

STILLAGE AS HEAT SOURCE IN ABSORPTION REFRIGERATION SYSTEM (H₂O-NH₃) APPLIED ON COOLING FERMENTATION IN THE ETHANOL PRODUCTION

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Abstract. When a heat source at low temperature is available, water-ammonia absorption refrigeration (AAR) system is preferred to traditional vapour compression. The fermentation process, in ethanol production process, is characterized by an exothermic reaction that need temperature control of the process to prevent several problems. The increase of temperature in fermentation process leaves to yeast inhibition, promote infection, flocculation, decrease the ethanol content in wine, increasing the energy consumption in distillation and stillage production. Nowadays, a common value of temperature in fermentation process is 34°C, however, several studies shows some advantages to keep the temperature in 28°C. In this work, the option to use AAR system, taking the energy from stillage as heat source, has been evaluated in a case study considering ethanol production of one vat with 800 m³ capacity, fermentation temperature of 28°C, ethanol content in wine equal to 13°GL. Several parameters of the system such as coefficient of performance (COP), cooling effect and equipment's irreversibility rate were calculated. The cycle's performance coefficient evaluated is 0.66. The preliminary result shows that evaporator and regenerator were the equipments more irreversible. Another important result showed that energy from stillage is sufficient to produce cooling effect required by fermentation process, keep it at 28°C temperature.

Keywords: Absorption refrigeration, ethanolic fermentation, stillage, ethanol fermentation

1. INTRODUCTION

According to agricultural frontier are migrating to warmer regions, such as the northwest paulista (Brazil's interior), the cooling of the fermentation vats is a critical step in the ethanol production process, since the process is characterized by an exothermic reaction. Dias (2008) showed that ethanolic fermentation at low temperatures (15-20°C) favors the ethanolic yield. However, the fermentation time would be high, making impossible the manufacturing process. In the range of 25°C and 30°C the fermentation rate is higher and above of 35°C decreases cell viability, Torija (2003).

The wine produced at low temperature and higher ethanol content compared to wine produced at high temperature, provides higher yields in the fermentation and distillation step. The greater amount no fermented sugar, the greater will be the amount ethanol lost, e.g., decrease at final ethanol production. This is one of the advantages of producing wines at high ethanolic level, Dias (2008).

Thus, fermentation at lower temperatures than those currently used (32°C), increasing the ethanol content in the wine, leads to advantages to the ethanol production process, as follow:

- Increase fermentation and distillation yield;
- Decrease the costs of stillage processing and transport;
- Energy consumption reduction in fermentation and distillation process.

Absorption Refrigeration Systems (AAR) is one manner to provide the required cooling effect in fermentation process at high ethanolic content. This cooling system is commonly known to be driven mainly by low quality thermal sources such as can be found in the sugarcane manufacturing process, for example, stillage, condensed steam at temperatures below 100°C, etc.

Despite the increase in equipment's costs through from the acquisition of new cooling devices, the benefits that can be obtained shows a great potential justifying further investigation.

2. ABSORPTION REFRIGERATION SYSTEM

The refrigeration cycle based on absorption have experienced up and downs since its first application around in 1859, Bjurstrom & Raldow (1981). Predominantly in refrigeration and air-conditioning industry, these systems became no competitive when the advent of electric energy distribution at low cost between the end century 19th and beginning century 20th. Newly, has seen a renewed interest in the absorption cycles in face to growing concerns about energy and environmental matters.

Similar to vapor compression cycle, the basic absorption cycle operates at two pressure levels correspondent to the condensation and evaporation temperatures, Niebergall (1981). In absorption cycle, the compressor is replaced by a binary solution, refrigerant (NH₃) + absorbent (H₂O), and plus three components: absorber, where the mixture absorbs

the refrigerant, recirculation pumps where raises the solution's pressure and generator where occurs the refrigerant separation from solution through the addition of heat. Apart from these differences, the refrigerant has the same processes of condensation, expansion and evaporation in a vapor compression cycle.

An absorption cycle (with regenerative heat exchanger) and main components are shown in figure 1. This work considers the use of stillage as heat source at generator (points 11 and 12) and the cooling effect at evaporator cools the water that circulates through of the vats during the fermentation process.

