

Valorization of the waste heat from a sulfuric unit for the refrigerated storage of ammonia

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Abstract

In the Tunisian Chemical Group, the production of sulfuric acid by the contact process yields important waste heat that measure about 22 MW of 1500 tons /day. This heat is discharged into the sea which, in addition to the resulting losses, constitutes a nuisance to the environment. To overcome this problem, it was proposed to recover part of this waste and use it for an absorption refrigeration machine. Now, ammonia is stored at atmospheric pressure and a temperature of -33 °C. So that it remains in the liquid state, significant amounts of heat must be eliminated continuously. A compression refrigeration cycle is designed for it, but consumes a huge amounts of electricity. Unlike absorption heat pumps, which consume thermal discharges of the sulfuric unit. This paper presents a technical feasibility study for the use of waste heat generated by the sulfuric unit for the refrigerated storage of ammonia. It is proposed as a solution to conduct a heat recovery loop with ejector for the production of steam from this heat waste. This steam is then used for an absorption machine to keep ammonia at the liquid state. The simulation of the loop was done by Hysys and for the absorption refrigeration machine, the calculations were done by using EES as well as Oldham and Merkel diagrams. The obtained results indicated that the generator temperature must be higher than 134 °C for the absorption machine to operate when ammonia-water is the working pair. Moreover, a COP of about 0.46 was obtained for a generator temperature of 145°C and a condensation and absorption temperature of 37°C. This COP is very satisfactory for a single effect water-ammonia refrigeration cycle which is cooling to such a low temperature.

Keywords: *Absorption refrigeration; Waste heat recovery; COP; EES; Oldham; Merkel.*

1.INTRODUCTION

The demand for refrigeration and air conditioning is responsible for the consumption of a great deal of electrical energy. According to the International Institute of Refrigeration, about 15% of the total energy generation is consumed by compression refrigeration systems [1]. Hence, several environmental problems are caused by the emission of an important volume of greenhouse gases, produced by large amounts of energy used to run the compressors in the conventional vapor compression refrigeration systems [2]. An alternative green technology to replace them is therefore highly needed [3]. The increased interest has been focused on innovative technologies that can either use renewable energy or recover waste heat [4]. Most of these technologies rely mainly on absorption refrigeration.

Absorption machines are characterized by the lack of internal moving parts, besides the pump, which guarantees a silent and vibration-free operation. Moreover, they work on fluids that cause no damage to the ozone layer and do not contribute to global warming as well. The most successful working fluids are still H₂O-NH₃ and LiBr-H₂O combinations [5,6]. The absorption system, employing water and ammonia, is one of the most reported in the literature, considering the data of enthalpy tables and diagrams[7].

There are several models of absorption machines [8]. The single stage machine, for instance, is quite similar to traditional vapor compression cycles. Both systems contain a condenser, where heat is extracted out of the system, and an evaporator, where heat is added to it. In absorption refrigeration, the compressor is replaced with an absorber, generator, pump, valve, and solution heat exchanger. The main advantage of absorption refrigeration compared to vapor compression is that it runs mainly on heat. This can be very interesting especially when low-grade heat is involved [9].

Absorption refrigeration machines have been the subject of several studies. Srihirin et al.[10] carried out a detailed review on vapor absorption cooling systems. A new method of generating shaft power and cooling simultaneously using water ammonia mixture based on solar energy was proposed by Shankar and Srinivas[11]. Chiranjeevi and Srinivas[12]carried out simulation studies on the impact of vapor absorption refrigeration

system on the performance of cooling systems in general. And other researchers as Alvares and Trepp [13]; Misra et al. [14]; Kouremenos [15]; Kang et al. [16]; Selahattin [17] and Riffat et al. [18] theoretically studied this machine with different configurations.

In this work, a technical feasibility study was carried out on the recovery of waste heat coming from a sulfuric acid production unit and its use for the refrigerated storage of ammonia. It is intended to replace the actual system which is based on vapor compression with an absorption machine.

2.CYCLE DESCRIPTION

2.1.Waste heat recovery

In the manufacture of sulfuric acid using the contact process, the acid has to be cooled in a heat exchanger train using seawater. As a consequence, roughly 22 MW of heat are released to the sea for a production of 1500 tons/day of sulfuric acid.

