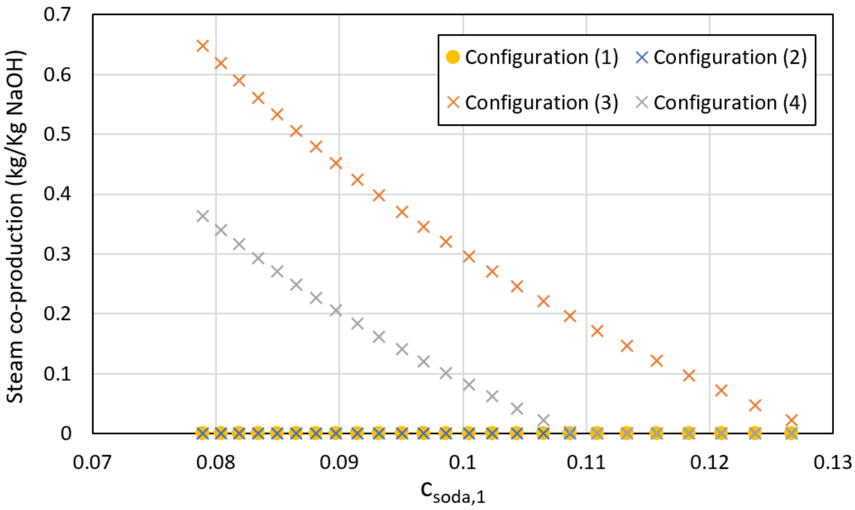

Figure 6: Specific steam surplus generated by the MVR system.

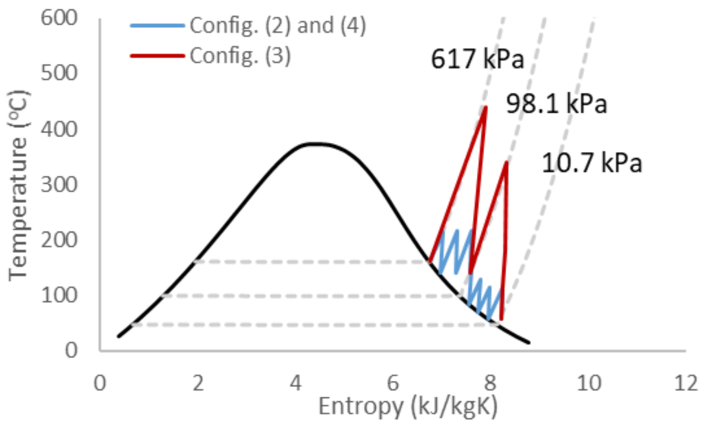

Figure 7: Temperature versus entropy (T x s) diagram for the compression process.

3.2. Exergy analysis

The Total Unit Exergy Cost methodology was applied, and the authors were able to calculate the total exergy inputs to the control volume shown in Fig. 4, and ultimately express it in terms of a unit of soda produced. It is important to discuss first what the exergy cost of a process means, as it is a lesser known exergy indicator. The exergy cost, as the name suggests, represents how much exergy was consumed in a process to produce a unit of exergy of a different product. It is intimately connected with the concept of exergy destruction, as it was made clear in the electricity example with Eqs. (14), (15) and (17) that the exergy destruction is the difference between the exergy input, or cost, and the desired output. Ergo, as the exergy cost increases, so does the exergy destruction in the same process.

Figure 8 presents the renewable, non-renewable, and total exergy costs per configuration. At first glance, it is already apparent that the exergy costs are far lower in the configurations with MVR than in the one without it, reaching up to 65% lower than the original scenario. Furthermore, while it is debatable which configuration is best at higher soda concentrations in the inlet, Configuration (4) is clearly the most exergetically efficient at lower concentrations, which are more usual on site. Configuration (2) is the one with the lowest renewable exergy cost among all cases, but the use of renewable and widely available resources to produce the caustic soda is not nearly as punishing as consuming the non-renewable ones. On the other hand, configuration (2) becomes the most expensive of the RMV scenarios when it comes to non-renewable and total exergy cost, mainly due to the higher amount of steam generated at the boiler since there is no addition of mass to the recompressed steam. The scenarios that rely more on the use of the boiler to generate steam are apparently the least thermodynamically efficient.