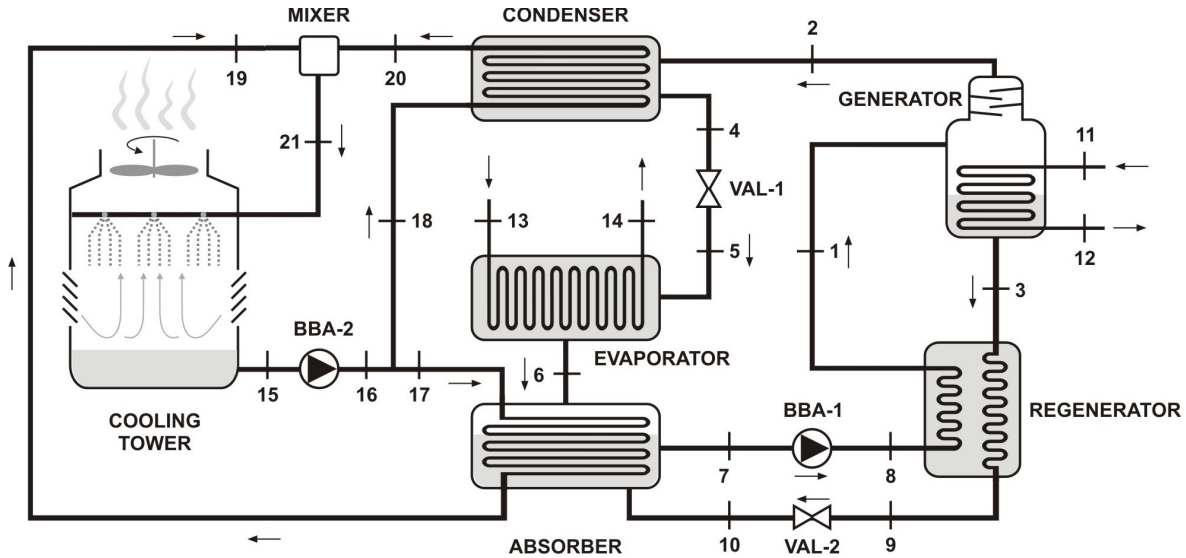


Figure 1. Basic absorption system (with regenerative heat exchanger) coupled to cooling tower.

3. THERMODYNAMIC MODELING

The most classic procedure to evaluate the thermal system performance is through of the 1^a Law of Thermodynamic, Horlock (1997). This analysis allows defining, from the energy view, the thermal efficiency of each equipment as well as the overall system. Although very popular, this methodology has limitations because it not counts the energy quality, e.g., not concerned with the inherent irreversibility of the processes. Considering this aspect, the thermal evaluation ought to consider the 1^a and 2^a Law of Thermodynamic coupled, known as Exergy Analysis, Kotas (1995).

Around the each device shown in Figure 1 is drawing one imaginary line represented a control volume and for continuity, 1^a and 2^a Law of Thermodynamics, Wylen (1994), by equations 1, 2 and 3, respectively. The following considerations are observed:

- I. The cycle operates under steady state.
- II. Variations of kinetic and potential energy are negligible.

$$\sum \dot{m}_s - \sum \dot{m}_e = 0 \quad (1)$$

$$\dot{Q}_{V.C.} + \sum \dot{m}_e h_e = \sum \dot{m}_s h_s + \dot{W}_{V.C.} \quad (2)$$

$$\sum \dot{m}_s s_s - \sum \dot{m}_e s_e = \sum_{V.C.} \left(\frac{\dot{Q}_{V.C.}}{T} \right) + \dot{S}_{ger} \quad (3)$$

The total exergy has been evaluated as follows:

$$\psi_i = \psi_i^{ch} + \psi_i^{ph} \quad (4)$$

Chemical exergy for the mixture H₂O-NH₃ (points: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10) has been calculated according to Rossa & Bazzo (2009), equation 5:

$$\psi_i^{ch} = \frac{x_{NH_3}}{M_{NH_3}} e_{o,NH_3}^{ch} + \frac{(1-x_{NH_3})}{M_{H_2O}} e_{o,H_2O}^{ch} \quad (5)$$

Where e_{o,NH_3}^{ch} and e_{o,H_2O}^{ch} are the chemical exergies of ammonia and water, respectively, as given by Szargut *et. al.* (1988). The chemical exergy unit is $kJ/kmol$. x_{NH_3} , M_{NH_3} and M_{H_2O} represents the mass fraction of ammonia, ammonia's and water's molecular mass, respectively.

