Study of Using Waste Heat of a Sulfuric Acid Plant to Concentrate the Phosphoric Acid

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ABSTRACT

This paper is a contribution to the waste heat recovery in a diammonium phosphate production plant. Such plant is made of sulfuric acid, phosphoric acid and diammonium phosphate production units. The production of sulfuric acid by the contact process rejects about 150 t/h of gas at a temperature of 70°C and about 30 MW of heat in sea water. This work is a contribution to the valorization of this energy wasted. It deals with the opportunity of its recovery by providing some of the hot utility requirements of a phosphoric acid production unit which belong to the same factory.

Keywords: Waste energy, heat recovery, phosphoric acid, sulfuric acid, spray column.

1. INTRODUCTION

There exist today worldwide concerns about the excessive use of fossil fuels and the pollution problems that come with it [1, 2]. The process industries are responsible for 27% of global energy consumption, and annual demand for heat and electricity is expected to grow by 1.9% and 2.4%, respectively [3, 4]. In spite of the increasing demand, depleting reserves of fossil fuels and increasing energy prices, energy in the form of low-grade heat is still being wasted. Using energy more efficiently could reduce demand for fuel; thereby conserving resources, reducing operating costs and reducing CO_2 emissions [4]. Some recent control methods are discussed in [12-16].

Heat recovery systems can significantly increase the efficiency of industrial plants thereby contributing to the reduction of energy consumption.

This study investigates the feasibility of utilizing waste heat from a sulfuric acid production unit for the purpose of covering a part of utility required in the phosphoric acid production plant.

2. PROCESS DESCRIPTION

The case study process consists of a diammonium phosphate (DAP) production plant. This plant includes:

- two sulfuric acid production units
- a phosphoric acid production unit
- two DAP production units.

The present work is especially interested in the heat wasted in the sulfuric acid production unit. This unit uses the double absorption contact process [5].

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The process (Figure 1) could be divided into four main sections: combustion, conversion, absorption and cooling.

At the first section, the atmospheric air is dried in a drying tower, and then it is sent to the oven. In this device the liquid sulfur is burned with the dried air to produce hot SO_2 gases, which then are cooled in a waste-heat boiler producing a steam at 60.105 Pa. This steam is, then, superheated with the hot gases leaving the first converter bed to produce the high pressure steam.

At the second stage, the cooled SO2 enters into a 4-bed catalytic converter to produce SO3.

The reaction is highly exothermic and generally it is carried out under adiabatic conditions, so the temperature of the solid catalyst bed increases. The SO2-SO3 equilibrium becomes increasingly unfavorable for SO3 formation as temperature increases, consequently, to achieve a high final SO2 conversion, the total catalyst mass is divided up into four catalyst beds.

The hot gas leaving each bed is cooled, respectively in the super heater, the GGH heat exchanger, the GGC heat exchanger and the economizers, to the minimum working temperature of the catalyst before it enters the next bed. At the third section, sulfur trioxide gasses are absorbed in both intermediate and final absorption towers. In the intermediate absorption tower (I. Abs tower) gases pass from third bed of conversion, after being cooled, from the bottom to the top through the absorber, which is uniformly irrigated from the top with liquid-phase sulfuric acid. The H_2SO_4 liquid stream absorbs the SO_3 gasses and it reacts with existing water to form more sulfuric acid with a desired concentration.

Similarly, in the final absorption tower (F. Abs tower), the gases leaving the forth bed conversion passes from the bottom to the top to be absorbed by sulfuric acid. The final section is acid cooling where concentrated acid and the final product are cooled using sea water in acid cooler heat exchangers.

