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Trabajo Fin de Grado

SELECTION OF ADSORBENTS FOR CO_2 RECOVERY FROM PROCESS GAS STREAMS USING PRESSURE SWING ADSORPTION PROCESSES

(SELECCIÓN DE ADSORBENTES PARA LA RECUPERACIÓN DE CO_2 A PARTIR DE GASES DE PROCESO MEDIANTE ADSORCIÓN CON OSCILACIÓN DE PRESIÓN)

Para acceder al Título de

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Autor: Sergio Castro González

RESUMEN

Este Trabajo Fin de Grado se enmarca dentro de las prácticas realizadas en la empresa Solvay de Torrelavega. El objetivo es el estudio de la técnica de adsorción por oscilación de presión (PSA) para su aplicación en la captura y concentración de CO_2 en corrientes de proceso, así como la realización de un estudio preliminar para la elección del adsorbente en dos casos representativos de la industria química.

En este trabajo fin de grado se ha realizado una revisión del estado del arte sobre los materiales adsorbentes de CO_2, principalmente carbonáceos y zeolitas. El segundo punto estudiado es la configuración del ciclo PSA, tanto el ciclo básico como las modificaciones que se pueden realizar. En el último apartado de este Trabajo Fin de Grado se realiza una selección preliminar entre los dos adsorbentes más empleados en la industria: carbón activo y zeolita 13X. La principal conclusión que deriva del estudio preliminar realizado es que la zeolita 13X es más ventajosa desde el punto de vista operacional que el carbón activo.

ABSTRACT

This Degree Final Project is part of the practices in the company Solvay Torrelavega. The aim is to study the technique of Pressure Swing Adsorption (PSA) for application in capture and CO_2 concentration in process streams as well as conducting a preliminary study for the choice of adsorbent in two representative cases in chemical industry.

In this Degree Final Project it has conducted a review of the state of the art on CO_2 adsorbent materials. We can distinguish two main types: carbonaceous and zeolites.

The second important issue is the configuration of the PSA cycle. In this document the basic cycle and the possible modifications are studied.

In the last section a preliminary study of the adsorbents zeolite 13X and activated carbon is performed. The main conclusion obtain is that the zeolite 13X is more advantageous from an operational point of view than the activated carbon.

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1. INTRODUCTION

1.1. MOTIVATION

The emission of $C0_2$ from power plants that burn fossil fuels is the major cause for the accumulation of $C0_2$ in the atmosphere, which causes long-range environmental problems as the global warming.

To avoid serious catastrophes, many countries agreed in some commitments (Kyoto protocol) to stabilize the greenhouse gases (GHG) concentration in the atmosphere, for carbon dioxide, methane, NO_x, SO_x, etc. Separation can play a key role in alleviating these problems.

In its purified form, CO_2 has found many uses in the chemical industry. It can be used in solid form (dry ice), liquid form (e.g. refrigeration equipment) or gaseous form (e.g., for carbonated beverages, fire extinguishing equipment). It can also be used as a reactant in many important chemical reactions or as an inert blanketing gas to prevent oxidation (e.g., for food packaging). Today CO_2 is produced as a by-product of fermentation and lime-kiln operations and by separations from flue gases by gas-liquid absorption processes. Typical flue gases contain around 17 % $C0_2$, the balance being N_2 (79 %) and 0_2 (4 %). Trace amounts of SO_x and NO_x, can also be found, but they are usually much less than 1% in total.

The capture of CO_2 in industrial streams is actually being performed by many processes, namely absorption in monoethanolamine (MEA) and solvent extraction. The first process is a proven technology used in natural gas sweetening and steel industry. The problems to extend this technology to CO_2 sequestration from flue gases are the global economics of the process, which is not very suitable for low molar fractions of CO_2 (Rao and Rubin, 2002), extensive solvent corrosion of the MEA and also the high energetic demand of the process. Solvent extraction with different chemicals was also considered although little detail about power consumption was given and also these processes are always based on proprietary solvents (Iijima et al., 2004). Capture of carbon dioxide from flue gases by Pressure Swing Adsorption (PSA) has been considered recently as an alternative to the absorption process.

In Table 1 it can be observed a comparison between different technologies used to capture CO_2:

Table 1: Comparison between various technologies used for CO_2 capture (Songolzadeg et al., 2014).

TECHNOLOGY	ADVANTAGES	DISADVANTAGES	SCALE
Absorption	-React rapidly. -High absorption capacities. -Very flexible.	-Equipment corrosion. -High energy required for regenerating solvent.	Industrial
Adsorption	-Low energy consumption and cost of CO_2 capture. -Suitable for separating CO_2 from dilute stream	-Low adsorption capacities (in flue gases conditions).	Pilot
Cryogenic destillation	-Liquid CO_2 production -Not requiring solvents or other components. -Easy scale-up to industrial-scale application.	-Require large amount of energy.	Pilot
Membrane separation	-Clean and simple process. -Continuous, steady-state technology.	-Require high energy for post-combustion CO_2 capture.	Pilot

PSA processes have been widely studied for the removal of CO_2 from various feed gas mixtures. For example, the CO_2 in the steam reformer off gas, landfill gas, and natural gas, are successfully removed by PSA technologies.

Other regeneration strategies for CO_2 adsorbents, apart from PSA are: Temperature Swing Adsorption (TSA), Vacuum Swing Adsorption (VSA), Electric Swing Adsorption (ESA) and a combination of Vacuum and Temperature Swing Adsorption (VTSA). In PSA applications, the pressure of the bed is reduced. VSA is preferred to the especial PSA application where the desorption pressure is below atmospheric, whereas in TSA, the temperature is raised while pressure is maintained approximately constant, and in ESA the solid is heated by the Joule effect (Songolzadeh et al., 2014).

Most commercial applications of PSA technology are related to the purification of the less-adsorbed (termed as light) species. However, it is possible to design the PSA unit in order to concentrate the most adsorbed gas. In the case of removing CO_2 from flue gases, CO_2 will be one of the most adsorbed gases and the scheduling of the PSA technology should be based on this phenomenon.