The other points of the cycle shown in figure 1, only the physical exergy have been considered, and calculated according to Szargut *et. al.* (1988), equation 6:

$$\psi_i^{ph} = (h_i - h_0) - T_0(s_i - s_0) \quad (6)$$

Irreversibility rate of each device has been calculated according to Wylen (1994), equation 7:

$$\dot{i}_{V.C.} = \left(\sum \dot{m}_e \psi_e - \sum \dot{m}_s \psi_s \right) + \sum \left(1 - \frac{T_0}{T} \right) \dot{Q}_{V.C.} - \dot{W}_{V.C.} \quad (7)$$

Cycle's coefficient of performance (COP) has been calculated as follow, equation 8:

$$COP = \frac{\dot{Q}_E}{\dot{Q}_G + |\dot{W}_{BB1}|} \quad (8)$$

Remark: The stillage is the main residue in the ethanol production. According to Glória (1976), the stillage contains more than 93% water, being very rich in potassium, organic matter and considerable amount of other elements essential to plant nutrition, such as: Ca, Mg and SO₄. Thus, the thermodynamic modeling of the stillage has been evaluated, simplified, like water's properties.

3.1. Mixture's Properties H₂O-NH₃

The performance of an absorption refrigeration system is critically dependent on the chemical and thermodynamic properties of working fluids, Perez-Blanco (1984). A fundamental characteristic of the pair absorbent/refrigerant is that, in liquid phase, the pair is soluble within the cycle temperature range. The mixture should also be chemically stable, non-toxic and non-explosive. Further it follows:

- The difference between the fusion points of the pure refrigerant and mixture, at the same pressure, should be as large as possible.
- The refrigerant should have high vaporization heat and high concentration in the absorbent in order to maintain low rates recirculation between the generator and absorber per unit cooling capacity.

Several working fluids are suggested in the literature. Marcriss (1988) suggests that there are at least 40 kinds of refrigerants and 200 kinds of absorbent for application in absorption refrigeration systems. However, the most common pairs are: ammonia-water and water-LiBr.

Since the discovery of absorption refrigeration system, the water-ammonia pair has been widely used. Both ammonia (refrigerant) and water (absorbent) are highly stable over a wide operating temperature and pressure range. The mixture can be used in application requiring low temperatures, because the freezing temperature of ammonia is close to -77 °C. However, as ammonia and water are volatile, the cycle requires a rectifier between the generator and condenser to condense the evaporated water and return to generator. Without the rectifier, the water would accumulate in lower parts at evaporator harming the cycle's performance.

In this work, the mixture's properties NH₃-H₂O have been calculated according to the correlations proposed by Ibrahim & Klein (1993) and implemented into the software EES[®] (Engineering Equation Solver) developed by Klein & Alvarado (1995). This software enables the rapid resolution of equation systems through the thermodynamic properties evaluation, such as: enthalpy and entropy, making it unnecessary access the thermodynamic tables.

3.2. Pressures and Concentrations of the Absorption Refrigeration System

The project assumptions define the pressure levels of the cycle. Niebergall (1981) suggests that the evaporation pressure (low pressure) should be defined by the evaporating temperature and condensing pressure (high pressure) by the condensation temperature. Thus, it is possible write:

$$p_{low} = p_{sat}(T_{evap}, NH_3) \quad (9)$$

$$p_{high} = p_{sat}(T_{cond}, NH_3) \quad (10)$$

Where: p_{sat} represent the saturated pressure.

Niebergall (1981) also suggests that the weak solution concentration should be defined by the pressure and temperature at generator, while the rich solution concentration by pressure and temperature at absorber. Thus, the concentrations have been calculate according to simplified formulation proposed by Pátek & Klomfar (1995) where the mixture temperature is function of the pressure and molar fraction of ammonia in liquid phase, equation (11).

$$T(p, x) = T_o \sum_i a_i (1-x)^{m_i} \left[\ln \left(\frac{p_o}{p} \right) \right]^{n_i} \quad (11)$$

Where: $T_o = 100K$ and $p_o = 2MPa$. The parameters are shown in the table 1.

Table 1. Parameters of the equation (10) by Pátek & Klomfar (1995).

i	m_i	n_i	a_i
1	0	0	$+0.322302 \times 10^1$
2	0	1	-0.384206×10^0
3	0	2	$+0.460965 \times 10^{-1}$
4	0	3	-0.378945×10^{-2}
5	0	4	$+0.135610 \times 10^{-3}$
6	1	0	$+0.487755 \times 10^0$
7	1	1	-0.120108×10^0
8	1	2	$+0.106154 \times 10^{-1}$
9	2	3	-0.533589×10^{-3}
10	4	0	$+0.785041 \times 10^1$
11	5	0	-0.115941×10^2
12	5	1	-0.523150×10^{-1}
13	6	0	$+0.489596 \times 10^1$
14	13	1	$+0.421059 \times 10^{-1}$

