

CO₂ Adsorption Process Simulation in ASPEN Hysys

Cristian DINCA, Nela SLAVU, Adrian BADEA

Energy Generation and Use Department
University POLITEHNICA of Bucharest
Bucharest, ROMANIA
crisflor75@yahoo.com

Nela SLAVU, Adrian BADEA

Academy of Romanian Scientists
Bucharest, ROMANIA

Abstract—The main objective of the paper consists to analyze the adsorption process for capturing the carbon dioxide generated from the fossil fuel power plants. For simplifying our analysis, we have considered that the stream contains only carbon dioxide and nitrogen in a mole concentration of 13/87 %. The adsorption process was simulated in the Aspen Adsorption V9 considering silica gel impregnated with amine and activated carbon. In this case, an adsorption column of 10 cm length was used according to the exhaust gases flow in order to achieve a CO₂ capture efficiency of 85 %. However, the CO₂ capture efficiency of 85 % was obtained only for silica gel due to its chemical properties. In the activated carbon case, the CO₂ capture efficiency was 77 %. In both cases, the maximal efficiency was obtained after 10 s due to the adsorption capacity of the bed.

Index Terms—Activated carbon, CO₂ Adsorption Process, Polyethyleneimine, Temperature Swing Adsorption, Silica gel.

I. INTRODUCTION

Globally the fossil fuels are the primary source for electricity generation and consequently the CO₂ emissions generated by fossil fuels combustion represents about 50% from the CO₂ emissions worldwide [1], [2]. In this context, for CO₂ emissions diminishing, the integration of the Carbon Capture and Storage (CCS) technologies are required. The CO₂ capture technologies developed in the present are based on: chemical absorption and adsorption; physical absorption and adsorption; membrane; and chemical looping combustion [3]-[5]. The integration into a power plant of these technologies are not possible yet due to the amount of flue gases generated by the fossil fuel combustion [2]. Today, the most developed CO₂ capture technology which can be applied in an existent power plant or a new power plant is chemical absorption process based on aqueous alkanolamine [6]-[8]. The main drawbacks of CO₂ capture post-combustion by chemical absorption are: the high thermal energy required for solvent regeneration, the high equipment degradation due to the corrosivity of the chemical solvent and the large surface occupied by the absorption column [9], [10]. Therefore, in the last years, more researchers are concentrated to develop the adsorption technology to separate the CO₂ from a stream gas [11]-[14]. The gas adsorption process consists to separate the active component from a stream by using a solid material. The adsorbents have a great advantage due to their adaptation for

capturing the carbon dioxide post- or pre-combustion according to many factors. The adsorption efficiency is determined by the physical and chemical properties of adsorbents. Prior the adsorption process, the flue gases passes through a stage of pre-treatment for removing the impurities, such as NO_x, SO_x and dust, because most of the adsorbent materials have also a selectivity for these impurities. After the adsorption process, the adsorbents are regenerated for separating the CO₂. We found in literature that the most developed methods for regenerating the solid adsorbents are: pressure swing adsorption (PSA), temperature swing adsorption (TSA) and vacuum swing adsorption (VSA) [12]. Several adsorbent materials was developed and studied like as zeolites, activated carbon, mesoporous silica, metal-organic frameworks (MOFs) and chemical adsorbents (amine based and amine impregnated) [13].

For adsorption process based on zeolites, the capacity of adsorption can reach up to 0.022 g_{CO₂}/g_{zeolite} for the temperatures in the range 0 – 100 °C, and pressure between 0.1 – 1 bar [15]. The studies has shown that the capacity adsorption of zeolites decreases in presence the impurities and the humidity from the stream gas which are treated [13]-[15]. The method applied for regeneration is TSA, due to the physical and chemical process for CO₂ adsorption at the adsorbent surface [15]. The adsorption with zeolites is suitable for capturing CO₂ from the flue gases post-combustion due to the kinetics adsorption of zeolites and the operating conditions specified above.

Activated carbon can be procured from many sources such as biomass, coal, industrial by-products etc. Although, the large raw materials variety used for obtaining the activated carbon represents an advantage, its structure, size and pores distribution depends on the nature of the material used, as consequently the performances of adsorption process. As in the zeolites case, the impurities must be removed prior the adsorption process [13]. The adsorption capacity of the activated carbon is higher for a CO₂ partial pressure higher than 1.7 bar and for a temperature between 25 – 75 °C [16], thus the activated carbon can be applicable for capturing the CO₂ in the post-combustion processes. The method used for regeneration the adsorbent is PSA, due to lower adsorption heats [17]. The activated carbon continue to be a competitive

adsorbent, due to the low cost with raw materials and the method of regeneration.

The MOFs are a promising method for CO₂ adsorption due to its capacity of adsorption, variation of the structures as well as the size of the pores. The previous studies are shown that MOFs have higher capacity of CO₂ adsorption comparative to zeolites or activated carbon for high partial pressure of CO₂ and a temperature of 25 °C [18]. For example, in the same conditions of pressure and temperature, 35 bar and 25 °C, the capacity of adsorption for each adsorbent was of 1.47 gCO₂/gMOF, 1.13 gCO₂/g_{activated_carbon} and 0.32 gCO₂/g_{zeolites} [18], [19]. Thus, the adsorption process by MOFs is suitable for pre-combustion CO₂ capture and the optimal method for regeneration of adsorbent is PSA.