Pressure Swing Adsorption technology shown great results in CO_2 capture and concentration. When the concentration of CO_2 in the feed is high, above 25%, 99% CO_2 is easily obtained with relatively high recovery, over 70% using a one-stage PSA. However, when the concentration of CO_2 is low as it happens in the flue gas of a coal power plant, which ranges 10-15%, it is difficult to recover 99% CO_2 with high recovery using the one-stage PSA. Thus, a two-stage PSA is employed to enrich CO_2 from low concentration CO_2. At the first stage of the two-stage PSA, CO_2 is concentrated to 40-60% and then concentrated to 99% at the second stage (Park et al., 2002).

1.2. OBJECTIVE

The objective of this Degree Final Project is the study of the Pressure Swing Adsorption technology (PSA) for CO_2 capture, as well as a preliminary study for the use of this technique in the concentration of CO_2 in two gas streams combustion of a plant.

This Degree Final Project was elaborated in collaboration with the Ambient Technologies and Bioprocess University of Cantabria investigation group and with the chemical industry Solvay Torrelavega.

The specific objectives are:

- Literature review about CO_2 adsorbent materials that can be used in Pressure Swing Adsorption processes.
- Preliminary design of a PSA process for two representative cases of study of the chemical industry.

2. DEVELOPMENT

2.1. SEARCH AND ANALYSIS OF INFORMATION ON CO_2 ADSORBENT MATERIALS

The first and most important issue in any adsorption process is to find the appropriate sorbent for the proposed separation. In the present case this sorbent must possess a high selectivity for $C0_2$ over both N_2 and 0_2, with fast uptake rates in order to achieve a reasonably high throughput.

In several excellent reviews on CO_2 capture by adsorption (Choi et al., 2009; Sayari et al., 2011), it can be understood that the development of an appropriate CO_2 capture adsorbent should satisfy this points:

1. Low-cost raw materials.
2. Low heat capacity.
3. Fast adsorption kinetics.
4. High CO_2 adsorption capacity.
5. High CO_2 selectivity.
6. Thermal, chemical, and mechanical stabilities under extensive cycling.

Carbonaceous adsorbents and zeolites are the most typically employed physical adsorbent use in PSA processes.

Though carbonaceous adsorbents such as activated carbon (Plaza et al., 2010) have been widely used for CO_2 capture due to their wide availability, low cost, high thermal stability and low sensitivity to moisture, their application is limited to treat high pressure gases. The weak CO_2 adsorption onto carbonaceous materials in a range of 50–120°C leads to high sensitivity in temperature and relatively low selectivity in operation. As a consequence, current research focuses on how to improve the CO_2 adsorption capacity and selectivity via two ways (Yu et al., 2012):

1. To improve surface area and pore structure of the carbonaceous adsorbents either using different precursors or fabricating different structures such as ordered mesoporous carbon (Saha and Deng, 2010), single-wall Carbon Nanotubes (CNT) (Cinke et al., 2003), multi-walled CNT (Su et al., 2009), graphene (Ghosh et al., 2008), etc.
2. To increase alkalinity by chemical modification on surface.

Zeolite materials have been widely studied for CO_2 capture from flue gases in fossil fuel power plants, natural gas and biogas facilities. According to the literature on CO_2 capture using different types of natural and various types of synthetic zeolites such as Y, X, A, 13X zeolite shows superior performance for CO_2 separation from N_2 at relatively low temperatures. Some researchers have considered zeolite 5A in TSA processes because of its higher volumetric capacity and high working capacity between low and high temperatures (Ling et al., 2014).

Zeolite 13X, which has been studied for more than two decades, is the benchmark material for CO_2 VSA systems because of its high working capacity and selectivity for CO_2 at the prevailing conditions of the process (Ling et al., 2014).

Zeolite 13X has the chemical formula Na_{86} $[(AlO_2)_{86}$ $(SiO_2)_{106}]$ • H_2O and a pore diameter of 8 Å approximately.

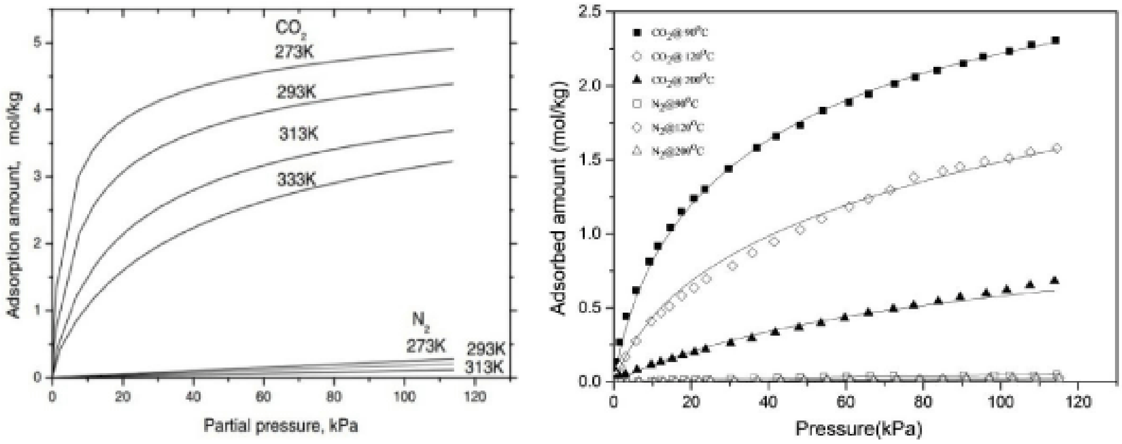


Figure 1: Isotherms of CO_2 and N_2 on zeolite 13X at low temperature [22] (left) and high temperature [30] (right). (Ling et al., 2014)

From the isotherms of CO_2 and N_2 adsorption on zeolite 13X, both CO_2 and N_2 adsorbed amount increases as their partial pressures increases (Figure 1) in the usual way for a physic-sorbent. As the temperature increases, the adsorbed amount for both CO_2 and N_2 decreases, indicative of exothermic adsorption. Although zeolite 13X is a physical sorbent for CO_2 and as such should be restricted to modest temperature application, we have found that it presents a relatively high CO_2 working capacity even over 120ºC. Therefore, it is an ideal adsorbent for CO_2 and N_2 separation as it has a wide operating temperature range (Ling et al., 2014).

