Is MVR an efficient alternative to optimize the energy use in an evaporation unity of electrolytic caustic soda production? An exergy approach to the diaphragm arrangement

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Abstract:

Energy and Exergy analysis were applied in an evaporation unity of electrolytic caustic soda production using the diaphragm arrangement. The objective of the vaporization is increase the concentration of caustic soda from entrance concentration which is at the order of magnitude of 10% (mass basis), until the ternary mixture of caustic soda, water and sodium chloride reaches the commercial level, which is 50% in mass of caustic soda. The evaporation process has three stages and one flash tank, which makes the steam consumption to be high. To reduce this consumption it was proposed to use mechanical vapor recompression (MVR) in two different stages of the process, making it possible to the decrease the steam consumption in 80% with the necessity of additional 14.3MW electrical power. In energy basis the reduction in the plant consumption would be about 50%. Moreover, there would be a reduction in the cost of the operation of the plant with the new configuration. Nevertheless, from the exergy consumption point of view the original configuration consumes 75% of the plant configuration with the vapor recompression. This can be explained by the difference in the quality of the electrical energy when compared with the steam used in the plant. When it is taken into account the energy and exergy necessary to produce the electricity and the steam (using a boiler with natural gas inside the factory), the mechanical vapor recompression uses less energy sources. Moreover, from the perspective of exergy analysis the costs were lower.

Keywords:

Exergy analysis, Caustic soda production, Mechanical vapor recompression

1. Introduction

The Brazilian production of caustic soda in 2010 were estimated in 1,536 thousands of tons, being 63.4% originated from diaphragm process, 22,2% from the membrane process and 14.4% using mercury process. All processes use the electrolysis of aqueous solution of sodium chloride to obtain the caustic soda [1]. In the diaphragm process, the membrane has a poor permeability, and typically, the resultant product of the electrolysis has a mass concentration of caustic soda of 12% and a high concentration of sodium chloride. Therefore, there is a necessity of increase the concentration of caustic soda and decrease the concentration of sodium chloride to the commercial level, which is 50% and 1% in mass basis, respectively. To this aim, the method commonly used is a multi-stage vaporization process, and since it is a ternary mixture, it is used hydrocyclones and centrifugal systems for the removal of NaCl crystals. Nevertheless, the vaporization process has a high steam consumption as driving energy.

According to Lara et al. [2] the vapor compression has been used in desalination problems because of its capacity to treat large volumes of water with a wide range of salt concentrations, nevertheless it has high operating and capital costs. Moreover, separation problems such as distillation [3] and

evaporation are widely used in chemical industry and the separation problems can represent about one third of the total energy consumption of the overall process [4]. Therefore, reduce the energy consumption of the vaporization process can lead to significant savings.

Authors such as Hamed et al. [5] claim that the unique characteristic of vapor compression is the energy reuse of the vapor generated in the last effect to act as an energy source in the first effect. There are two different ways to recompress the vapor, thermally in a steam ejector and mechanically in a compressor. Nhien et al. [3] applied mechanical vapor recompression (MVR) in a mixture of acetone, methanol and water, from which it was proposed the use of two recompressions integrated with the distillation system. The saving obtained by the authors achieved values as high as 60% in energy basis when compared with regular extractive distillation. It is important to highlight that the pressure ratio was 2.5 for each compressor used.

Several authors applied mechanical vapor recompression for different processes, from desalination processes [5-9] to chemical industry using distillation process [3]. Some of these articles applied the energy, exergy and thermoeconomic analyses. In the desalination process [9] obtained that multi effect evaporation with mechanical vapor compression resulted in lower unit product costs in comparison of thermal vapor compression, whereas [6] obtained that the later results in lower destroyed exergy and higher exergy efficiency.

2. Original arrangement and mechanical vapor recompression

Figure 1 indicates a schematic representation of the vaporization process, from which, the liquor enters as a mixture of sodium hydroxide, sodium chloride in water, represented by stream 0. This schematic representation is classified by [10] as a typical triple effect diaphragm cell evaporator. Therefore, this schematic representation will be named in the text as conventional evaporation system.

