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DEVELOPMENT OF A FIXED BED ADSORPTION SYSTEM THAT OPERATES IN PSA / TSA MODE FOR PRODUCTION OF PURIFIED HYDROGEN FROM THE SYNTHESIS GAS

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Abstract. *The hydrogen has been showed as a promisor fuel in the world energetic scenario. Industrially, can be obtained from thermochemical conversions, follow by a purification step of product's current by adsorption cycles. Were developed a separation system from an assembly of simple and cheap equipments that allows the study of steps in TSA/PSA adsorption cycle for produce hydrogen purified. The column was filled with activated carbon VW 1050 and fed with syngas. Simulations of adsorption steps were developed using the software gPROMS®. The system was capable of heat the column until regeneration temperature of the bed and maintain it. The bed cooling after the heating column and its refrigeration until low temperature were too possible. The bed showed fast saturation in adsorption step.*

Keywords: *Hydrogen production, TSA/PSA Cycle Adsorption, Syngas, Activated Carbon*

1. INTRODUCTION

Hydrogen production has been the subject of studies and technical improvements since the last century. Besides being an important reagent in the chemical, petrochemical and food industries, this is an advantageous fuel from a technical and environmental point of view. It has high specific enthalpy and clean burning, without emission of particulates, toxic substances and carbon dioxide (Atkins & Jones, 2005). There are many several ways to obtain hydrogen, and different routes: chemical, electrolytic, thermochemical, photovoltaic and biological (da Rosa, 2009).

In thermochemical conversions, it can be produced from the Steam Reform, Partial Oxidation and Auto Thermal Reforming of hydrocarbons, resulting in a mixture of H_2 and CO, known as synthesis gas (Basu, 2013). In order to maximize its production, the current of products can be submitted to the shift reaction, obtaining a new gas stream, composed mainly by H_2 and CO2.Bastos-Neto (2011), after a bibliographic search from Yang (1997), Sircar & Golden (2000) e Ribeiro *et al* (2008), presented the following range of compositions for the final product of the steam reform of natural gas, followed by the shift reaction: 70-80% hydrogen, <1% water vapor, <1% nitrogen, 3-6% methane, 1-3% carbon monoxide, 15-25% carbon dioxide and traces of hydrogen sulphide. This stream is then subjected to a PSA process to obtain hydrogen with purity of 98-99.999% at the exit of the adsorption column. The gases captured in the bed are discarded into the atmosphere, because they do not present commercial value and calorific value for reuse, due to the high concentration of carbon dioxide. Although a greater volume of H2 production can be achieved, the disposal of CO2 into the atmosphere is a negative point because this is one of the agents that cause the greenhouse effect.

The process studied in this work was aimed at the production of purified hydrogen, in an adsorption system, from a synthetic synthesis gas mixture. This mixture can be obtained from the steam reform of natural gas, without the shift reaction. Such a process route would be interesting, since it could provide besides the hydrogen current, one of carbon monoxide also with high purity, since this is the compound adsorbed in the bed. To achieve this objective, a Fixed Bed Adsorption Separation System was constructed, filled with activated carbon WV 1050.

At industrial level the adsorption processes are operated cyclically, having as main characteristic, for each type of cycle, the way the adsorbent is regenerated (Ruthven, 1984). In order to regenerate the adsorbent by temperature and pressure variation, TSA and PSA cycles, respectively, were coupled to the adsorption column with relatively simple and commonly used equipment. The purpose of this construction was to make possible the study of process operating conditions in the wide range of values for these variables.

2. EXPERIMENTAL

This section was divided in four subsections: Material and Methodology, Results and Discussion and Conclusion.

2.1 Material and Methodology

Activated Carbon WV1050 was supplied by the North American mining company MeadWestvaco and the synthetic gas (50% H_2 - 50% CO) by the brazilian company White Martins.

The developed system consists of three distinct subsystems: cooling, heating, adsorption and sampling.

- Cooling subsistem
  A metal tank filled with water and cooled by means of a cooling serpentine (Figure 1). Inside there is a pump for recirculating water, causing the water to leave the tank and travel the copper serpentine that surrounds the adsorption column and finally returns to the tank.

Figure 1. Cooling subsystem

- Heating sub-system
  Consists of a varivolt connected to a resistive wire that surrounds the adsorption column (Figure 2). With the varivolt the ddp can be manually adjusted up to 100V, generating an electric current that will run through the wire. This, due to its resistive nature, heats considerably, yielding heat by indirect exchange to the adsorption system.