4. RESULTS

Considering the production of conventional distillery using batch fermentation, vats of 800m³ capacity, fermentation temperature of 28°C and ethanol content of the wine equal to 13°GL, Dias (2008) showed that during 15 hours of fermentation is need to remove an average of 1455 kW (for each vat) to maintain the fermentation processes at 28°C. The removal of the heat generated during fermentation has been done accomplished by Absorption Refrigeration System (AAR), figure 1. Water used to cool the vat is to have an inlet temperature of 17°C (point 14), and an outlet temperature of 26°C (point 13), in order to maintain the wine temperature at 28°C.

In conventional distillery, the stillage is removed at lower part of the distillation column, around at 109°C. Often, the stillage is used to heat the yeast wine, thus after the release heat to wine the stillage reaches at temperature of 90°C. The stillage at 90°C provides heat to generator (point 11, figure 1). The cooling effect generated by evaporator cools the water that circulates between the vat and evaporator, keeping the fermentation temperature at 28°C.

The table 1 shows the results for each points of the cycle proposed or base line (BL).

Table 2. Operation conditions at each point of the cycle as shown in the figure 1.

Point	$\dot{m} \left(\frac{kg}{s} \right)$	$P(bar)$	$T(^{\circ}C)$	x_{NH_3}	x	$h \left(\frac{kJ}{kg} \right)$	$s \left(\frac{kJ}{kg.K} \right)$	$\psi^{ch} \left(\frac{kJ}{kg} \right)$	$\psi^{ph} \left(\frac{kJ}{kg} \right)$
1	3.620	15.55	41.6	0.6332	CL	-27.9	0.4805	12581	1577
2	1.333	15.55	41.6	0.9999	1	1299.0	4.188	19839	1798
3	2.287	15.55	87.0	0.4195	CL	157.6	1.08	8352	1584
4	1.333	15.55	40.0	0.9999	0	190.5	0.6583	19839	1742
5	1.333	6.15	10.0	0.9999	0.117	190.5	0.6846	19839	1735
6	1.333	6.15	15.2	0.9999	1	1282.0	4.522	19839	1682
7	3.620	6.15	29.0	0.6332	0	-87.1	0.2931	12581	1574
8	3.620	15.55	29.1	0.6332	CL	-85.4	0.2941	12581	1575
9	2.287	15.55	67.0	0.4195	CL	66.6	0.8199	8352	1570
10	2.287	6.153	62.0	0.4195	0.01569	66.6	0.8235	8352	1569
11	18.0	2.00	90.0	-	-	377.0	1.192	-	1770
12	18.0	2.00	61.0	-	-	255.2	0.8428	-	1752
13	36.8	3.00	26.0	-	-	109.2	0.3809	-	1744
14	36.8	3.00	17.0	-	-	69.7	0.2466	-	1744
15	40.0	1.00	30.0	-	-	125.8	0.4365	-	1744
16	40.0	3.00	30.1	-	-	126.0	0.4367	-	1744
17	20.0	3.00	30.1	-	-	126.0	0.4367	-	1744
18	20.0	3.00	30.1	-	-	126.0	0.4367	-	1744
19	20.0	2.25	56.0	-	-	234.8	0.7812	-	1750
20	20.0	2.25	47.7	-	-	199.9	0.6737	-	1747
21	40.0	1.00	52.0	-	-	217.4	0.7282	-	1748

CL: Compressed Liquid. $T_o = 25^{\circ}C$ and $P_o = 1$ bar

Table 3. Heat exchanged by devices and pump's mechanical works and irreversibility.

Device (Absorption cycle)	$\dot{Q}(kW)$	$\dot{W}(kW)$	$i(kW)$
Generator	2193	-	5.5
Condenser	1477	-	11.1
Expansion Valve: VAL-1	-	-	10.4
Expansion Valve: VAL-2	-	-	2.4
Evaporator	1455	-	51.4
Absorber	2176	-	12.6
Regenerator	208	-	23.9
Pump: BBA-1 ($\eta = 0.75$)	-	5.9	1.1

The points 2, 6 and 4, 7 have been taking as boundary conditions and represents saturated vapour and liquid, respectively. The coefficient of performance (COP) for these conditions resulted in 0.66, according to equation 8, for a cooling effect of 1455 kW and consume of stillage of 18.0 kg/s.