A loop has been designed in this work to recover some of the waste heat through the production of steam (see Figure 1). The main component of this loop is exchanger E-100 where the sulfuric acid (A), which is available at 114 °C, is cooled to 104 °C. Water (1A) available at 3 bar is heated from 98 to 105 °C in this exchanger.

The heated water (1) passes through an expansion valve where it is flashed to 1 bar (2). Then it is separated in V-100 into vapor (2A) and liquid (2B) streams both at 1 bar. The liquid is pumped back to the water loop where it is mixed with make-up water (3A) at 30 °C. Vapor (2A) goes through an ejector OP-100 where its pressure is raised to 4.8 bar using steam (2C) at 14 bar. This ejector is necessary to raise the condensation temperature of the produced steam (5) to the level required by the absorption machine.

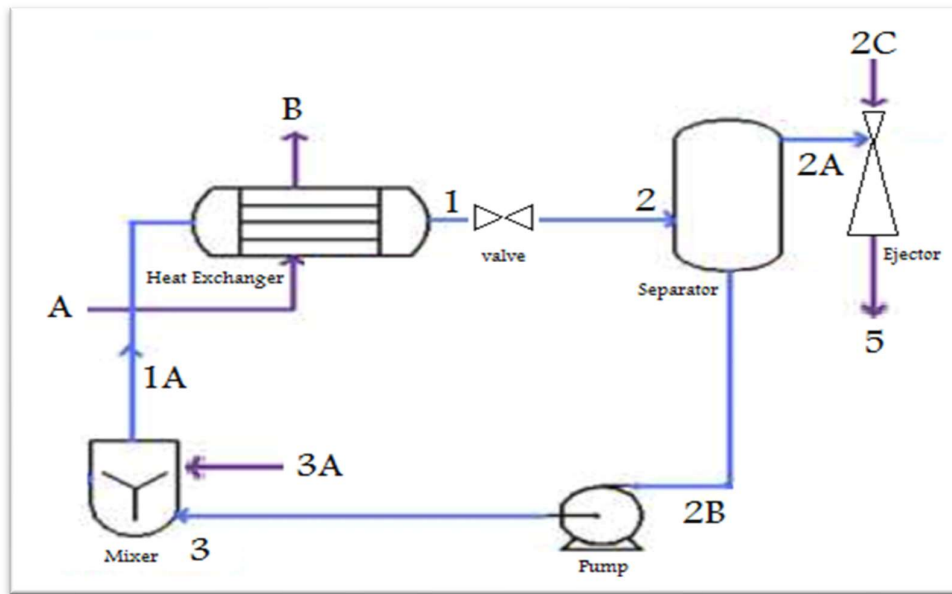


Figure 1. Hot water loop.

2.2.Absorption refrigeration machine

The absorption refrigeration cycle is represented in Figure 2. Ammonia vapor (1) at high pressure is separated from the rich solution (7) in the generator. Then, it goes to the condenser where saturated liquid ammonia (2) is obtained. This liquid is expanded in a throttling valve and the obtained vapor-liquid mixture (3) is sent to the evaporator where cooling takes place. The ammonia leaves this equipment in the vapor state (4) before it goes to the absorber. The lean solution (8) coming from the generator is first cooled, in the solution heat exchanger, then throttled in a second valve. The resulting stream (10) is sent to the absorber where it absorbs the ammonia coming from the evaporator to produce the rich solution (5). This solution is then pumped back through the solution heat exchanger towards the generator to close the cycle [2].

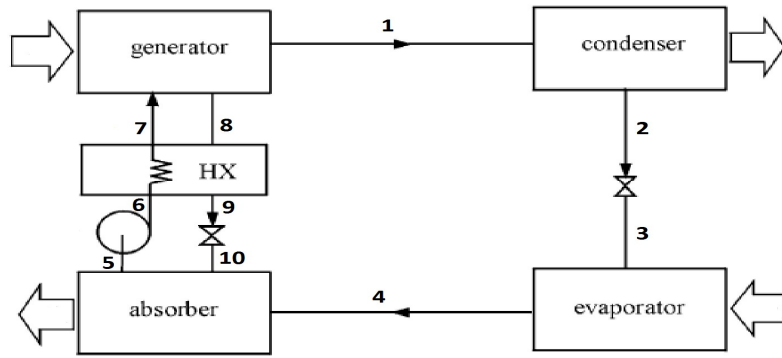


Figure 2. Absorption refrigeration machine [19].