Figure 2. Heating subsystem

- Adsorption subsystem

  Consists of the aluminum column (52.6x300mm) which was filled with activated carbon and percolated by the gas (Figure 3). The column contains on its exterior grooves and semicircular canals so that the heating and cooling system can be coupled, respectively. Also, a pair of thermocouples, located at the base and at the top of the column, to accompany the temperature at these points.

Figure 3. Column of adsorption

- Sampling Subsystem

  Consists basically of five gas capture cells, interconnected by means of thermoplastic hoses (Figure 4). Each cell consists of a copper tube with inner diameter of ¼ in, with a length of approximately 25 cm, having a valve at each end, thereby allowing both the passage and the entrapment of gas therein.

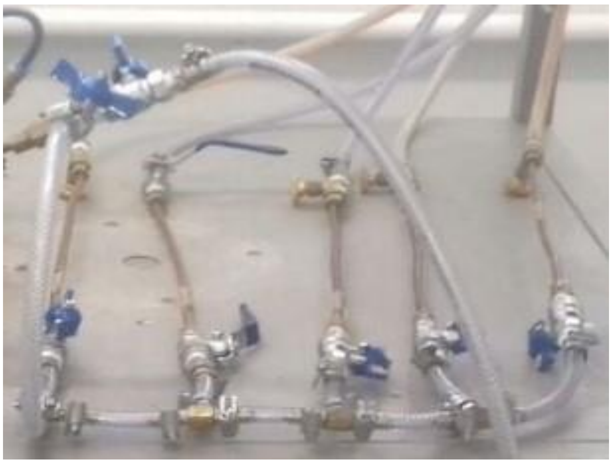

Figure 4. Sampling subsystem

Figures 5 and 6 present real photos of the developed system and a schematic drawing, for better observation and understanding of its operation.

The composition of the gas stream leaving a column, was analyse on a gas chromatograph (*490 Micro GC Biogas Analyzer – Agilent Technologies*).

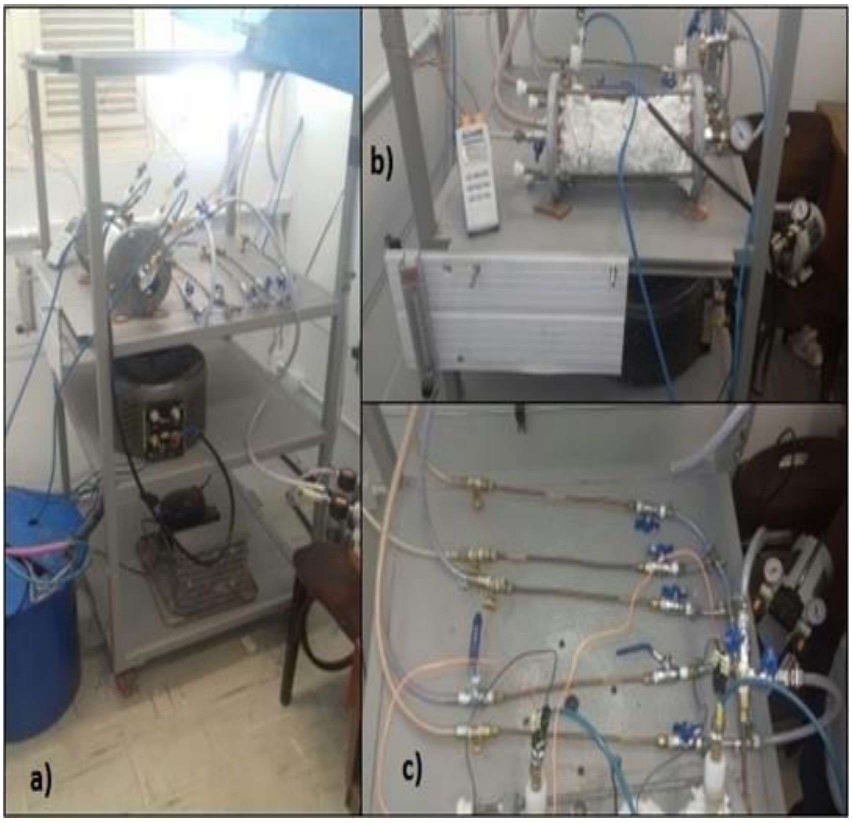

Figure 5. Pictures of the developed system: a) Front View. b) Side view e c) Top View