CO_2 adsorption capacity on zeolite 13X is reduced significantly by water vapor because water is strongly adsorbed onto the hydrophilic sodium cations within the supercage, displacing CO_2 from adsorption sites. As a result, a guard layer must be employed to avoid moisture contamination of zeolite 13X (Ling et al., 2014).

For CO_2 adsorption for moisturized gases, activated carbon presents a better performance because it contains both hydrophobic and hydrophilic sites on its surface. That means that water vapor can be adsorbed onto the surface by hydrogen bonding to the surface functional groups, but this bonding is very weak so that the water vapor can be removed by reducing its partial pressure and as a result activated carbons are often regarded as more suitable for wet flue gas treatment. The isotherms of water vapor and CO_2 adsorption on activated carbon are shown in Figure 2 (Ling et al., 2014).

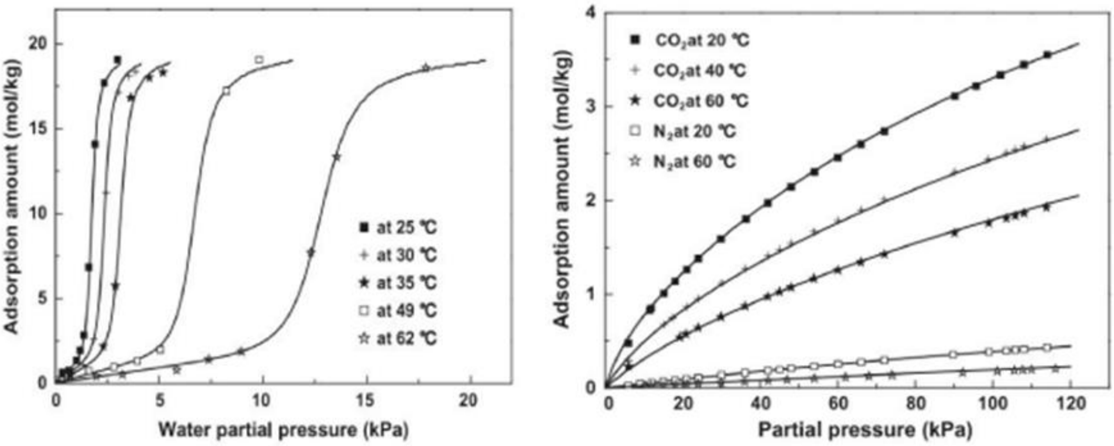


Figure 2: Isotherms of water vapor and CO_2 on activated carbon: water vapor (left) and CO_2 (right). (Ling et al., 2014)

CO_2 adsorption capacity on activated carbon is much lower compared to that of zeolite 13X particularly at the lower range of partial pressure. However, its ability to moderately withstand water vapor makes it a promising material in the application of CO_2 capture from wet (real) flue gases (Ling et al., 2014).

Others groups of adsorbents, like Metal-organic frameworks (MOFs), have attracted significant interest in the recent years, but they are being studying nowadays (*Yu et al., 2012*).

In real flue gases, apart from CO_2, N_2 and O_2, it can be present SO_x, NO_x, water vapor and others. These compounds are common impurities in flue gases from power plants, and these negatively affect CO_2 adsorption capability. Capturing CO_2 by pressure swing adsorption may be complicated by the existence of these impurities when commercial CO_2 selective adsorbents are used. Conventional process designs rely on using a pretreatment process to remove water, SO_x and NO_x, which adds considerably to the overall cost (Ling et al., 2014).

In most cases these impurities are removed in a pretreatment. Sometimes a multilayered column is used where the first bed contains an adsorbent with high selectivity to the impurity which is going to be removed, and the second part of the bed contains an adsorbent to removed CO_2. In some cases the multilayered column contains 3 types of sorbents (Li et al., 2014).

Another item that should be considered is the number of cycles the adsorbent is able to perform. It is related with the operating cost.

2.2. ANALYSIS OF THE PSA PROCESS STEPS

The second important issue is the design of a proper PSA cycle in order to attain the desirable concentration rate of the target component from the mixture.

The basic PSA cycle principle is to have two or more beds that undergo cyclic adsorption and desorption (Bolland, 2012). However, as the operating cycle is critical to the performance, there have been many different attempts to modify the basic cycle. This includes adding cycle steps, the number of beds (Ruthven, et al., 1994) and even adding another PSA stage, meaning that the adsorbed product passes through a secondary PSA process (Liu, et al., 2011).

There are several factors that determine how the process should be modified such as the nature of adsorption selectivity (equilibrium or kinetics) and the trade-off between CO_2 purity and recovery *(Moen and Stene, 2014).*

The typical steps in a PSA cycle are:

(1) Pressurization. The pressure in the bed is increased to the feed pressure as fresh feed gas is introduced co-currently into the bed. The product end is closed during this step in order to achieve the rise in pressure. The pressurization can also be counter-current, but then with the raffinate gas entering counter-current into the bed (Liu, et al., 2011). If the latter step is employed this is carried out prior to the co-current pressurization with the feed gas, with the purpose of improving the purity and recovery of the raffinate product (Ruthven, et al., 1994).