3. WASTE HEAT SOURCES

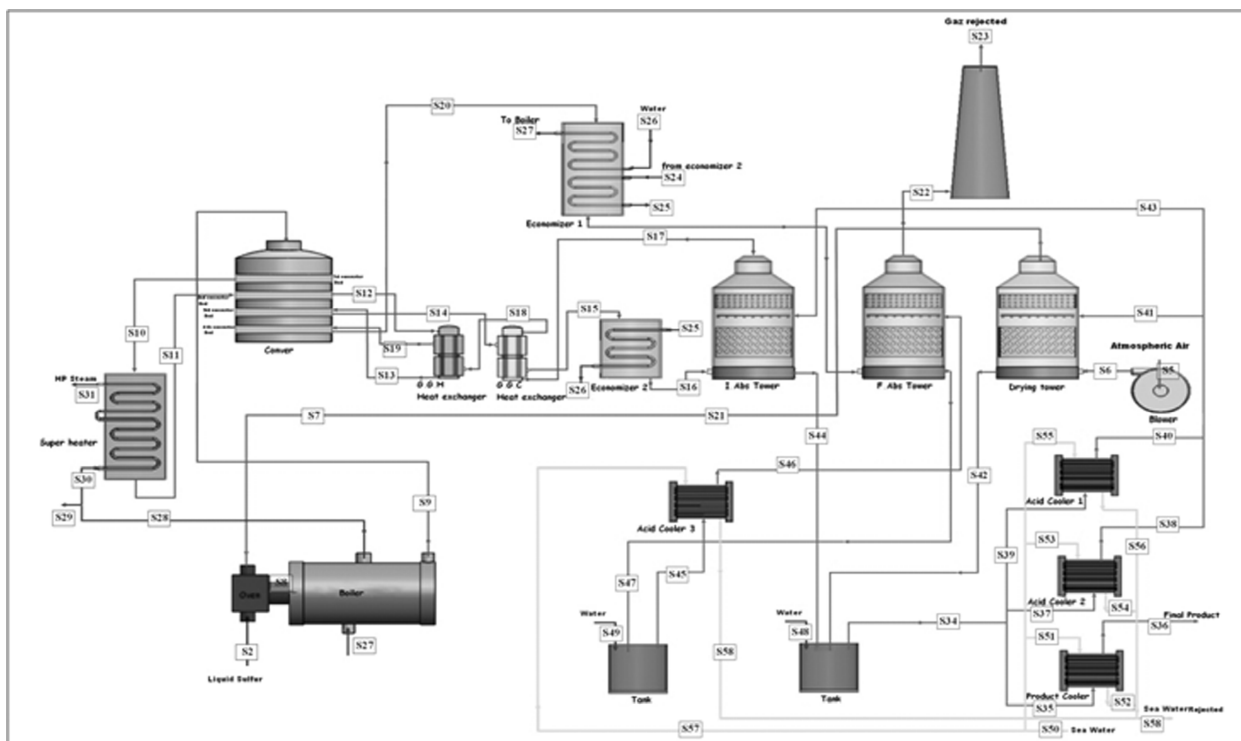The sources of waste heat in the sulfuric acid production unit are specially:

Figure1: Sulfuric acid production unit.

- the waste heat from the cooled acid, which is rejected in sea water
- the gas rejected from the final absorption tower to the environment. This dry gas is at 70°C.

These sources of energy can be used, even partly, to supply the requirements in hot utilities for the other units of the same factory.

In this work we will study the opportunity of using these sources of wasted heat to cover some of the hot utilities of the phosphoric acid production unit.

4.   USING WASTE HEAT TO CONCENTRATE PHOSPHORIC ACID

4.1. Water flow to the saturation

The considered rejected gas is described in Table 1 as follows.

Table 1
Discharged gaseous characteristics.

Designations	Value
Temperature (°C)	70
Pressure (bar)	1,07
Molar Flow (kmol /h)	5498,3
Mass flow (kg/h)	155366,13
Molar fraction	
SO_2	382 PPM
O_2	5,8
N_2	94,2

Until the weak phosphoric acid is in contact with the gas rejected from the sulfuric acid unit, same of the water contained in the acid evaporates. It would be interesting to know the maximum flow of water that can be evaporated by the gas.