Some amount of refrigerant evaporated before entering the evaporator, losses of 11.7% of cooling effect. Niebergall (1981) suggests that to minimize this loss the low pressure must be decreased; in this BL case a good value of low pressure would be 5.0 bars. Considering the points from 1 to 10, the chemical exergy represented the largest amount of the total exergy, notably at points where the mass fraction of ammonia is greater. This conclusion verifies the great importance in consider the chemical exergy in the thermodynamic modeling of absorption refrigeration system and just no the physical portion in the total exergy.

When the pair ammonia-water is considering in absorption refrigeration system, some researchers says that would be necessary a rectifier between generator and condenser because some amount of water evaporates together ammonia. However, the results from table 2 show that no rectifier is required because the mass fraction of ammonia at point 2 is 0.9999. This result evidence the importance of the thermal equilibrium condition imposed at the points 1 and 2. Obviously, this condition depends on the device's constructive characteristics.

Considering the data from table 3, the figure 2 is plotted and the device's irreversibility (%) has been compared.

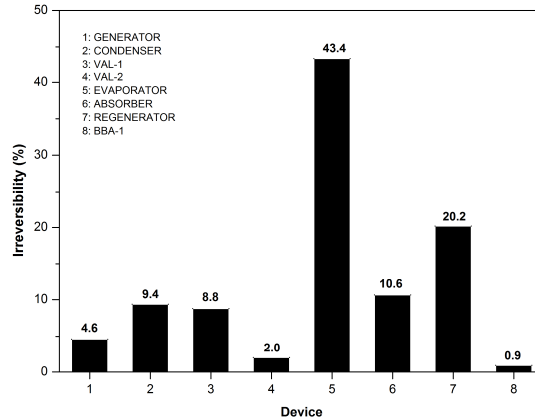


Figure 2. Irreversibility generated in each device (BL case).

The evaporator (43.4%) is the device with the highest irreversibility followed by regenerator (20.2%). Considerable irreversibility have been also observed in the absorber (10.6%), condenser (9.4%) and expansion valve 1 (8.8%). Especially at evaporator, the high water mass flow is the main cause for irreversibility generation. At regenerator, the high temperature at point 3 is the main cause for irreversibility generation.

Following, the figure 3a-d shows the cycle behavior in function of the evaporating temperature. These informations are very important during project phase of the absorption refrigeration system.