The diaphragm electrolysis produces a solution with low concentrations of caustic soda and with impurities. According to [10] a typical concentration of the solution stream in the output of the diaphragm cell, in mass basis, varies from 10-13% and 10-15% of NaOH and NaCl, respectively. The concentrations adopted in the present analysis are 10.2% of NaOH and 16.5% of NaCl. For the sake of simplicity, the components for the crystals removal, such as hydrocyclones and centrifugal systems were removed from the schematic representation of Figure 2, as well as the heat exchangers and preheaters for the solution vaporization process. Nevertheless, they were taken into account for mass, energy and exergy balances.

The stream 1 is the end of the vaporization process, with a concentration of 49.4% of sodium hydroxide and 2.8% of sodium chloride. Other processes are involved until the final product of 50.4% of NaOH and 0.9% of NaCl. The pressure and temperature at stage 3, 2, 1 and flash tank are, respectively: (9.9kPa, 58°C), (30.6kPa, 87.1°C), (98.1kPa, 140°C) and (10.7kPa, 91.62°C).

Ejectors and barometric columns are used to guarantee the vacuum, where steam and liquid water are used to operate these components. The stream 7 that leaves the evaporation process undergoes condensation process into liquid water.



Figure 1. Conventional evaporation plant schematic representation

The liquor enters in the process by the evaporator 3, as indicated in Figure 1 (in red), from which the vapor that comes from the evaporator 2 remove a fraction of the water. In this process, the heat exchangers and pre-heaters are used to increase the temperature of the solution before it enters the evaporator. These processes are repeated until the solution reaches the evaporator 1 where the input energy is provided by the process steam (which is indicated by the stream 5), bought or produced elsewhere. Moreover, the last effect is the flash tank that does not use heat exchangers, because of the low temperature and pressure that lead to spontaneous vaporization of the water content in the solution. Therefore, the energy inputs in the process of vaporization are the enthalpy of steam 5, the steam to operate the ejectors (stream 6), and the liquid water (stream 4) for the barometric column.

Figure 2 indicates a proposal to reduce the vapor consumption using the mechanical vapor recompression to increase the temperature and the pressure from the thermodynamic state of the steam leaving the evaporator (stream 7) to the process steam. This pressure ratio would be extremely high ($P_5/P_7=37.4$) to perform MVR in a single stage. The present solution breaks the process in two stages, first, from the stream 7 to the state that the steam leaves evaporator 1 (stream 8), which results in a compression ratio of 9.9. The second compression is from the stream 8 to the process steam state (stream 5), which results in a pressure ratio of 6.7. The energy input would be electrical current (compression power) – W_{mvr} . Since the compressions are in different stages (Figures 3 and 4), the term ΔH_{cool} is the intermediate heat transfer to the environment between the stages of compression. Additionally, the exergy content in ΔH_{cool} could be used as a source in some process in the factory.

Another option of vapor compression could be the use of thermal vapor compression, but since the objective is to reduce steam consumption and the flow rates of 7, 8, 9 and 10 are the same order of magnitude of the process steam flow rate, this technique would not lead to a significant reduction in the vapor consumption.



Figure 2. Modification using mechanical vapor recompression - MVR

The pressure ratios of 6.7 and 9.9 are still high for regular compressors; therefore, it was adopted that each compression stage must not exceed a ratio of 2.0. This solution leads to the necessity of the use of different stages with intermediate cooling. The schematic representation of the compressors that takes the vapor from the state of the stream 7 to the state of the stream 8 is indicated in Figure 3. The state after the compression is called cp_i and after the cooling r_i , where i indicates the number of compressions and cooling already performed, i=1, 2 and 3 (cp_4 is the stream 8).



Figure 3. Mechanical vapor recompression in four stages with intermediate cooling

Using the same process, Figure 4 represents a schematic representation of the recompressions that take the vapor at state of the stream 7 to the state of the stream 5, which is the process vapor (usually bought from other plants). At this point depending of the actual disposal of the evaporators it is possible to connect directly the stream 8 to the compressors, or reuse it in evaporator 2 and compress the steam of evaporator 1 in compressors 2. The difference m_8 - m_9 should be added to the stream that enters the compressors 2. This last solution is the one that is indicated in Figure 2.