3.MASS AND HEAT BALANCE EQUATIONS

The mass and heat balances will be written only for the absorption refrigeration machine. They won't be needed for the heat recovery loop because its simulation will be done using Hysys where these equations are already programmed in the software.

3.1.Mass balance

The mass balance equations for the absorber are as below [20] :

$$m_w + m_e = m_a \quad (1)$$

$$m_a \cdot x_r = m_e \cdot x_e + m_w \cdot x_w \quad (2)$$

m_w and m_e as a function of m_a and the compositions of the rich and lean solutions, can be determined as follows:

$$m_e = m_a \cdot \frac{x_r - x_w}{x_e - x_w} \quad (3)$$

$$m_w = m_a \cdot \frac{x_e - x_r}{x_e - x_w} \quad (4)$$

3.2. Heat balances

The heat balance equations can be used to estimate the duties of the various components of the cycle (generator, absorber, pump, etc) from which the coefficient of performance can be calculated.

The heat balance on the whole cycle can be written as:

$$Q_a + Q_c = Q_e + Q_g + W_p \quad (5)$$

If we consider each component individually, we can write:

Condenser:

$$Q_c = m_c (h_2 - h_1) \quad (6)$$

Evaporator:

$$Q_e = m_c (h_4 - h_3) \quad (7)$$

Generator :

$$Q_g = m_c h_1 + m_w h_8 - m_a h_7 \quad (8)$$

Absorber :

$$Q_a = m_a h_5 - (m_w h_{10} + m_c h_4) \quad (9)$$

Solution pump :

$$W_p = m_a (h_6 - h_5) \quad (10)$$

The results of the mass and heat balance can be used to calculate the coefficient of performance (COP) of the machine using the following equation [21]:

$$COP = \frac{Q_e}{Q_g + W_p} \quad (11)$$

Note that the mass and heat balance equations will be used with the Merkel diagram and programmed in EES.

4.CALCULATIONS OF THE ABSORPTION CYCLE

These calculations will be done for the absorption machine first because the required temperature and flowrate of the steam produced by the water loop depend on them.

The main assumptions are the following:

- The absorption refrigeration machine is operating at steady state.
- There is no pressure drop in the pipes.
- The refrigerant is saturated vapor after the evaporator and saturated liquid after the condenser.

Note that it is necessary for the ammonia leaving the generator to be almost pure so that practically no water will be sent back to the storage tank.

4.1. Calculations using the diagrams

To study the performance of the absorption refrigeration cycle besides simulation software, two diagrams are paramount. Oldham is used to determine the concentration of the state points. While Merkel determines the enthalpy at different points of the machine [22].

Oldham diagram

The data required for these calculations are shown in Table 1. The Oldham diagram was used first to determine the minimum generator temperature that is needed to run the absorption machine. It was found that this temperature is equal to 134 °C. Accordingly, a temperature of 145 °C was chosen for the generator which is sufficiently higher than the minimum value so that the coefficient of performance would be acceptable.

Figure 3 represents the cycle of the absorption machine with Oldham diagram using a generator temperature of 145 °C.

Table 1.Oldham diagram Input Parameters.

Designation	Value
Evaporator temperature [°C]	-33
Condenser temperature [°C]	37
Absorber temperature [°C]	37