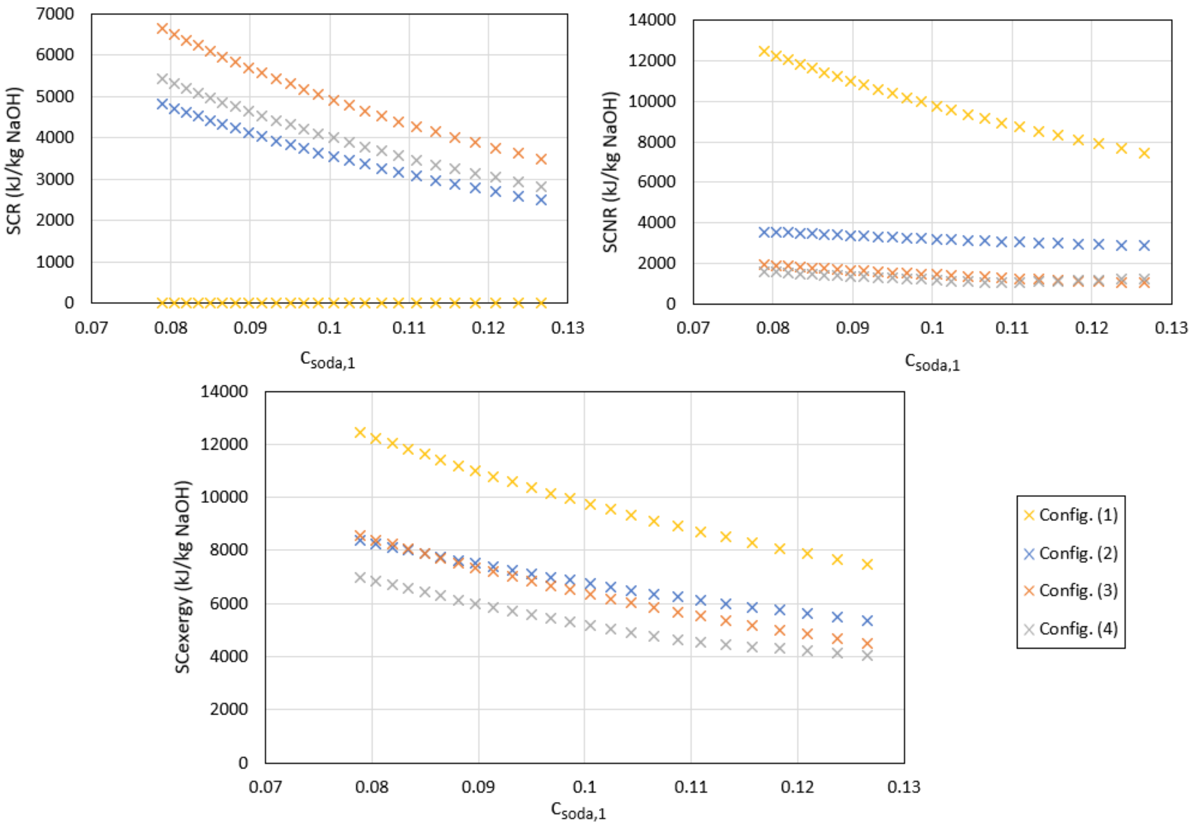

Figure 8: Renewable, non-renewable, and total exergy cost by configuration.

To elaborate on the discussion regarding thermodynamic efficiency of the processes, Fig. 9 was elaborated to compare the exergy destruction in each process for each configuration while keeping the operating parameters fixed. The main goal of this work was to establish a comparison between the steam generated in the boiler and the steam that is recuperated using MVR and de-superheating. Firstly, boilers are known to not be excellent in terms of thermodynamic efficiency. The temperatures on them do not reach remarkably high values, and thus they are restricted by the Carnot limit, while also containing heat exchanges and several passes in tubes which lead to unpleasantly high exergy destruction. On the other hand, the process of de-superheating consists of mixing water in ambient condition with high-pressure steam, which is high-quality exergy. Combined with the exergy destruction in the heat exchanges and compression stages, the overall process is not expected to lead to low exergy destruction rates. Finally, the exergy destruction on the heat exchange intercooling considered heat transfer to cooling water at 25 º C with an allowable increase of 10 degrees, which punishes this configuration severely as most of the exergy is destructed when the product leaves the control volume at such a low temperature. However, as demonstrated in Fig.9, the boiler dominated scenario presents the highest exergy destruction rate by far. Considering that on all these cases the total plant steam demand is met, and that configurations (2) and (4) produce in these conditions additional 0.53 and 0.27 kg of steam per kg of soda produced, it becomes very clear that generating steam by injecting water into steam is more efficient, under the stated conditions, than doing so in a boiler.