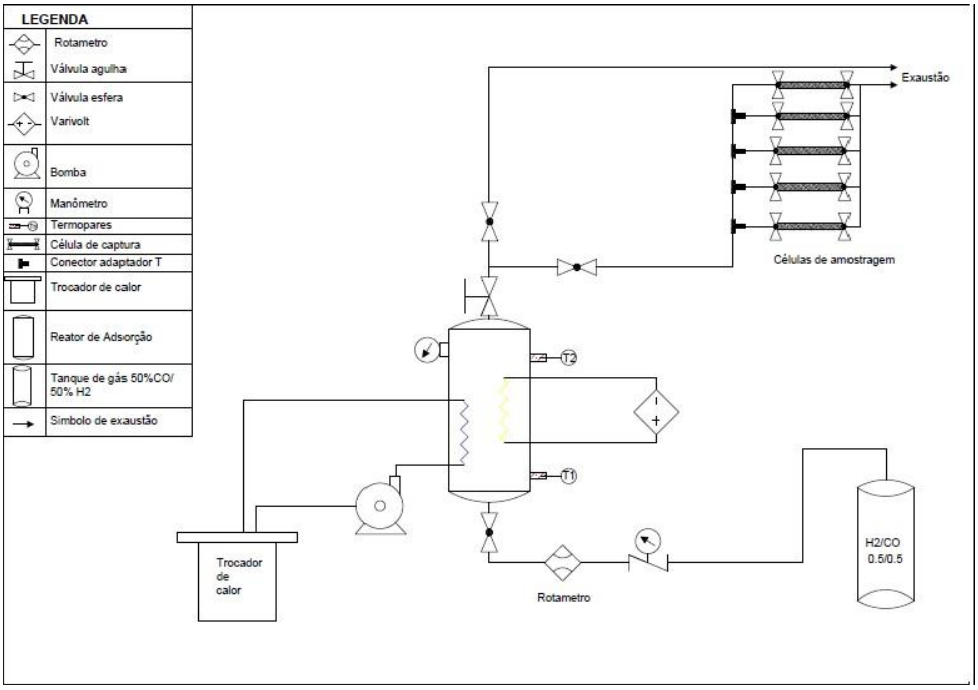

Figure 6. Schematic Drawing of the Built Separation System

Simulated curves, representing a concentration of CO at the adsorption column output as a function of time, were calculated for adsorbent / adsorbate, under specific operating conditions. The software used was gPROMS® (*Process System Enterprise, London, UK*) and modeling of the adsorption step had base in works of Cen & Yang (1986), Ribeiro *et al* (1986) and Bastos-Neto (2011). Equations (1) and (2) referred to mass balance, Equations (3) and (4) referred to energy balance, with which the adsorption and the temperature variation are modeled, respectively. In Eq (1) we obtain the concentration of CO in fluid phase along the bed and in Eq (3) the energy balance is made in the solid part obtaining temperature variation along the bed.

Mass Balance:

$$\varepsilon\frac{\partial C_g}{\partial t}+\left(\frac{\partial u C_g}{\partial z}-D_{ax}\frac{\partial^2 C_g}{\partial z^2}\right)+(1-\varepsilon)\left[\rho_s\frac{\partial \bar{q}}{\partial t}+\varepsilon_p\frac{\partial C_g}{\partial t}\right]=0 \tag{1}$$

$$\frac{\partial \bar{q}}{\partial t}=k_{ef}(q-\bar{q}) \tag{2}$$

Where:

- ε and ε_p correspond to bed and particle porosity, respectively.
- u and C_g correspond to flowing velocity and adsorbate concentration in gas phase.
- ρ_s and $\bar{q}$ correspond to particle density and adsorbate concentration in adsorbed phase.
- D_{ax} correspond to axial dispersion coefficient in the mass transfer zone.
- $\partial\bar{q}/\partial t$ correspond to adsorbate accumulation on solid surface (adsorbed phase).
- k_{ef} correspond to mass transfer effective coefficient.
- $\bar{q}$ correspond to adsorbate average concentration in adsorbed phase.
- q is the adsorbate concentration in adsorbed phase that corresponds to thermodynamic equilibrium fluid phase