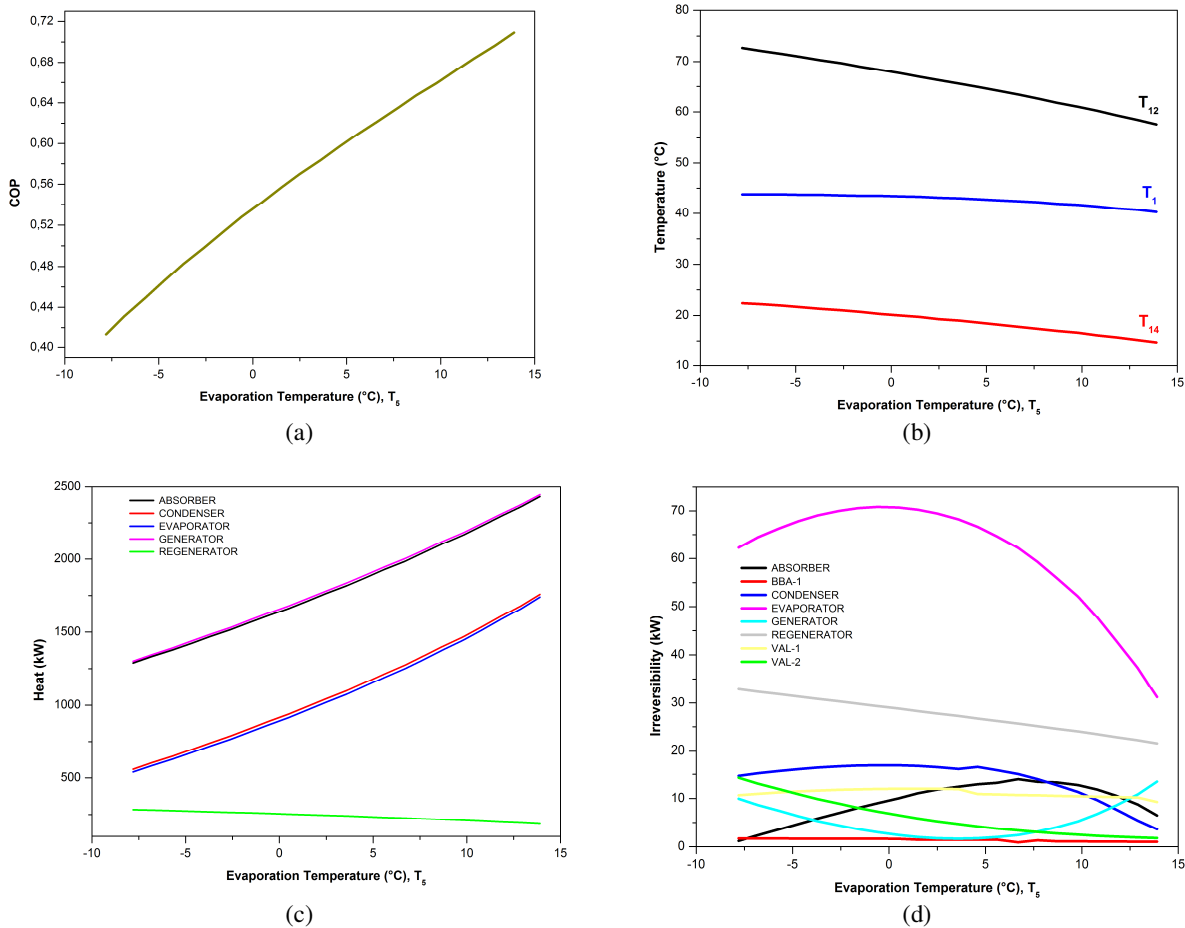


Figure 3. Results considering boundary conditions from BL case (table 2). (a) Coefficient of performance behavior. (b) Temperature at points 1, 12 and 14. (c) Heat exchanged by absorber, condenser, evaporator, generator and regenerator. (d) Irreversibility generated by devices.

The figure 3a shows that there is a high relation between COP and evaporating temperature, e.g., the higher the evaporating temperature the higher the cycle's COP. The limitations for increase the evaporating temperature is meet $T_6 < T_{13}$ so that evaporator's size is minimized.

The figure 3b shows the temperature behavior at points 1, 12 and 14. Considering the evaporating temperature range, the temperature T_1 hardly changed. However, the temperatures T_{12} and T_{14} were fully dependent. Decreasing the temperature T_{12} is one goal this refrigeration system, however, the temperature T_{14} is related with fermentation temperature, e.g., the lower the temperature T_{14} , lower the fermentation temperature inside vats, making impossible the manufacturing process.

The figure 3c shows the heat behavior at each device (generator, absorber, evaporator, condenser and regenerator). Only regenerator's heat decreased with the increase the evaporating temperature, in other devices the heat rate always increased. This fall in regenerator's heat is provoked mainly by fall the mass flow of poor solution (point 3), as can be seen in figure 4.

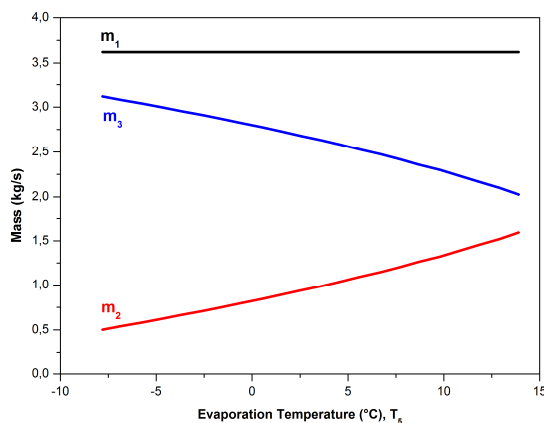


Figure 4. Results considering boundary conditions from BL case (table 2). Mass flow of rich solution (m_1), poor solution (m_3) and "pure" ammonia (m_2).

Finally, the figure 3d shows the irreversibility behavior for devices. Clearly, it possible observed the high relations between irreversibility generated by absorber, generator and condenser in function of increase evaporating temperature, however, the opposite trends, e.g., the increase of evaporating temperature provokes the increase of generator's irreversibility, whereas at evaporator and condenser provokes the strong fall.

5. CONCLUSIONS

Overall, in this work have been presented an alternative project for fermentation temperature control counteroffer to current absorption chiller, which reveals itself as "black box" at Brazilian industry.

The results showed that is possible to operate an absorption refrigeration system utilizing heat from stillage as a thermal energy source to produce cooling effect for maintain fermentation temperature at 28°C.

The critical devices were identified evaluating the irreversibility generated, as well as the cycle operation conditions, according to project assumptions.

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