This flow is equal to the partial flow of water in the gas to saturation. It is given by [6]:

$$\overset{\bullet}{m}_{water} = Y_s \times \overset{\bullet}{m}_{gaz} \tag{1}$$

where Ys is the absolute humidity of the gas at saturation (kg water / kg dry air) which can be calculated by:

$$Ys = \frac{M_A \times P_{H_2O}^0}{M_B \times (P - P_{H_2O}^0)} \tag{2}$$

Where

- $P^0{}_{H2O}$: saturation steam pressure at the gas outlet temperature (mmHg)
- P: total pressure (mmHg)
- M_A: molar mass of the vapor (g / mol),
- M_B: molecular weight of gas (g / mol).

The saturation steam pressure is given by the Antoine equation as [6, 7]:

$$\log P_{H_2O}^0 = A - \frac{B}{T + C} \tag{3}$$

where A, B and C are Antoine Parameter which are functions of temperature and T is the water temperature.
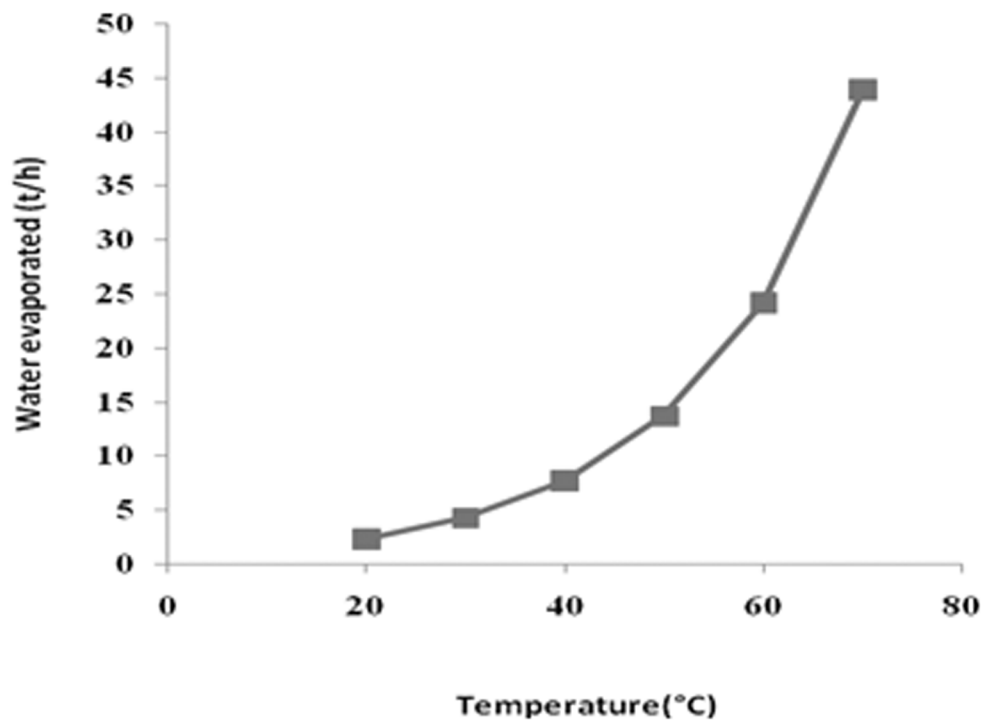
Figure 2: Water flow evaporated at saturation by the gas as a function of temperature.

The water flows evaporated at saturation by the gas rejected from the sulfuric acid production unit are calculated, using equation (a), (b) and (c), for different temperature between 20 and 70 °C. The results are summarized in Figure 2.

It is noted from these results that the moisture saturation as well as the water flow increases according to the temperature. Thus, it is advantageous that the gas will be to the highest possible temperature after contact with phosphoric acid. This can be achieved by heating the phosphoric acid before it's contact with the gas.

In this work we will study two cases:

- A first case that consist in evaporating a part of the water contained in the phosphoric acid by contact with gaseous rejected from sulfuric unit

- A second approach that involves heating the phosphoric acid by the sulfuric acid and its concentration by the exhaust air.