Energy Balance:

$$\left[\varepsilon C_g\tilde{c}_g+(1-\varepsilon)\rho_s\tilde{c}_s\right]\left(\frac{\partial T_g}{\partial t}+\frac{\partial u T_g}{\partial z}\right)-(1-\varepsilon)\rho_s\left[(-\Delta H)\frac{\partial \bar{q}}{\partial t}\right]+\frac{4h_w}{d_i}\left(T_g-T_w\right)=0 \tag{3}$$

$$\rho_w c_w \frac{\partial T_w}{\partial t} = \alpha_w h_w \left(T_g - T_w\right) \tag{4}$$

Where:

- $\tilde{c}_g$ and $\tilde{c}_s$ correspond to heat capacity of gas and solid, respectively.
- T_g e T_w correspond to temperature of gas phase and wall column, respectively.
- d_i correspond to column internal diameter.
- ΔH e h_w correspond to heat adsorption and heat transfer coefficient from gas phase to wall column.
- ρ_w and c_w correspond to wall tube's density and heat capacity.
- α_w is a parameter that depends of bed geometry.

2.2 Results and discussions

After the assembly each component of system had its specific work tested into a separation process. Were did heating tests in the bed, filled with activated carbon, using different voltages to identify the best condition to achieve the temperature of 150ºC. That is the temperature of solid regeneration (Rios, 2015). Figure 7 shows graphics of bed's heating for ddp of 20 and 30V.

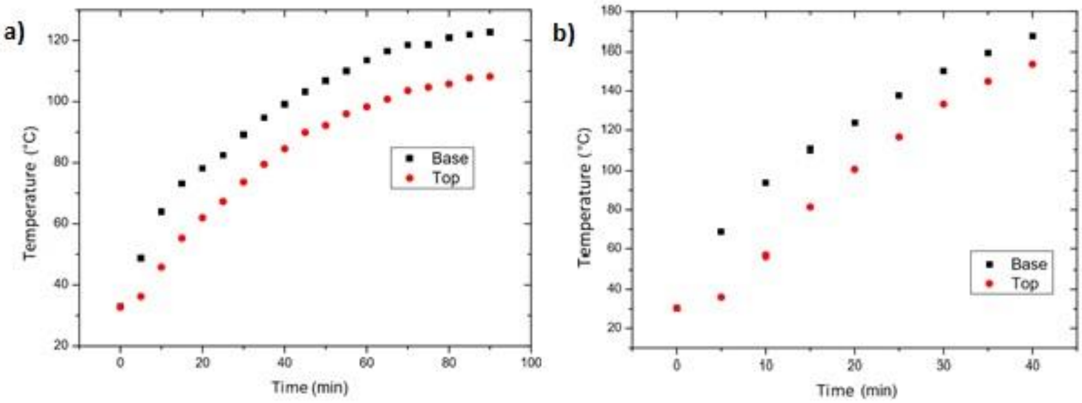

Figure 7. Heating of the Bed: a) ddp of 20V and b) ddp of 30V

Looking these graphics, can be realized that to ddp of 20V, after 90 min, the bed reached a temperature plateau in the bottom and in the top of 120 and 100ºC, respectively. In different way, to ddp of 30V, at 40 min the whole bed already was up of 150ºC. So to develop a step of bed regeneration and carbon monoxide recuperation (adsorbed product), in temperature of 150ºC, must be choice a ddp of 30V. Although an increase of ddp reduces the time of heating, realized that for values up to 30V the resistive wire became incandescent, coming to break in one of the experiments. So by security questions was preferred didn't exceed this value.

After the bed's heating in ddp of 30V was did its cooling, fundamental step of an TSA process. The temperature historic of the bed and the water in the tank was showed in Figure 8. Was used a water flow of 1,67 L/min.

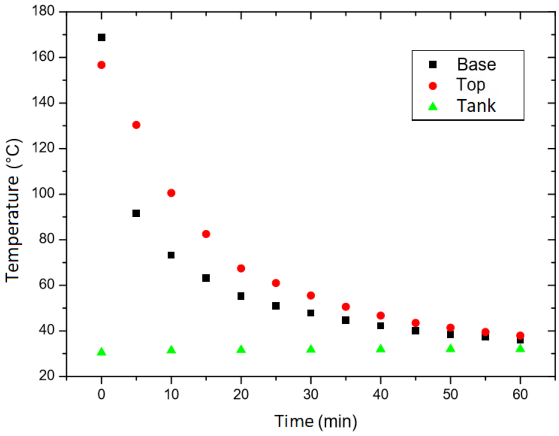

Figure 8. Historic temperature of cooling bed

After 60 min the bed came back to environment temperature and during all process the water, temperature into the tank maintained constant, maximizing the heat transfer inside the bed. Knowing that the adsorption phenomenon is favored by the decreasing of temperature (Do, 1998), was added to the separation system a refrigerator. This way it would be possible reduces the water temperature into the tank and operates the adsorption phase at low temperatures, increasing the bed capacity. The Figure 9 showed the temperature variation of water into the tank and for two distinct points of the bed, top and bottom, soon as the refrigeration was turn on. Was used once again a water flow of 1,67 L/min.