Figure 4 Mechanical vapor recompression in three stages with intermediate cooling

To calculate the thermodynamic states between the stages it was used an isentropic efficiency of 85% from which it was possible to determine these several thermodynamic states after each compression and cooling. The cooling had the objective to take the steam to the same temperature before the compression, or when this temperature is lower than saturation temperature, take to the to the saturation temperature at the same pressure. This energy can be used as an input to other processes in the factory, nevertheless, here this exergy is considered as lost since it has not be applied to a process yet. Table 1 represents these intermediate states.

Comp. from 8 to 5				Comp. from 7 to 8		
	P (kPa)	T (°C)		P (kPa)	T (°C)	
cp ₁	185	219	cp ₁	17.6	116	
\mathbf{r}_1	185	140	\mathbf{r}_1	17.6	58	
cp_2	349	218	cp_2	31.6	116	
\mathbf{r}_2	349	140	\mathbf{r}_2	31.1	70	
срз	659	214	cp ₃	55.3	130	
r ₃ =5	659	163	r ₃	55.3	84	
-	-	-	cp4=8	98.1	145	

Table 1. Thermodynamic states of the recompression, cooling process

2.1. Energy and Exergy analysis

The mass, energy and exergy equations can be applied for Figures 1 and 2, considering:

- Steady state operation.
- Heat transfer to environment negligible.
- No pressure drops in pipes; therefore, the pumps power has been neglected.

For Figure 1 it is possible to calculate the destroyed exergy as: $B_d = B_{input} - B_{output}$. Hence, the exergy analysis is indicated according to Equation 1.

$$B_d = B_0 + B_5 + B_6 + B_4 - B_3 - B_2 - B_1,$$
⁽¹⁾

The exergy efficiency allows a comparison between the performance of different system and technologies in one single thermodynamic basis. Nevertheless, there is still not a consensus about its addressing in processes such as a separation, evaporation and others. In the present analysis, the exergy efficiency is indicated by Equation 2, and can be defined as the ratio of the exergy output to the exergy input.

$$\eta = \frac{B_{out}}{B_{in}} = \frac{B_1 + B_2 + B_3}{B_0 + B_5 + B_4 + B_6},\tag{2}$$

For Figure 2 the destroyed exergy and exergy efficiency are calculated by Equations 3 and 4. For these equations, the exergy associated with the intermediate cooling, $B_{cooling}$, is considered to be destroyed in the environment or used in some other process in the factory. Moreover, W_{mvr} is the total energy used in the vapor compression, from stream 7 to 10.

$$B_d = W_{mvr} + B_0 + (m_6 - m_{10})B_5 - B_3 - B_2 - B_1 - B_{cooling} , \qquad (3)$$

$$\eta = \frac{B_{out}}{B_{in}} = \frac{B_1 + B_2 + B_3 + B_{cooling}}{B_0 + (m_5 - m_{10})B_5 + W_{mvr}},\tag{4}$$

To apply Equations 1 to 4 it is necessary to calculate the total exergy of each stream. For the vapor, it is possible to calculate accordingly to Equation 5, taking into account physical (b_{ph}) and chemical (b_{ch}) exergy. The water was considered as liquid state in the reference environment.

$$B_{vap} = m_{vap} b_{ch,water} + m_{vap} b_{ph,water} = m_{vap} [b_{ch,water} + (h - h_0 - T_0(s - s_0))],$$
(5)

Considering the solution of sodium hydroxide, sodium chloride in water, Equation 6 can be used to calculate de physical exergy of the solution taking into account the presence of crystals, when necessary.

$$B_{ph,sol} = \left(m_{sol} c_{sol} + m_{cryst} c_{cryst} \right) \left[T - T_0 - T_0 \ln \left(\frac{T}{T_0} \right) \right], \tag{6}$$

From the enthalpy of the solution it was possible to calculate the specific heat c_{sol} , considering that in the reference state (0°C) the enthalpy of the solution and crystals are considered zero. Thus, Equation (7) demonstrates the determination of specific heat of the solution (NaOH, NaCl and H₂O).

$$c_{sol} = \frac{H_{sol} - H_{solref}}{T_{sol} - T_{solref}} = \frac{H_{sol}}{T_{sol}},$$
(7)

The crystals are analyzed in a similar manner, in which the specific heat can be obtained by the expression $c_{cryst} = H_{cryst}/T_{cryst}$.