(2) Feed. This step is also called the adsorption step, and usually follows the pressurization step. The feed gas is passed through the adsorbent at the highest cycle pressure level with the product side valve open. This step causes the raffinate gas to become enriched in the less adsorbed species as the strongly adsorbed species are taken up by the adsorbents (Rodrigues, et al., 1988). It is important that the feed stops before breakthrough is reached. Breakthrough can be said to be occurring when the concentration of the strongly adsorbed species in the raffinate product starts to

increase dramatically. It is therefore very important to select the correct feed step time in order to achieve high recovery (Choi, et al., 2003). During the adsorption step the pressure can either be kept at a constant level or be allowed to be slightly reduced. By reducing the pressure the recovery of the raffinate gas is increased (Ruthven, et al., 1994). For CO_2 PSA this should mean that the purity of the adsorbed CO_2 would increase, but at the expense of the recovery *(Moen and Stene, 2014).*

(3) Depressurization: before CO_2 breakthrough, feed is stopped and the pressure of the column is reduced (normally, co-currently to feed). This process is carried out by putting in contact two columns at different pressure levels in order to save energy. This procedure is known as pressure equalization and can be repeated several times (*Zhen Liu et al., 2011).*

(4) Desorption. The desorption can be performed with different modes of operations.

One is to have counter-current desorption with raffinate purge, which was the method of choice in the basic Skarstrom cycle (Ruthven, et al., 1994). This is done by using a fraction of the raffinate product to flush the void spaces in the bed. By doing this one can ensure that the raffinate at the end of the bed, which is recovered in the next cycle, is completely free of the strongly adsorbed species. This result in increased extract recovery at the expense of decreased extract purity (Ruthven, et al., 1994). Counter-current purging is often carried out at the lowest cycle pressure, but it is also possible to employ this step at intermediate pressures (Liu, et al., 2011).

An alternative to purging is to use a counter-current evacuation, also known as blowdown (Ruthven, et al., 1994). During the evacuation step the extract product is recovered. With the blowdown step a high extract purity and recovery can be obtained. The disadvantage with this step compared to the raffinate purging is that when evacuation is performed at near vacuum pressure the increase in the recovery of the raffinate is at the expense of additional mechanical energy needed for the evacuation step (Ruthven, et al., 1994). It should be noticed that blowdown and purge may be used in the same PSA cycle.

(5) Purge: in order to remove the heavy gas from the gas phase, a counter-current purge with inert gas (or the less adsorbed one) is carried out. This step is also carried out at the lowest pressure of the system, although some intermediate pressures can be employed (*Zhen Liu et al., 2011).*

(6) Rinse. The rinse step is a form of purging, but instead of purging with the raffinate product the extract product is used. This step often follows the pressure equalization step as seen in several papers (Choi, et al., 2003), (Na, et al., 2002). The aim is to improve the extract product purity when less adsorbing (lighter) species are co-adsorbed with the more strongly adsorbed (heavier) species (Ruthven, et al., 1994). The rinse step is carried out by using a fraction of the adsorbed gas and recycling it co-currently into the bed. The rinse can be performed with the valve at the other end of the bed first closed, then open (Choi, et al., 2003), or open during the entire step (Na, et al., 2002). As with the adsorption step time, the rinse step time is important to optimize. If the rinse is allowed to proceed for too long time, the recovery of the extract product is significantly decreased as a large portion of the heavy species disappears with the raffinate (Na, et al., 2002).

(7) Pressure equalization. During this step the pressure between two beds is equalized by connecting a high pressure bed with a low pressure bed. The high pressure bed goes through a depressurization, which starts before breakthrough of the strongly adsorbed species (Liu, et al., 2011). The low pressure bed is pressurized. This step saves energy since the work needed for the pressurization step can be reduced (Choi, et al., 2003).

Figure 3 shows the different steps mentioned previously in order to get a global idea of a configuration of a PSA cycle where different steps are present:

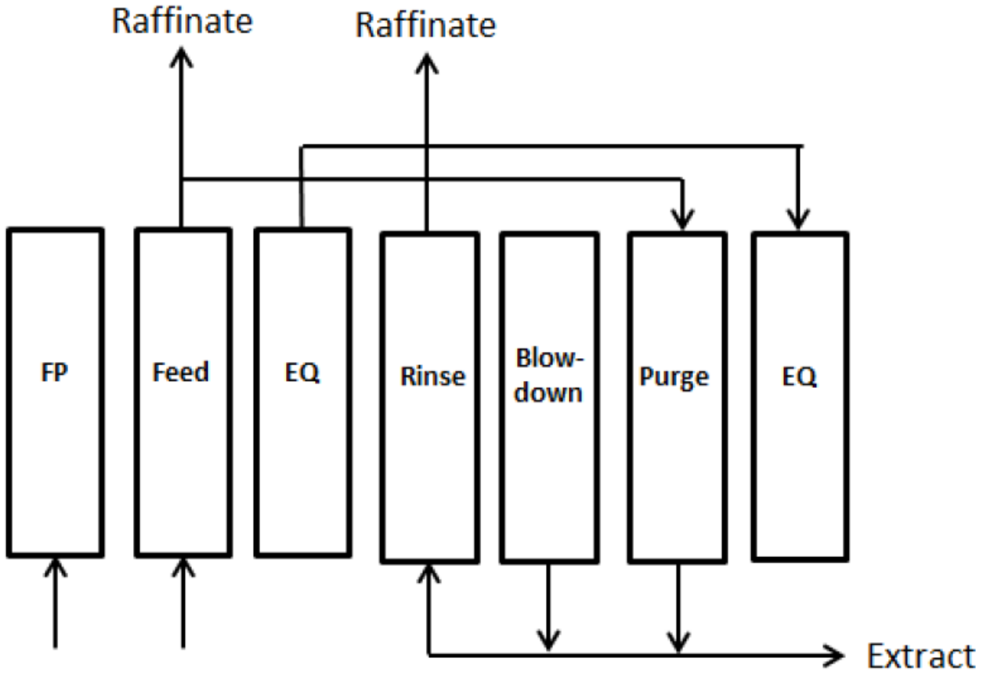
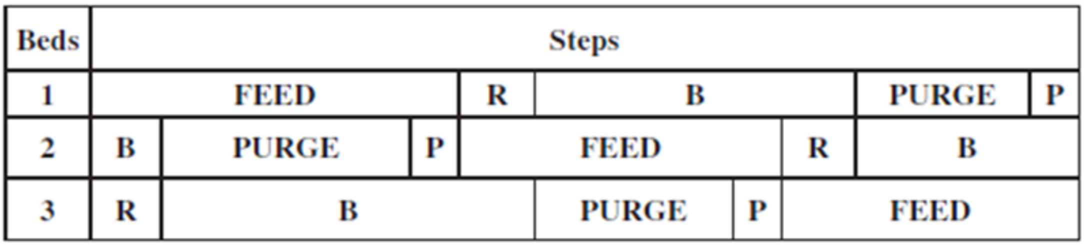


Figure 3: PSA cycle steps.