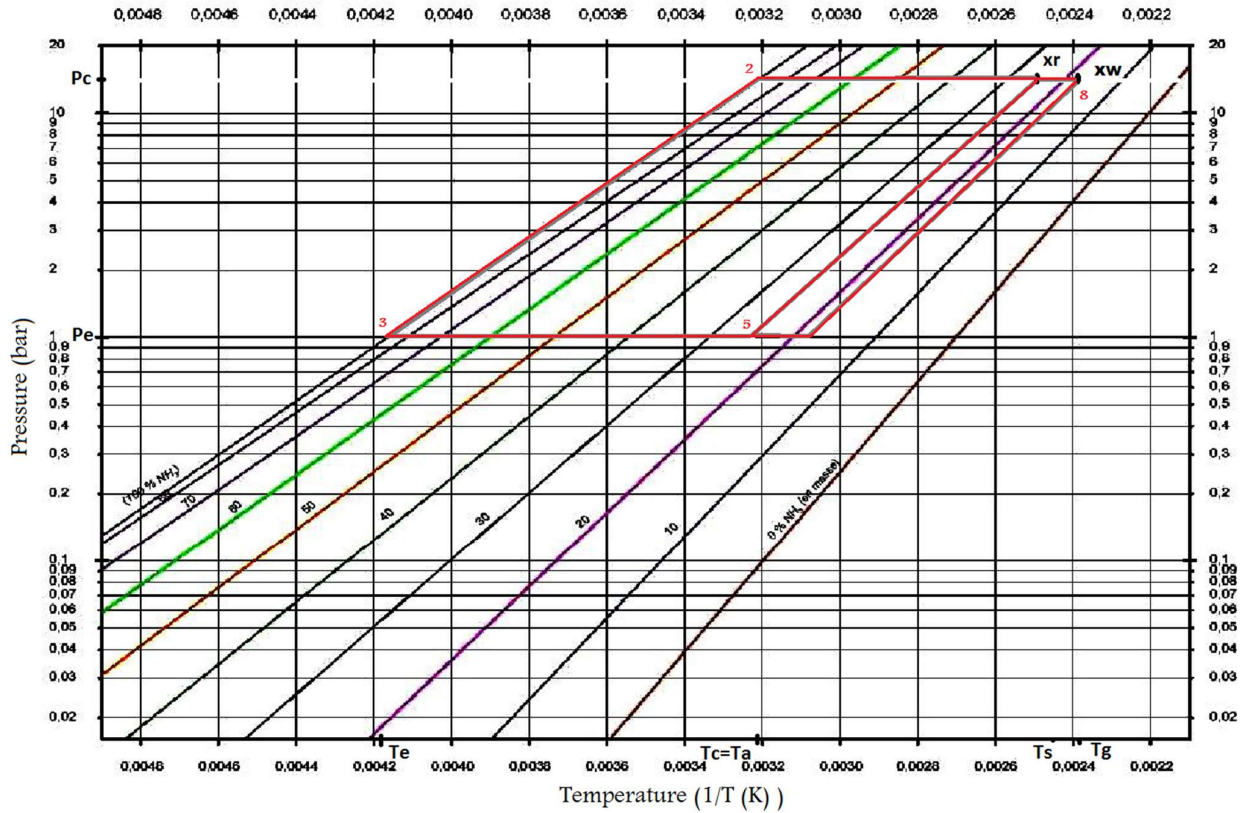


Figure 3. Oldham Diagram for the studied cycle.

The main results of this diagram are shown in Table 2.

Table 2. Results of the Oldham diagram

Designation	Value
Low pressure [bar]	1
High pressure [bar]	15
Ammonia mass fraction of the rich solution	0.26
Ammonia mass fraction of the lean solution	0.19

Merkel diagram

To determine the calculations for Merkel diagram, Oldham results are used. This diagram is shown in Figure 4 for the studied cycle. Merkel diagram shows the enthalpy at various points of the cycle. For that, it is possible to determine the heat duties according to the heat and mass balance equations.