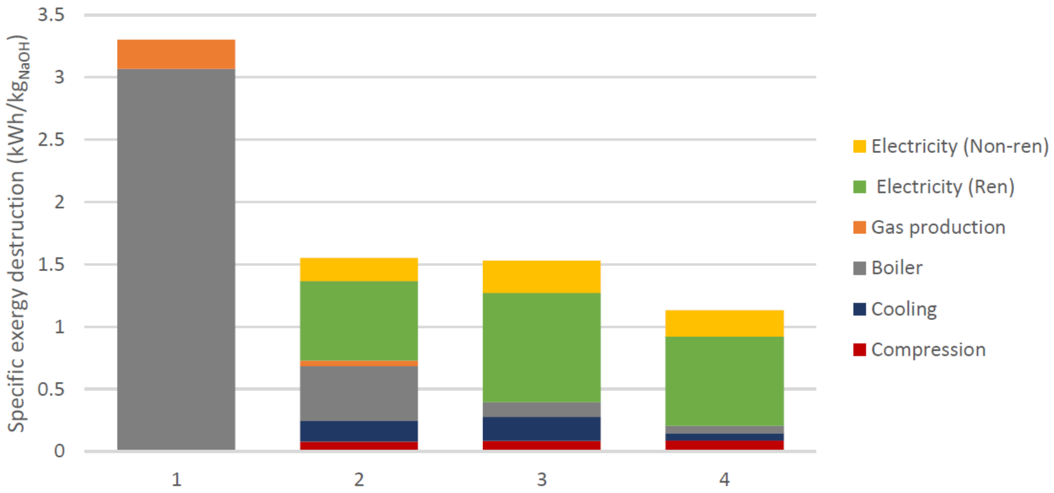

Figure 9: Specific exergy destruction breakdown by configuration and process. Fixed parameters as p11 = 10.7 kPa and c_{soda_1} = 8.5%. Real scenario where $m_{membrane}$ = 10000 t/h.

Proceeding further in the environmental analysis, the total CO_2 emissions for every configuration are shown in Fig. 10 with varying soda concentration in the evaporation system inlet. This encompasses the direct emissions from the boiler, and all the indirect emissions that are consequence of using electricity. Again, the environmental impact is strongly related to the usage of the natural gas-fired boiler, and the configurations that do not generate steam through injection of water in the steam are heavily punished. Generating steam in a boiler is particularly punishing in the Brazilian context since most of the electricity is generated in hydro power plants, with a very low non-renewable exergy and emissions footprints overall.

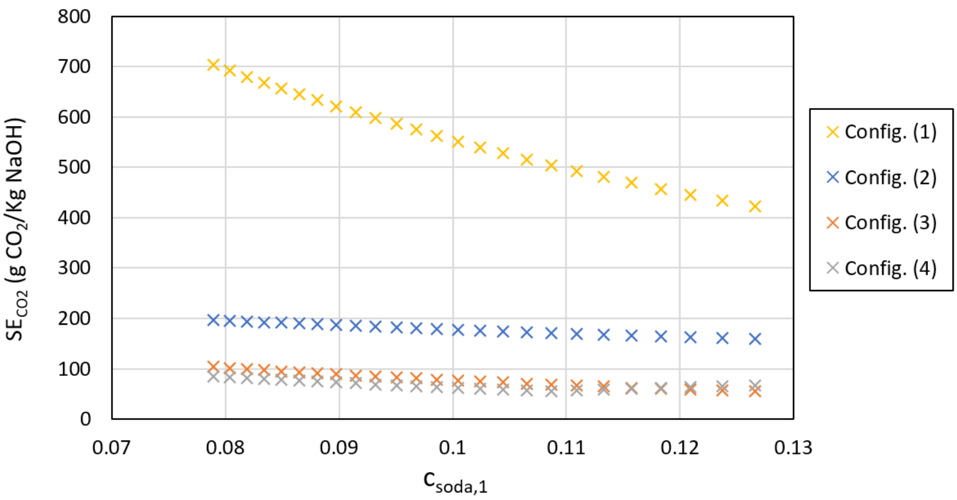

Figure 10: Specific CO_2 emissions with varying inlet soda concentration. Fixed parameters as p11 = 10.7 kPa.