4.2. First case study

In this part we will study the possibility of using only the gas rejected from sulfuric unit to evaporate a part of the water contained in the phosphoric acid. The contact can be done in a spray absorption column (see figure3).

In such configuration, the gas actually rejected from the chimney (S23, in figure1), is aspired by a fan. Then, the weak phosphoric acid is pumped from the filters. These two streams circulate in counter flow with the hot gases rejected from sulfuric unit.

As soon as they are in contact, a quantity of water will be evaporated and the phosphoric acid will be more concentrated.

Since the discharged gas is dry, it is thus very useful for the evaporation of water contained in the phosphoric acid and therefore its concentration.
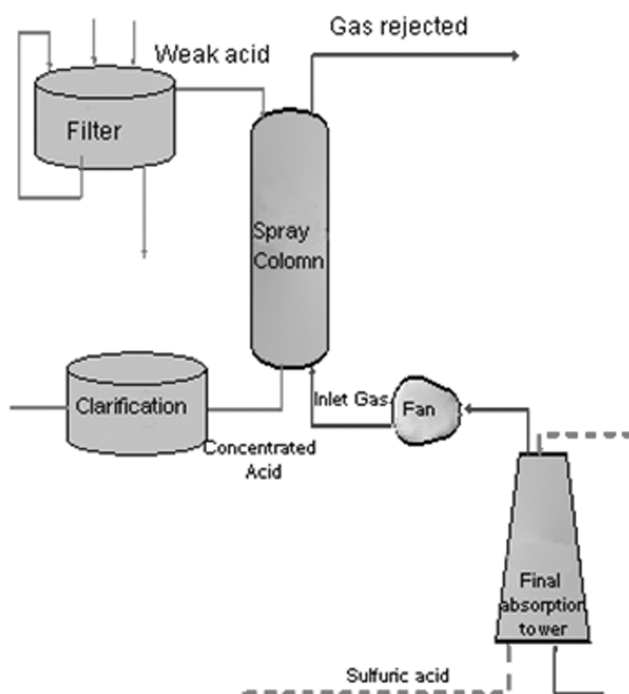
Figure 3: Concentration of phosphoric acid.

Table 2
Flows characteristics.

	Weak acid	Dry gas	concentrated acid	wet gas
Temperature (°C)	25	70	28.4	35.2
Pressure (bar)	1.2	1.2	1.2	1
Mass flow (t/h)	70	155	65	160
Mass fraction				
H_2O	66.2	0	63.3	3.4
H_3PO_4	33.8	0	3.7	1
N_2	0	93.3	0	90.2
SO_2	0	866 PPM	0	827 PPM
O_2	0	6.6	0	6.3

The results of the simulation of the column, using the 'ASPEN Plus' software, are given in Table 2.

The simulation of the spray column shows that after contact with the gas, the concentration of the phosphoric acid move from 24% to 27% by weight P_2O_5. This allows us to achieve the concentrations that were obtained when the plants treated better quality of phosphates.

4.3. Second case study

As it is shown in Figure 2, the water flow evaporated at the saturation is more important when the phosphoric acid is heated.

Heating will be provided in a heat exchanger with sulfuric acid, which is actually cooled by sea water. In this way we will use waste heat associated with gas and sulfuric acid simultaneously. The proposed configuration is illustrated in Figure 4.
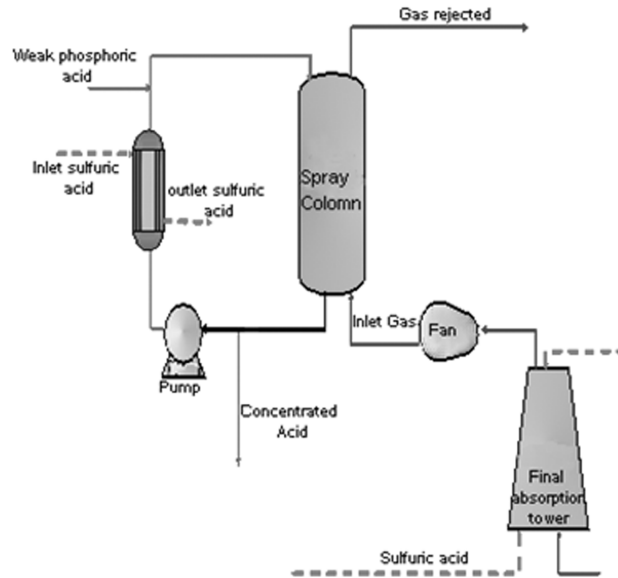
Figure 4: New concentration loop.