As it can see in the figure 4, PSA is discontinuous process: the feed step only occurs for a period of time. In order to make the process continuous, in a real plant there would be several trains of PSA processes (three in figure 4) to be able to accommodate all the flue gas. That means when a column is in the feed step, another column is in other step like pressurization or desorbing step.



<table>
<tr><th>Beds</th><th colspan="9">Steps</th></tr>
<tr><td>1</td><td colspan="3">FEED</td><td>R</td><td colspan="3">B</td><td>PURGE</td><td>P</td></tr>
<tr><td>2</td><td>B</td><td>PURGE</td><td>P</td><td colspan="3">FEED</td><td>R</td><td colspan="2">B</td></tr>
<tr><td>3</td><td>R</td><td colspan="3">B</td><td>PURGE</td><td>P</td><td colspan="3">FEED</td></tr>
</table>

Figure 4. Three column five steps PSA (Liu et al.,2011). R: Rinse; P: Pressurization.

The cycle configuration is going to depend on the objective of the separation. Steps can be selected in order to increase the recovery or de purity of the CO_2 (more adsorbed) or the other gases (less adsorbed).

In order to increase the purity and recovery of CO_2 it can be used a second PSA process (Liu et al., 2011).The CO_2 obtain as a product in the first PSA is the feed of the second PSA. To assume that the flow rate and composition entering the second stage was constant, a tank can be used between the two PSAs. It should be noticed that the number of columns and steps can be different in both PSA, principally because the gas it has be treat in the second PSA is minor than the gas threat in the first PSA (Moen and Stene, 2014).

The duration of the steps should be optimizing to obtain higher performance parameters (Liu et al., 2011).

To summarize, the main objective is make the process continuous. To achieve this objective it should be get an agreement between the number of columns, the steps of the cycle, the duration of each steps and the size of the column.

Table 2 shows a compilation of PSA processes with different configurations, steps, flow rates, CO_2 concentration at the inlet and pressures as well as the purity and recovery obtain in order to compare them with each other.

As it can verify, purity levels of 99% and recovery levels of 98.9% can be achieve under some specified conditions. It is prouf that a higher purity is not compatible with a higher recovery. Examples of a compromising solution between purity and recovery are the 4-steps cycle configuration of Kikkindes et al., (1993) and 2-bed 6-step cycle configuration of Park et al., (2002).

Table 2. Post-combustion PSA configurations from literature.

CYCLE CONFIGURATION		STEPS SECUENCE	FLOW RATE (SLPM)	CO_2 % FEED	ADSORBENT	PH atm	PL atm	CO2 PURITY %	CO2 RECOVERY %	STUDY TYPE	REFENCES
3-bed 7-step	Rinse, Pressure equalization	fPR,AD,PEo,cRN, oRN, EVn, PEn	10	13	13X	1.5	0.05	90	78	Exp	Choi et al, 2003
4-step	Rinse recycle, raffinate presurization	rPR, AD, oRN, Evn	-	17	AC	1.2	0.1	90	85	Sim	Kikkindes et al, 1993
3-bed 6-step	Rinse recycle, Pressure equalization	fRP, AD, PEo,oRN, EVn, Pen	83	13	AC	1.97	0.1	99	59	Exp	Na et al, 2002
2-bed 4-step	Skarstrom cycle	fPR, AD, Bn, Pn	0.8	15	SA	1.48	0.1	50.67	95.04	Sim	Lui et al, 2011
2-bed 6-step	Skarstrom cycle with pressure equalization	fPR, AD, PEo, Bn, Pn, PEn	0.8	15	SA	1.48	0.1	58.23	93.62	Sim	Lui et al, 2011
3-bed 5-step	Skarstrom cycle with rinse	fPR, AD, oRN, Bn, Pn	0.8	15	SA	1.48	0.1	69.15	98.92	Sim	Lui et al, 2011
4-bed 7-step	Skarstrom cycle with pressure equalization and rinse	fPR, AD, oRN, PEo, Bn, Pn, PEn	0.8	15	SA	1.48	0.1	77.14	91.46	Sim	Lui et al, 2011
4-bed 8-step	Skarstrom with pressure equalization and rinse	fPR, AD, oRN, PEo, EVn, Pn, PEn, O	-	13	NaX	1.18	0.1	56.93	87.96	Exp	Takamura et al., 2001
2-bed 4-step	Skarstrom	fPR, AD, Bn, Pn	135	10	13X	1.13	0.07	55	87	Sim	Park et al., 2002
2-bed 6-step	Skarstrom with pressure equalization	fPR, AD, PEo, Bn, Pn, PEn	135	10	13X	1.13	0.07	64	85	Sim	Park et al., 2002
3-bed 5-step	Skarstrom with rinse	fPR, AD, oRN, Bn, Pn	135	10	13X	1.13	0.07	64	89	Sim	Park et al., 2002
3-bed 8-step	Pressure equalizationand rinse	fPR, AD, Bo, PEo,cRN, oRN, EVn, PEn	10	17	AC	1.5	0.1	91.2	46.1	Exp	Na et al., 2001

Legend: fPR = feed pressurization, rPR = raffinate pressurization, AD = adsorption, PEo = co-current pressurization, PEn = counter-current pressurization, cRN = closed end rinse step, oRN = open end rinse step, Bo = co-current blowdown, Bn = counter-current blowdown, EVn = counter-current evacuation, Pn = countercurrent purge.