After 240min (4h) the water into the tank and the whole bed reached a temperature plateau. In these conditions the bed will operate in a strict temperature range between 5 and 7,5 ºC, as the tank will be at 2,5ºC.

Due to the high time that tank and bed stabilized their temperature, will be more interesting keep a tank of water under low temperature. Therefore, in the desired moment the water circulation will be turn on, reducing the bed's temperature in a low time.

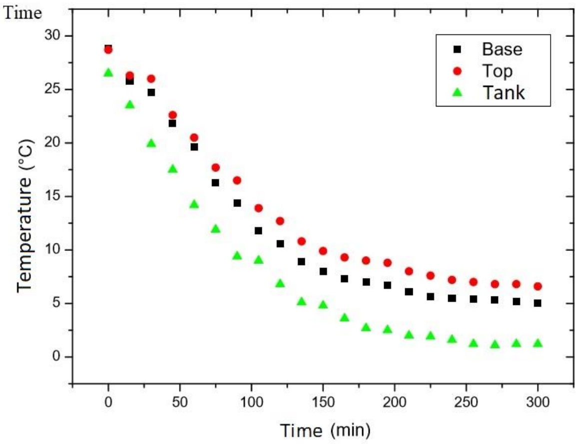

Fig 9. Refrigeration of the system

To available the adsorption and sample system were did adsorption runs in the bed. In each test were caught and analyzed samples from the output gas current of the bed.

Were developed two experiments, where the bed was pressurized with the mixture that would be fed (50%H_2 / 50%CO, during the adsorption run. These were denominated Run 1 and Run 2, operated at 3,5 and 5 bar, respectively. The feed was fed to the column in the same pressure of adsorptions' phase, at environment temperature and volumetric rate of 3,24L/min. The Table 1 shows the composition data obtained by sample caught and the Figure 10 the respective curves of concentration of CO versus operation time, called breakthrough curves, for each run.

Table 1 - Relative molar percentage composition of H_2 and CO in Runs 1 and 2.

	Run 1		Run 2	
t (s)	H_2	CO	H_2	CO
0	0	0	0	0
20	0,57	0,43	0,65	0,35
50	0,45	0,55	0,54	0,46
80	0,46	0,54	0,53	0,47
110	0,45	0,55	0,48	0,52

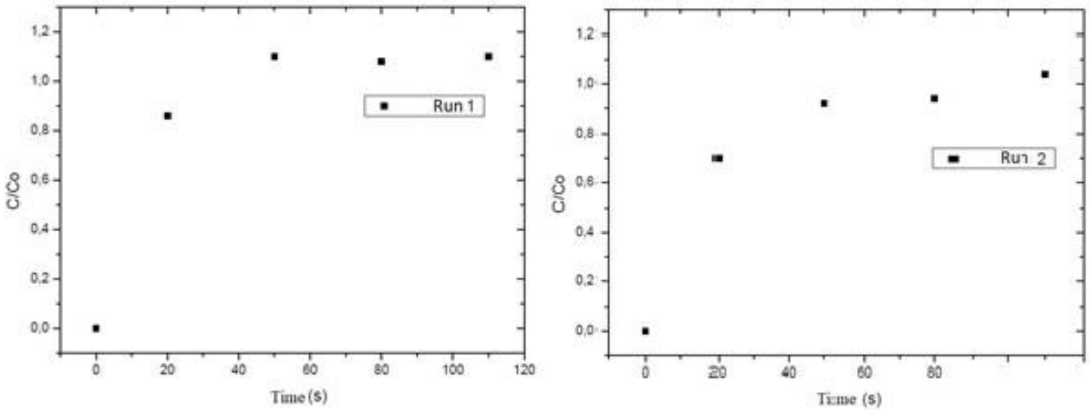

Figure 10. Breaktrough curves for Run 1 and Run 2

How we can look in Table 1 the compositions of H_2 and CO are very close and, besides the generated curves (Figure 9), didn't possible to identify a period of purified hydrogen product. In tested conditions the system undergoing a fast saturation and the obtained curves well didn't reproduce the evolution of CO's concentration in the product's current. This fact impossible the kinetic study of the system to predict the model of adsorption in the bed and parameters involved.