The main differences between this loop and the existing one are the substitution of the evaporator by a column, the removal of the barometric condenser and substitution of the heating steam by sulfuric acid.

5.   DETERMINATION OF THE P_2O_5 WEIGHT FRACTION

Following the evaporation of a quantity of water contained in the phosphoric acid circulating in the loop, this acid will be more concentrated. The weight fraction of P_2O_5 in the acid is calculated using the following equation [8, 9]:

$$\frac{1}{C_1} - \frac{1}{C_2} = \frac{\overset{\bullet}{m}_{eau}}{\overset{\bullet}{m}_{P_2O_5}} \tag{4}$$

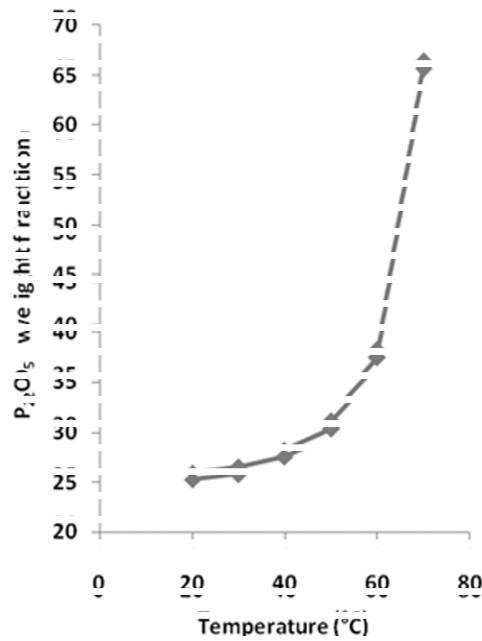where C_1 and C_2 are the P_2O_5 concentration respectively in the weak and concentrated acid.

Figure 5: P2O5 weight as a function of temperature.

The mass flow rate of the weak phosphoric acid is about 70t/h. The treatment of this charge in the proposed loop led to weight fractions on P_2O_5 shown in Figure 5.

These results show that it is possible to achieve high concentrations of P_2O_5 if the gas leaves the column at elevated temperatures.

6. DETERMINATION OF THE P2O5 WEIGHT FOR THE PROPOSED LOOP

The studied phenomenon is similar to that of a humidification tower. Then, in what follows, we will adopt a similar methodology. We can determinate the P2O5 weight fraction according to various steps shown in the flowchart in Figure 6 [10].
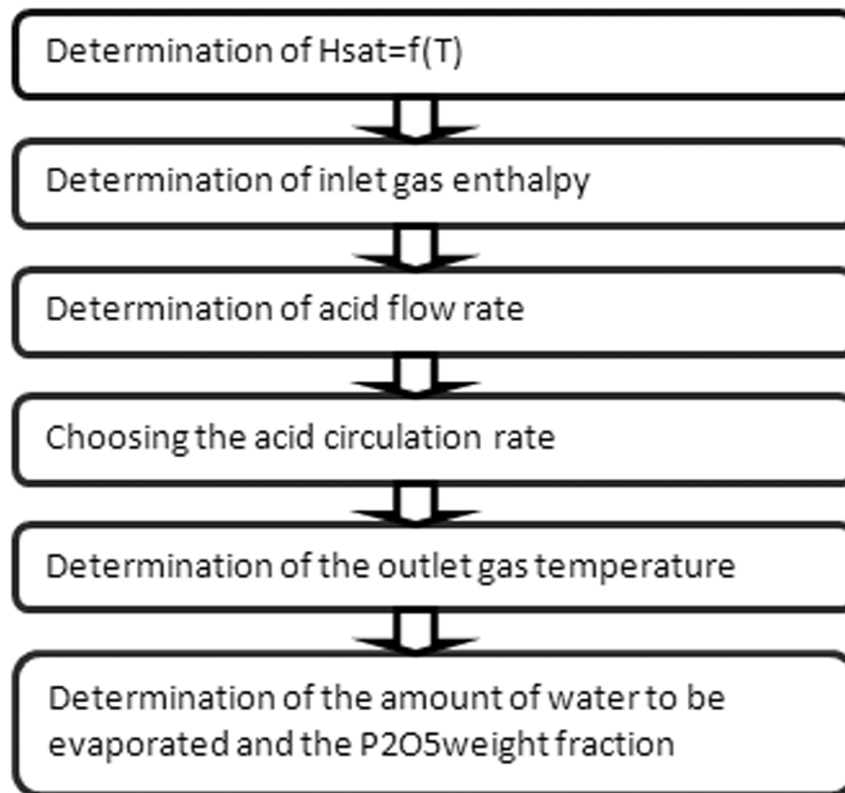