Adsorbent abbreviation legend: 13X = zeolite 13X, AC = activated carbon, 5A =zeolite 5A, NaX = NaX-type zeolite, NaA =NaA-type zeolite.

2.3. PRELIMINARY CALCULATIONS

In this section of the Degree Final Project a preliminary study for the use of PSA technique in the concentration of CO_2 is developed. The first important step in the design of a PSA process is the choice of a preferred adsorbent. In the next pages the adsorbent selection will be performed for two different case studies defined in Table 3. In case study 1, inlet CO_2 concentration is 10% and an output concentration of CO_2 of 40 % is sought. In case study 2, CO_2 in the inlet stream is 50% and a final CO_2 concentration of 95 % in the product is sought.

The characteristics of these output currents are:

Table 3: characteristics of output currents.

	CASE 1		**CASE 2**	
	INPUT	**OUTPUT**	**INPUT**	**OUTPUT**
FLOW RATE (m^3/h)	10	-	10	-
T (^oC)	100	-	100	-
P (atm)	1	-	1	-
CO_2 (% v/v)	10	40	50	95
N_2 (% v/v)	74	-	37	-
O_2 (% v/v)	5	-	2	-
SO_x, NO_x (% v/v)	1	-	1	-
H_2O (% v/v)	10	-	10	-

In present work two adsorbents, Activated Carbon (AC) and Zeolite 13X, are examined. Both candidate adsorbents are widely applied in PSA process.

In general, zeolites have higher adsorption capacities for $C0_2$ as well as higher equilibrium selectivity's for $C0_2$ over N_2 than activated carbon. On the other hand, the heat of adsorption of $C0_2$ on activated carbon is lower than on zeolite, so that the uses of activated carbon in a PSA process may result in less severe heat effect on the PSA performance. The temperature due to heats of adsorption and desorption is detrimental to the separation performance of a PSA process (Cen and Yang, 1986**;** Lu et al., 1993). Other differences that make one adsorbent more attractive than the other are the price and the renewal time.

First of all, to start the comparison of both adsorbents the equilibrium isotherms are required.

Table 4. Parameters of the Langmuir Adsorption Isotherms of pure Adsorbents. (Chue et al., 1995).

ADSORBENT	**ADSORBATE**	**A_0 (mol $Kg^{-1}Pa^{-1}$)**	**A_1 (K^{-1})**	**B_0 (Pa^{-1})**	**B_1(K^{-1})**
Zeolite 13X	CO_2	2.38341	-0.02816	0.12266	-0.02352
Zeolite 13X	N_2	0.06355	-0.02934	$6.313x10^{-4}$	-0.01419
AC	CO_2	0.02381	-0.02007	$5.937x10^{-4}$	-0.00378
AC	N_2	0.00125	-0.02086	$1.271x10^{-4}$	-0.01452

Table 4 shows the parameters of the Langmuir equation that describe the adsorption isotherms of pure $C0_2$ and N_2 on zeolite 13X and activated carbon

Equilibrium data of pure $C0_2$ and N_2 were fitted with the Langmuir isotherm:

$$q = \frac{A\times P}{1+B\times P} \quad [mol/Kg] \qquad \textit{Equation 1.}$$

Pressure is measured in Pa. The parameters A and *B* are well correlated by an exponential function of temperature:

$$A = A_0 \times e^{A_1 x T} \quad [mol.Kg^{-1}.Pa^{-1}] \qquad \textit{Equation 2.}$$

$$B = B_0 \times e^{B_1 x T} \quad [Pa^{-1}] \qquad \textit{Equation 3.}$$

Once the adsorption isotherms are known, the next step is select the PSA flow diagram. In this case, the flow diagram proposed is represented in figure 5.

The process consists of a preliminary step where stream impurities (NO_x, SO_x and H_2O) are removed in order to avoid adverse effects on the adsorption process. For this purpose it is proposed to install a flue gas desulfurization unit (FGD) to remove SO_x and a dehydration unit to remove water vapor.

The temperature of the input current has to be lowered because high temperatures have a negative influence on the adsorption. Ling et al., (2015) says that both CO_2 recovery and purity are not adversely affected in a temperature range between 25 and 80 °C. We must bear in mind that the exothermic adsorption reaction increases the bed temperature during adsorption. On the other hand the regeneration is endothermic and thus it is enhanced a high temperatures.

To avoid operation with very high temperatures that could damage the adsorption step, it is proposed to use a heat exchanger that change the temperature of the input current from the output temperature of the dehydration unit to about 35-40 °C, in order to get a balance between the advantage gained by increased team productivity and energy consumption in this stage. Thus the flue gases enter at a temperature that does not substantially alter the adsorption process, while also discourages the desorption process to be introduced more or less at a higher temperature in the cycle and heating during adsorption by the exothermic character thereof.

The next step should be the compression of the flue gas in order to increase the pressure (atmospheric pressure) to 3 atm, which is the adsorption working pressure in this case. After the compression step, the flue gas enters the adsorption column. The cycle configuration is:

Feed pressurization → Feed/Adsorption → Blowdown → Purge

The columns are 0.5 m high. The adsorption pressure is 3 atm and the desorption pressure will be calculated.