The second causes could be contributed to that was realized:

a. Due to the use of the very mixture to would be fed in column pressurization, before the adsorption run the bed already semi filled.
b. The mixture feed had a high concentration in the adsorbed component, contributing to its rapid saturation.
c. The activated carbon doesn't have elevated capacity for carbon monoxide.

A solution for this problem can be pressurize the bed with an inert gas (doesn't adsorb), the very hydrogen or others like helium, before the beginning of adsorption step. Simulated breaktrough curves for Run 1 and Run 2 were developed, considering pressurization with inert gas and rapid saturation of the bed with CO. They are called Sim 1 and Sim 2, respectively.

The parameters used are in Table 2 and the curves produced are in Figure 11.

Table 2 – Input data for simulations.

L (m)	0,3	ρ_s (Kg/m^3)	1745,2
d_i (m)	0,040	k_{ef} (s^{-1})	3
ν (L/min)	3,24	ρ_w (Kg/m^3)	2600
P (bar)	3,5/5	c_w (J/Kg /K)	921,8
T_o (K)	303	m_s (g)	100
ε	0,5	ΔH_{ads} (KJ/mol)	-15,20
ε_p	0,479	h_w (W/m^{2}K)	2,9629
d_p (μm)	700	c_s (J/Kg/K)	820

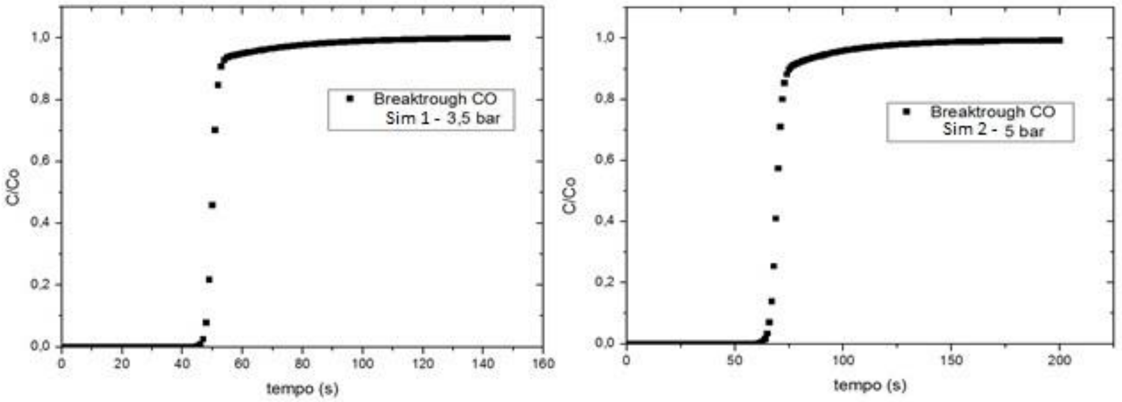

Figure 11. Simulated breaktrough curves

In both cases the bed will not operate in adsorption phase to produce hydrogen purified more than 1 minute. This fact illustrates the rapid saturation of this system adsorbent/adsorbate. Besides that, can be realize that an increase in an operation pressure leaves the same bed to a bigger time to reach its saturation. This is order to Adsorption Fundamentals, where an increase of pressure favors the occurrence of adsorption, high the adsorbent capacity and consequently the bed capacity (Ruthven, 1984).

2.3 Conclusion

The bed could be heated and maintained in a range of temperature desirable to operate the desorption of the carbon monoxide. The cooling of the bed, after its heating, could be operated until environment temperature. The refrigeration of the system reduced considerable the temperature of the column, however didn’t do this so fast. The adsorption system didn’t produce hydrogen purified when pressurized with the very mixture to be fed. A simulation of the system in experimental tested condition showed its rapid saturation for the pair adsorbent/adsorbate.

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4. RESPONSIBILITY NOTICE

The authors Igor Souza, Jean Faber, Francisco Nivaldo, William Magalhães, Welkson C. Araújo, Thiago Martins and José Welbson are the only responsible for the printed material included in this paper.