The chemical exergy of the solution is represented by the two terms in Equation 8, where the first is the standard chemical exergy [11]. In this equation, x_i is the mole fraction; γ_i is activity coefficient of the solution and the index *i* represents: water, sodium chloride and sodium hydroxide. These coefficients of the different components were obtained in [11, 12, 13]. For sodium chloride and caustic soda it was adopted as the activity coefficient the value of 0.6, and as a recommended by [11], for water it was adopted 1.0.

$$B_{ch,i} = \sum_{i} \frac{m_i}{M_i} \left(x_i b_{ch,i} + RT_0 x_i \ln \gamma_i x_i \right), \tag{8}$$

The total exergy of the solution is the summation of physical and chemical exergy indicated respectively by Eq. (6) and (7). Therefore: $B_i = B_{ch,i} + B_{ph,i}$.

Regarding the energy and exergy indicator, it was proposed three mathematical relations to compare the MVR with project condition. The first is a traditional index used in the field of sodium chloride, which is the ratio of mass of vapor consumed to produce certain mass of pure NaOH in the product (c_{mass}). Based on this index, two other indicators were proposed accordingly to Eq. (9) and (10), but in energy and exergy basis. Equation 9 is also traditionally used in the caustic soda production sector.

$$C_{energy} = \frac{E_{consumed}}{m_{NaOH, product}},$$
(9)

$$C_{exergy} = \frac{B_{consumed}}{m_{NaOH, product}},$$
(10)

3. Results and discussion

3.1. Evaporation unity

Table 2 indicates the exergy inlet and outlet of the project conditions and the modification using mechanical vapor recompression – MVR. The value of the exergy inlet in the project condition, which is 42% higher than the mechanical vapor recompression, is related to the high consumption of water in the barometric column. The destroyed exergy in the project condition is higher than using MVR; nevertheless, the percentage of the exergy input that is destroyed is lower in the conventional condition.

	Pro	Project		′R
	MW	%	MW	%
Exergy input	81.1	100	34.1	100
Exergy output	69.0	85.0	22.5	66
Destroyed exergy	12.2	15.0	11.6	34

 Table 2. Exergy input, exergy output and destroyed exergy for the conventional condition and MVR

In table 3 it is considered the values of mass and energy consumption of the project condition and using MVR. It is important to highlight that despite the power of compression be higher than the exergy variation of the process steam (Table 4), there is a reduction in the energy consumption of the vaporization process. The steam consumption would decrease from 38.5MW to approximately 14.4MW of electricity. The exergy content of the steam in the ejector is 263.8kW. From Table 3 it is possible to conclude that there is a significantly reduction of steam consumption and if the price of the electricity is lower than the price of the steam, there would be a considerable reduction in evaporation costs. Nevertheless, regarding the evaporation unity as control volume, the exergy used in mechanical vapor recompression is higher than in the project condition.

Table 3. Comparison in mass and energy basis for the conventional configuration and MVR proposal

	Conventional	MVR
	$\Delta H (\mathrm{MW})$	ΔH (MW)
Process steam	38.5	3.12
Steam to ejector	0.96	-
Liquid water to ejectors	-	-
Intermediate cooling	-	11.5
Compression power	-	14.3

In Table 4 it is demonstrated the difference between the steam consumption (process and ejectors) in the original configuration of the evaporator and using the mechanical vapor recompression (MVR); and it is also demonstrated the electricity consumption in the new configuration. This last decreases the energy consumption of evaporation plant in 53% (modification to use electricity instead of vapor). From the exergy analysis point of view, the steam exergy variation is 12MW, whereas the compression power is 14MW. In other words, if it is considered only the frontier of the evaporation unity as control volume, from the exergy analysis it is possible to conclude that the MVR has higher exergy costs that the original condition.

	Project	MVR
	MW	MW
Steam enthalpy variation	39.6	3.1
Steam exergy variation	12.0	0.9
Destroyed exergy	12.2	11.6
Compression power	-	14.0
Electricity consumption	-	15.6
Energy consumption	39.6	18.7

Table 4. Comparison of the energy and exergy consumption for the conventional configuration and MVR proposal

** Mechanical and electrical compression efficiency of 90%

Other possible solution not studied with details in this article is to use a desuperheater instead of the last cooling process of the Figure 4. The idea of this process is to increase the enthalpy of the steam adding some amount of water to the last stream, to guarantee that the specific enthalpy is in state 5, or the same absolute enthalpy, H_5 . With this procedure the energy available for the process of vaporization would be 37.6MW, being necessary only 2% of the original vapor consumption of the vaporization process. Nevertheless, it would demand some modifications in the heat exchanger in the first effect; therefore, these analyses were not conducted with higher details, bearing in mind that is a possible solution to decrease more the energy consumption of the vaporization process.