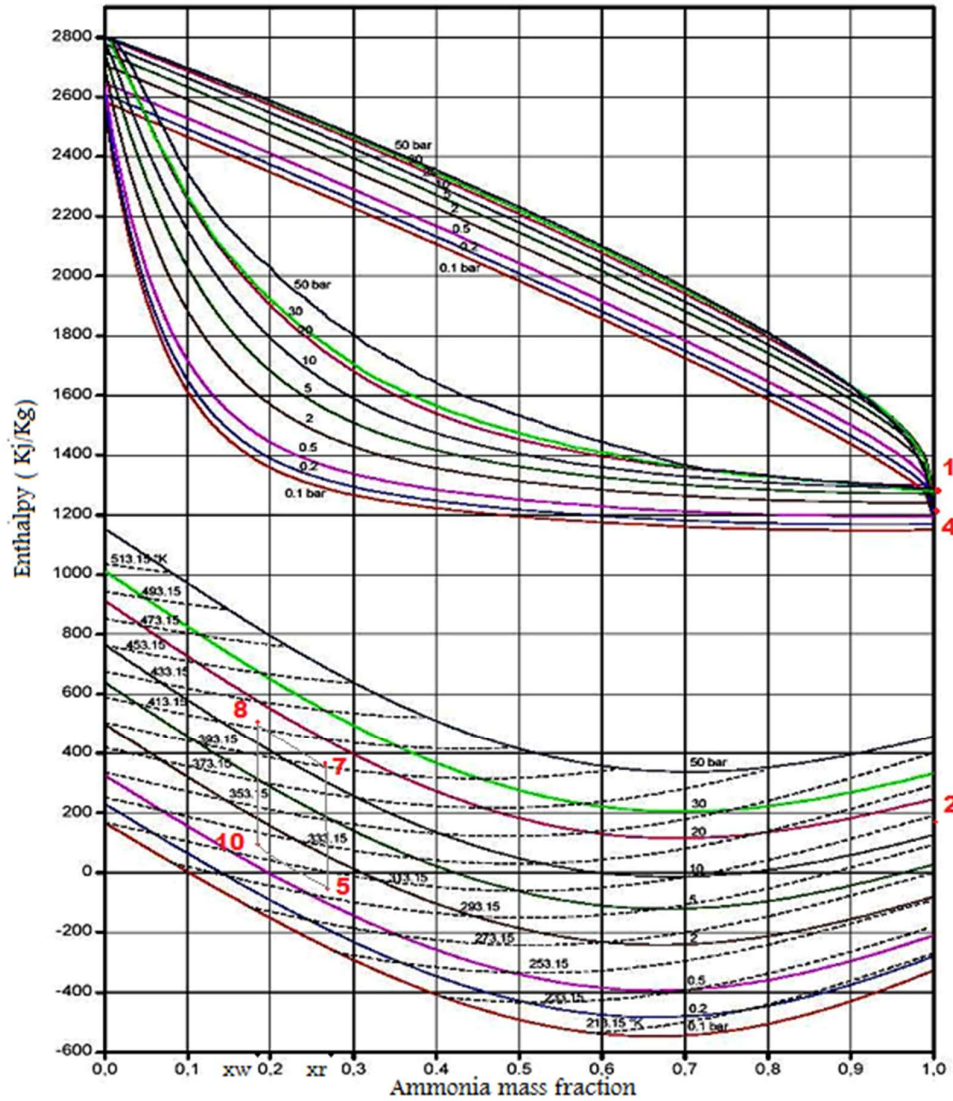


Figure 4. Merkel diagram for the studied cycle.

Table 3. Main results of the Merkel diagram

Designation	Value
Generator duty (kW)	479
Condenser duty (kW)	233
Absorber duty (kW)	598
Evaporator duty (kW)	220
Mechanical work of the pump (kW)	6

Depending on the results indicated in the table above, the coefficient of performance for this machine is about 0.46.

4.2. Calculations using EES

The Engineering Equation Solver (EES) is extensively used for absorption refrigeration cycles due mainly to its comprehensive internal/external libraries for Ammonia/Water properties[23].

Using the Oldham and Merkel diagrams, it was possible to fully study the performances of the cycle. The results of EES will be used in this case just for the sake of comparison. However, calculations using diagrams are often tedious and become impractical when a sensitivity analysis is conducted for example.

The required simulation data for EES are the same as those shown in Table 1. The results given by this software are presented in Table 4.

Table 4. Main results of EES.

Designation	Value
Generator duty (kW)	451.2
Condenser duty (kW)	231.8
Absorber duty (kW)	436.9
Evaporator duty (kW)	217.5

Table 4 indicates that the results given by EES are close to those obtained using the diagrams.

According to these results, the coefficient of performance calculated by EES is equal to 0.48 which is nearly equal to the previous value.

5. CALCULATIONS OF THE HEAT RECOVERY LOOP

The simulation of this loop was conducted using Hysys. The flow-sheet of the loop in Hysys is shown in Figure 5 and the simulation input data is given in Table 5. The most recommended thermodynamic model for the simulation and calculation of the acids properties in solution, electrolytes, is "Electrolyte NRTL".