A fictitious scenario was elaborated, considering that the remainder of the plant demands 22 t/h of steam, so that all the surplus steam is used in the plant for soda production. Naturally, since no additional soda production is being considered in this thought exercise, the plant will be less efficient as it consumes more energy to achieve the same production, but Fig. 11 allows for a fair comparison in terms of exergy destroyed per unit soda production.

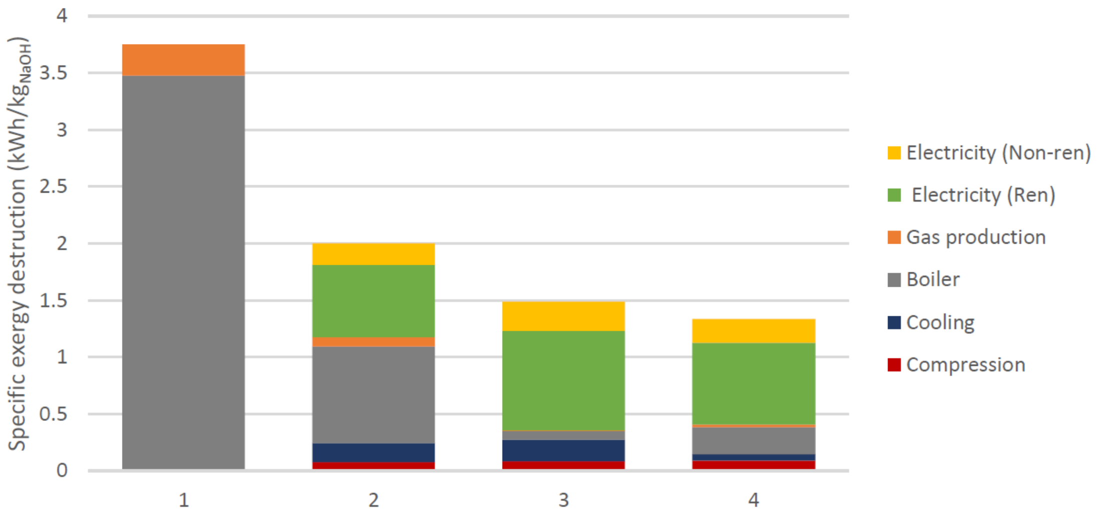

Figure 11: Specific exergy destruction breakdown by configuration and process. Fixed parameters as p11 = 11 kPa and c_{soda_1} = 8.5%. Fictitious scenario where $m_{membrane}$ = 22000 t/h.

4. CONCLUSIONS

The results shown demonstrate that the use of MVR is effective as a method of improving the thermodynamic performance of the system, as the exergy costs for the production of soda, and the exergy destruction in the overall control volume, are reduced when the low temperature steam is recuperated by mechanical compression. Furthermore, by generating high-pressure steam with the use of electricity instead of on a fossil fuel-fired boiler, thanks to the Brazilian hydropower-focused electricity supply this becomes a much more sustainable option, with lower CO_2 emissions and non-renewable exergy costs.

Due to the reality of the plant in question it was not possible to completely isolate the exergy costs for the caustic soda because a sub-product of steam arose in some scenarios. It is apparent that Configuration (4) is the most thermodynamically efficient, as the exergy destruction in that scenario is clearly lower than the others. This matches the expectations since the compression is performed with intercooling, the most thermodynamically efficient manner, and as mentioned before, the other intercooling configuration was punished by considering heat rejection to cooling water. By creating a fictitious scenario where the plant consumes all the steam generated, it becomes clear that from a point of view strictly considering the thermodynamic efficiency of the processes, configuration (4) is undoubtedly the best among the present scenarios. The next steps in implementing this system would need to consider a financial analysis, taking in consideration factors such as contract conditions and prices for steam and caustic soda, and the capital costs for the equipment and installation. However, it has become clear that from an exergy performance point of view, implementing MVR to a caustic soda evaporation plant is a viable option.

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6. RESPONSIBILITY NOTICE

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