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┌─────────────────────────────────────────────┐
│ Determination of Hsat=f(T)                  │
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│ Determination of inlet gas enthalpy         │
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│ Determination of acid flow rate             │
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│ Choosing the acid circulation rate          │
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│ Determination of the outlet gas temperature │
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│ Determination of the amount of water to be  │
│ evaporated and the P2O5weight fraction      │
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Figure 6: Steps of determining the P2O5 weight fraction.

6.1. Drawing the gas saturation curve

The gas saturation curve indicates the change in the saturation enthalpy versus temperature. This relationship is expressed by the following equation [8, 9]:

$$H_{ysat} = Cp_{gas}(T - T_{ref}) + y \times Lv \tag{5}$$

- Hysat : Gas enthalpy at saturation (kJ/kg),
- Cpgaz : gas heat capacity (kJ/kg K),
- T : temperature en (°C),
- Tref : reference temperature (taken equal to the water melting temperature) (°C)
- Lv : latent heat of vaporization at T_{ref} (kJ/kg),
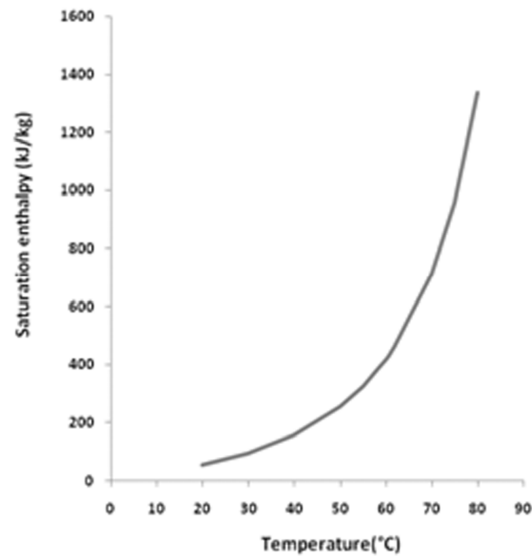- Y: saturation humidity.

Figure 7: Saturation enthalpy as a function of temperature

The results are given in Figure 7.

6.2. Determination of the inlet gas enthalpy

The inlet gas enthalpy is given by the flowing equation

$$H_1 = Cp_{gas}(T_{gas} - T_{ref}) + y \times Lv \tag{6}$$

In this equation (Y = 0) since the gas is wet.