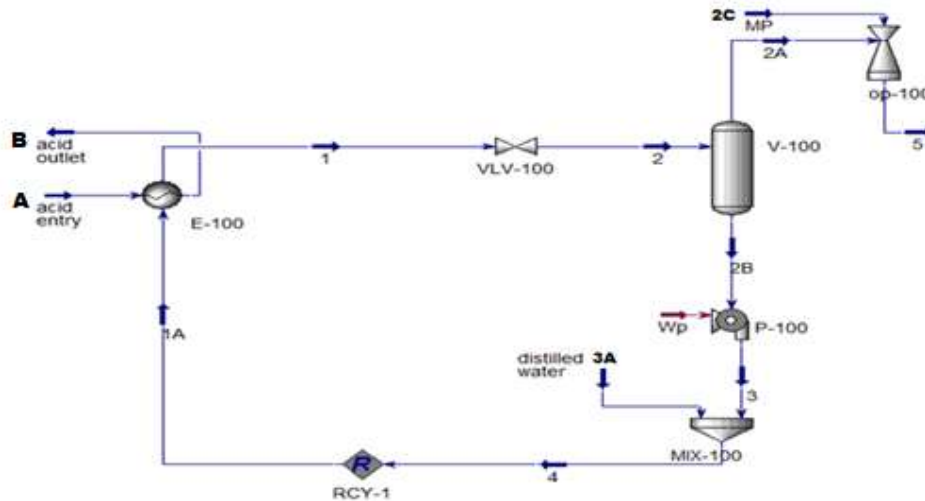


Figure 5. Flow-sheet of the loop in Hysys

Table 5. Simulation data for the heat recovery loop.

Designation	Value
Sulfuric-Acid mass fraction	98%
Sulfuric acid inlet temperature [°C]	114
Sulfuric acid inlet pressure [bar]	3
Discharge pressure [bar]	3
Water inlet temperature [°C]	30
water inlet pressure [bar]	3
Pressure of motive steam [bar]	14
Temperature of the produced steam [°C]	150
Pressure of the produced steam [bar]	4.9
Mass flow rate of the produced steam [kg/h]	770
Temperature of motive steam[°C]	195

Note that the temperature of the produced steam is deduced from the absorption machine calculations. It is equal to the generator temperature plus 5 °C. Its pressure is equal to the saturation pressure of steam at 150 °C while its flow rate is equal to the duty of the generator divided by the heat of condensation of steam at the same pressure.

The main results of this simulation are shown in table 6.

Table 6. Main results of Hysys for the heat recovery loop.

Designation	Value
Mass flow rate of sulfuric acid [kg/h]	10900
Mass flow rate of steam produced at 1 bar [kg/h]	70
Duty of the exchanger E-100 [kW]	50
Circulation rate of water [kg/h]	3000
Mass flow rate of make-up water [kg/h]	70
Mass flow rate of motive steam [kg/h]	700

Table 6 indicates that the hot water loop produces 70 kg/h of steam at 1 bar using 50 kW of the heat waste. This steam is compressed to 4.8 bar using 700 kg/h of MP steam so that the necessary heat duty can be delivered to the refrigeration absorption machine at the required temperature of 150 °C.

6. CONCLUSIONS

It was shown in this work that the refrigerated storage of ammonia using waste heat is technically feasible. In fact, according to the simulations, a temperature of $-33\text{ }^{\circ}\text{C}$ can be reached in the evaporator using the steam produced by the heat recovery loop.

The operating parameters of the heat recovery loop and the absorption refrigeration machine were estimated using Hysys, EES, and the appropriate thermodynamic diagrams. For the absorption machine, a coefficient of performance close to 0.5 was obtained which is very satisfactory for a single effect water-ammonia refrigeration cycle.

However, it would be better to find a solution that eliminates the need for vapor compression using an ejector. This will be the subject of another paper where steam produced at 1 bar is used to drive a double-stage absorption refrigeration machine that can operate on low-grade thermal energy.

Nomenclature

COP Coefficient of performance	p Pump
a Absorber	Q Heat
c Condenser	T Temperature
e Evaporator	T_i Inlet temperature
g Generator	W Work
h Specific enthalpy	x Mass fraction
MP Medium pressure	x_r Mass fraction of the rich solution
m Mass flow rate	x_w Mass fraction of the lean solution
P Pressure	

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