In Table 10 it is indicated the ratio of the indicators in mass (t_{vapor}/t_{soda}), energy (kJ_{energy}/kg_{soda}) and exergy (kJ_{exergy}/kg_{soda}) basis in the original configuration and considering MVR. The indexes are defined in Eqs. (9) and (10). The first two columns indicate that the mass and energy indexes would improve if the MVR were used. Nevertheless, the same indicator, but in exergy basis shows that the original configuration consume less exergy to produce the same amount of NaOH.

Table 5. Consumption indicator for the factory

Ratio	C _{mass}	Cenergy	Cexergy
MVR/Original	0.08	0.49	1.39

3.1. Effect of the energy generation

As indicated in [14] the Brazilian energy matrix has about 82% of its basis of hydro-electric power, the remain of the energy source is biomass and natural gas (10%), nuclear power (3%) and others. The same authors considered the conversion efficiency in a hydroelectric plant as 82%, whereas a cogeneration system using natural gas has a conversion efficiency of 45%. With these values, it is possible to make a comparison between the energy and exergy necessary to produce electricity (considering the energy source as hydroelectric or as natural gas), and the energy and exergy consumption of a boiler operated with natural gas as fuel (energy efficiency of 90% and exergy efficiency of 30%).

Table 6 indicates the results of energy and exergy consumption to produce the steam at the condition of the evaporator. For electrical energy (hydro and natural gas), it also considered the exergy necessary to produce the surplus of steam to satisfy the evaporator demand since MVR do not attend all the requirements as indicated by Table 3. From Table 6 it is possible to infer that the exergy costs considering the production of the steam is lower using mechanical vapor recompression. If transmissions lost were 16% for hydroelectric generation [14], the exergy required to evaporation

process would be 24 MW. Accordingly, considering the production chain of the electricity and steam, the MVR would be the best solution from the energy and exergy point of view. Nevertheless, this technique must be recommended in countries where a considerable part of the electricity matrix are obtained from hydro plants, nevertheless cogeneration system with natural gas would also have lower exergy cost if compared with steam production in the factory.

Table 6. Energy and exergy consumption of the factory considering the electricity and steam production

	Energy (MW)	Exergy (MW)
Boiler with natural gas	42.7	40.0
Electricity production natural gas	34.3	34.0
Electricity production Hydroelectric	20.9	20.6

4. Conclusions

In this article, mechanical vapor recompression technique was analyzed as an attempt to reduce steam consumption in an evaporator of sodium hydroxide and sodium chloride solution in water. It was performed the energy and exergy analysis of the evaporation system considering as a control volume the factory and the production chain of electricity, which is distinguished feature of this article. From the range analyzed, it is possible to conclude that:

- Mechanical vapor recompression saves 50% of the total energy consumption of the factory. The steam consumption of the solution reduces to 8% if compared with the consumption of the original configuration.
- From the exergy analysis point of view, the compression power is higher than the exergy variation of the steam, indicating that this modification has higher exergy costs to produce the same amount of caustic soda. Nevertheless, if the performance of production and transmission of electricity and steam were included in the analysis, the exergy costs of MVR would be lower than the conventional condition. This results highlights that, from the exergy point of view, MVR is a better solution.

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Nomenclature

- *b* specific exergy, kJ/kg
- *B* exergy flow rate, kW
- *c* specific heat, kJ/(kg K)
- C mass, energy and exergy index, kg/kJ, kJ/kJ
- *h* specific enthalpy, kJ/kg
- H enthalpy flow rate, kW
- m mass flow rate, kg/s
- P pressure (kPa)
- T temperature, K
- x mole fraction, -

Greek symbols

 η efficiency, -

 γ activity coefficient, -

Subscripts and superscripts

cool cooling

ch chemical

MVR mechanical vapor recompression

- ph physical
- sol solution

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