6.3. Delineation of the operating curve

The operating curve (see figure8) is delimited by the two following point:

- the first point ($T_{outlet,acid}$, H_1)
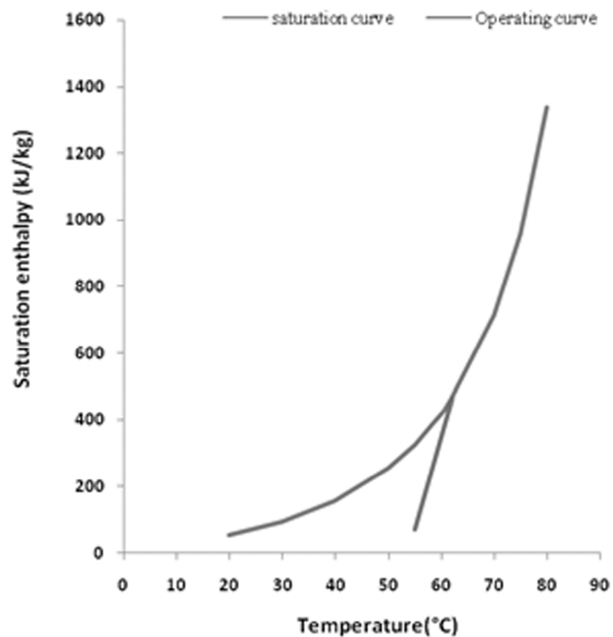- the second point ($T_{inlet,acid}$, H_{2sat})

Figure 8: Operating curve.

6.4. Determination of acid flow rate

The acid flow rate is given by the following equation [11]:

$$\dot{m}_{acid} = \frac{H_{2sat} - H_1}{Cp_{acid}(T_{acid,in} - T_{acid,out})} \times \dot{m}_{gas} \tag{7}$$

The acid flow rate calculated is about 2666 t/h.

Note that the acid flow rate must be less than the saturation flow rate so that the height of the tower is unlimited. So in what follows we will work with a circulation rate of phosphoric acid equal to 2400 t / h.

6.5. Determination of the outlet gas temperature

To calculate the gas outlet temperature we start by drawing the new operating curve with the new acid flow rate [11]. From this curve we can determine the new value of H_2 (see figure 9).

According to Figure9, Air enthalpy is about 425 kJ/kg, then it's temperature will be about 60.3 °C ant it's humidity reach 15.8 kg/kg dry air.

Consequently the gas rejected from the sulfuric acid unit can evaporate 24.64 t/h of water contained in the phosphoric acid. Then, according to equation (4) we can attain a P_2O_5 weight fraction about 37%.
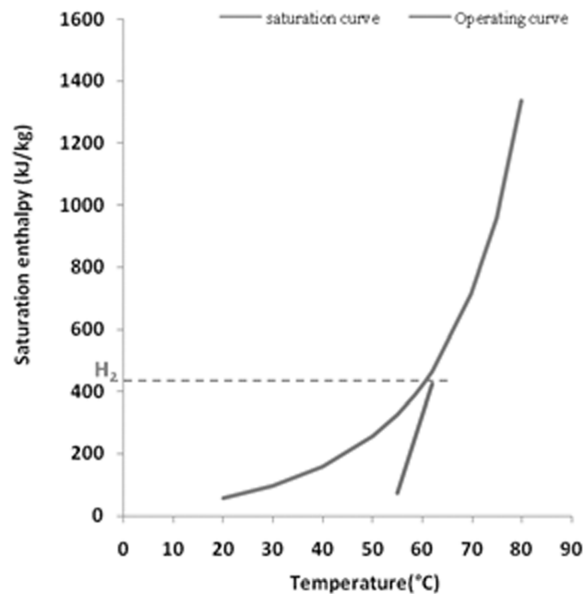

Figure 9: New operating curve.

7. CONCLUSIONS

In this work we studied the opportunity of using the waste heat from a sulfuric acid production unit to provide some of the hot utility of a phosphoric acid unit.

We start by using the gas rejected to concentrate the phosphoric acid in a spray column. The results show that we can pass from 24 to 27% (weight P_2O_5).

As a second alternative we studied using the heat, rejected when cooling the sulfuric acid by sea water, to heat the phosphoric acid in a heat exchanger. Then we use the gas rejected to evaporate a part of the water. By this way we can reach 37% weight P_2O_5.

A technical economic study must be achieved to assure the effectiveness of these projects.

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