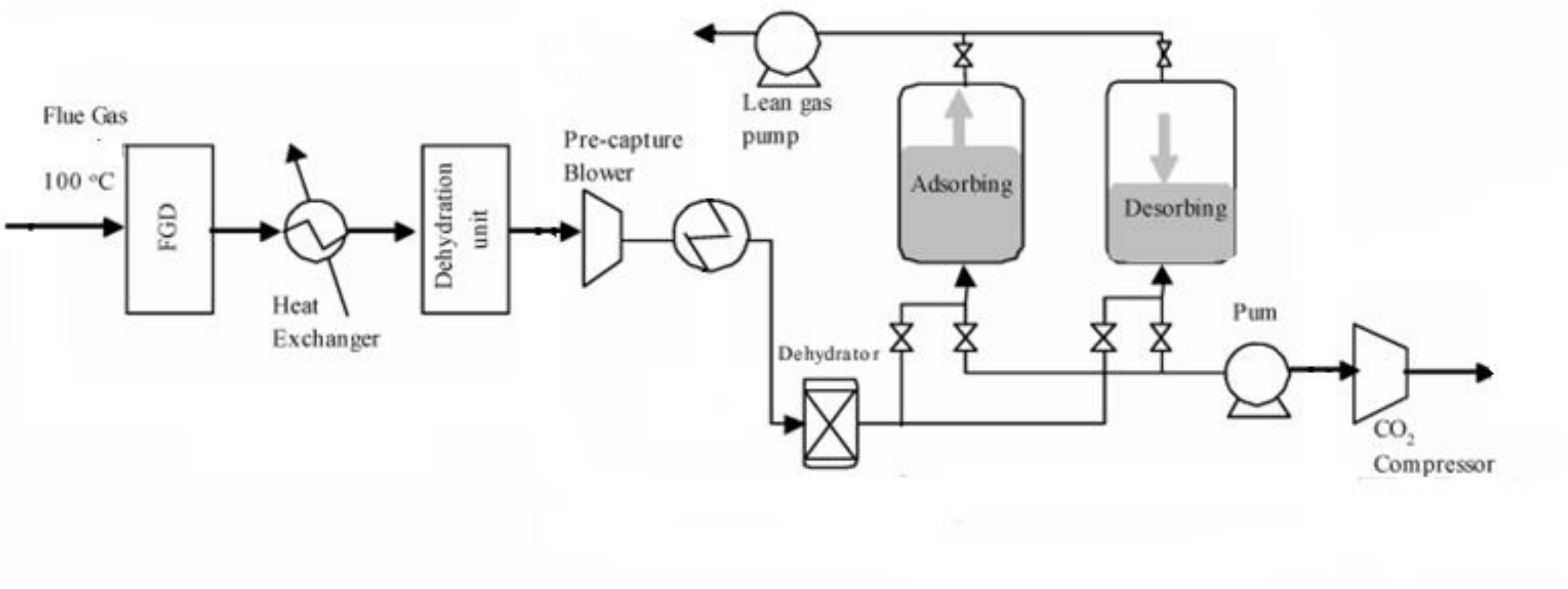


Figure 5. Process flow diagram for CO_2 capture process.

In the pressurization step the flue gases entering at high pressure (3 atm) to the column. The gas enters the bottom of the column whereas the superior exit is closed. After 1 second the head of the column opens and the flue gas continues entering: this is the Feed or Adsorption step.

Once this step finishes (different time for each adsorbent), pressure changes from the highest value, 3 atm, to the lowest. Once this occurs, blowdown stage starts. This step only occurs during 1 second.

During the purge the feed gas is used to drag the CO_2 adsorbed in the column. The duration is variable and outlet CO_2 concentration can be calculated. When this stage is completed, the cycle begins again.

The mathematical model equations used are shown below. First we define β, a parameter which relates the adsorbed fraction with the non-absorbed fraction in the column. This parameter is calculated for both types of adsorbents.

$$\beta = \frac{\mathcal{E}_e + (1-\mathcal{E}_e) x \mathcal{E}_p x K_{d,i} + (1-\mathcal{E}_e) x (1-\mathcal{E}_p) x \phi_s x K_{weak} x\ R\ x\ T}{\mathcal{E}_e + (1-\mathcal{E}_e) x \mathcal{E}_p x K_{d,i} + (1-\mathcal{E}_e) x \left(1-\mathcal{E}_p\right) x \phi_s x K_{strong} x R x T}$$

Equation 2.

For the case study K_{weak}=0 because nitrogen is not adsorbed, and R=8.314 $^{Pa.m3}/_{mol.K}$. $K_{d,i}$=1 because all the adsorption sites are accessible to small gas molecules.

Now we are in conditions to calculate the movement of the molar fraction of the CO_2, which is more absorbable than N_2 and O_2. The equation use to calculate the molar fraction is:

$$\frac{y_{after}}{y_{before}} = \frac{P_{after}}{P_{before}}^{\beta-1}$$

Equation 3.

The movement of the waves of solute can be determined with the equation 4:

$$\frac{z_{\text{after}}}{z_{\text{before}}} = \frac{P_{\text{after}}}{P_{\text{before}}}^{-\beta}$$

Equation 4.

Where Z is the axial distance within the adsorption column.

For a gas that can be considered as ideal, the solute velocity is calculated as:

$$V_{s,i} = \frac{v_{inter}}{1 + \frac{(1-\mathcal{E}_e)x\mathcal{E}_p x K_{d,i}}{\mathcal{E}_e} + \frac{(1-\mathcal{E}_e)x(1-\mathcal{E}_p)}{\mathcal{E}_e} x\phi_s xRxTxK_{strong}}$$

Equation 5.

This solute velocity is used to calculate the step duration, dividing the distance traveled by the CO_2 by the solute velocity.

The adsorbent properties, both Activated Carbon and Zeolite 13X, are summarized in table 5:

Table 5. Activated Carbon and Zeolite 13X properties.

	ACTIVATED CARBON	**ZEOLITE 13X**
($\mathcal{E}_p$)	0.33	0.5
($\mathcal{E}_e$)	0.43	0.36
Densidad (kg/m^3)	1800	1060
$K_{d,i}$	1	1
K strong (mol.Kg/Pa)	0.00001	0.0004

With all of this information we are prepared to plot the position of the adsorption front located in column height versus time diagram. The obtained diagrams of the adsorption cycle calculated for both adsorbents in case 1 are:

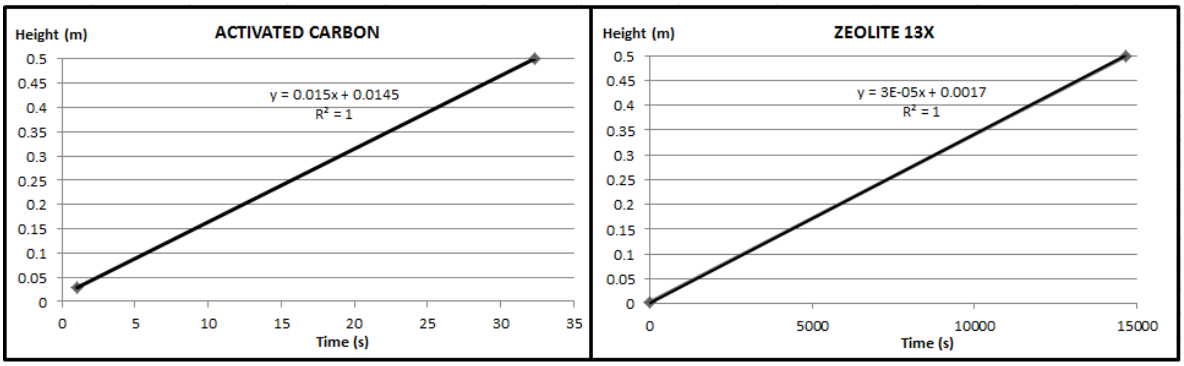


Figure 6. Column height versus time for Zeolite 13X and Activated Carbon.

As a result of the above analysis in figure X, it can be noted that zeolite 13X is more promising judging from the operation time. For each zeolite bed regeneration, the activated carbon bed is regenerated 400 times.

Zeolite 13X presents more promising from an economical point of view because the pressure change to regenerate the column means a high energy consume, approximately 400 times less in zeolite 13X than in activated carbon.

For the above reasons, the next calculations are going to be focus on Zeolite 13X.

The next step is the blowdown, where the pressure change to the lowers and the CO_2 started to desorb.

The equation 4 describes again the movement of the solute wave, and the closed end continuous in the top of the column, so calculating the new Z_{after} and introducing in equation 4 the value of Z_{before}, blowdown can be calculated. In this case the P_{after} is the lower pressure and P_{before} is the highest pressure, the opposite than in the adsorption step.

The exit molar fraction is well known for both cases, so the lower pressure can be calculated using equation 3 and the same modifications than for the solute movement wave. The highest the lower pressure value, the better adsorbent for our process, because the pressure reduction has an economical cost. The lower pressure obtains for case 1 using Zeolite 13X is 0.84 atmospheres.

The last stage is the purge. In this step the solute velocity increases. The new velocity is the same as the adsorption ones but multiplied by 1, 1.

$$V_{purge} = 1.1 \times V_{s,i}$$

To calculate the time spend in this step the distance traveled by the CO_2 is divided by the purge velocity. The process diagram for Zeolite 13X is:

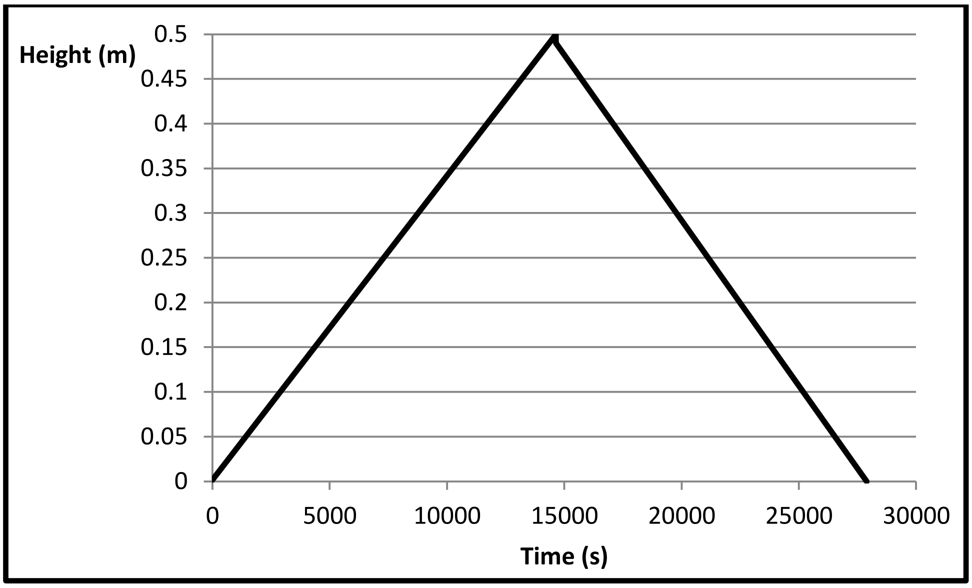


Figure 7. Solute movement in zeolite 13X cycle. Column height Vs time.

The different variables calculated for both adsorbents and for each case are summarize in table 6:

Table 6.Comparative results for both adsorbent and for each case.

	ADSORBENT	P_{lower} (atm)	Time $_{ad.}$ (s)	Time $_{des.}$ (s)	Time $_{total}$ (s)
CASE 1	AC	0.805	31.33	29.37	62.7
	13X	0.84	14647	13243.29	27892.29
CASE 2	AC	1.74	32.7	31.25	65.95
	13X	1.77	14691.14	13513.5	28206.64

3. CONCLUSIONS

Zeolite 13X has longer cycles than activated carbon. This cycle duration allow zeolite 13X bed been regenerated less times. Approximately, for each zeolite 13X cycle, 400 activated carbon cycles are complete.

This significant variation in the number of cycles can be translate in costs. A PSA cycle has associated energy cost because of the pressure variation. That means that for activated carbon the energy cost will be higher than for zeolite 13X, due to the number of cycles.

The energy cost is relation with the lower pressure. For vacuum pressures the cost is higher than for high pressures. In these cases, the lower pressure in both adsorbent is similar. For case 2 conditions, the lower pressures are 1 atm approximately higher than for case 1 conditions, so the pressures variation in cycle 2 is less because the high pressure is a fixed value for both cases.

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