The mesoporous silica bed is a physical adsorbent being characterized by the higher specific surface, the large volume of pores and the high thermal and mechanical stability [20]. For increasing the capacity of adsorption process in the case of mesoporous silica, often the amine is impregnated in the silica structure [20]. The adsorbents based on amine have the advantage that CO₂ adsorption capacity is not influenced by the CO₂ partial pressure, thus, the adsorbents can be applied for CO₂ capture post-combustion. The CO₂ is chemical adsorbed by the adsorbent, thus, the TSA method for bed adsorbent regeneration is required. Several researchers were analyzed the effects on the CO₂ adsorption capacity of different silica supports impregnation with polyethyleneimine (PEI) ratio [21], [22]. It was observed that the higher the PEI impregnation ratio is, the higher the amount of CO₂ adsorbed by silica support is [22]. Another factor that influences the adsorption process is the temperature of the flue gases that will be treated. It was reported that at temperature of 25 °C the capacity of sorbent is smaller than 75 °C [20].

In this study we evaluated and compared the performances of two adsorption beds based on silica gel impregnated with PEI at 50 wt. % and activated carbon.

II. METHODOLOGY

A. Process description

The adsorption process based on silica gel with PEI and activated carbon was studied for identifying the adsorption time influence on the CO₂ capture process. The physical properties of the adsorbents are presented in Table I.

Table I. Physical properties of adsorbents [23]

Properties	Value silica with PEI	Value activated carbon
Specific surface area (m ² /g)	845	800
Density (kg/m ³)	1216	2100
Desorption temperature (°C)	150	150
Pore volume (% of total)	~ 56	~ 32
Pore size (nm)	~ 35	~ 25
Pore volume (cm ³ /g)	0.38	0.57

The adsorption is thermodynamic exothermic process thus the thermal heat from external source decreases for equilibrate the heat produced of system. The temperature of adsorption process should be constant for an isotherm process. The

adsorption efficiency (adsorption capacity) of adsorbents is according to their surface characteristics and pores structures. The amount of gas adsorbed per gram of solid material at equilibrium depends the pressure and the temperature of the process and also the properties of adsorbent. The capacity of adsorption varies from a type of solid material to another even if apparently it have the same chemical composition.

The selection of adsorbent depends on the isotherm equilibrium of all constitutive elements of stream gas in the range operating pressure and temperature. The adsorption isotherms mainly based on the potential interaction and on the geometry/structure of adsorbent. The adsorption isotherms influences the design of separation process and it has impact on the following factors:

- The adsorption capacity of CO₂ in the operating range of pressure and temperature;
- The adsorbent length of the unused bed (LUB);
- The method of adsorbent regeneration;
- The purity of the CO₂ adsorbed after the bed regeneration.

In this study, the method used for bed regeneration (PEI impregnated silica gel and activated carbon) was TSA. The TSA cycle consists in variation of the temperature in the packing bed. As we know, at low temperature the CO₂ is adsorbed in the bed and at high temperature it is released from the bed. The partial pressure of the CO₂ in a transversal section of the bed is maintained constant. The principle diagram of the TSA process is shown in Fig. 1.

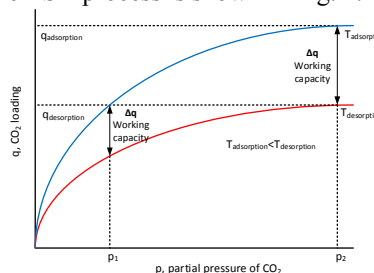


Figure 1. Temperature swing adsorption process [24]

B. Process Simulation in Aspen Adsorption

The TSA cycle for adsorption CO₂ in Aspen is based on the mathematical model of one-dimensional dynamic column. The model was validated by several researchers by comparing it with results obtained experimentally [25]-[27]. The assumptions underlying the mathematical model and the Aspen simulation are the following:

- The gas phase is represented by the ideal gas law;
- The heat dispersion and radial mass are neglected;
- The axial dispersion is considered;
- The superficial velocity is given by Darcy's law;
- The kinetics of mass transfer in solid phase are described by the linear driving force model (LDF);
- The particle size is uniform in the whole column;

- The adsorption equilibrium and the adsorption isotherms is based on the Langmuir isotherm model.

The adsorption process simulated in Aspen Adsorption is presented in Fig. 2. The TSA cycle consists of three steps: adsorption, heating (regeneration) and cooling (Fig.3). In this article, the CO₂ separation from a simulated gas (exhaust flue gases) was studied, the flue gases composition used contains 13 % CO₂ and 87 % N₂. The input parameters value of the flue gases as well as for the adsorbents used are shown in Table II. Also, the characteristics of the column used are presented in Table II.

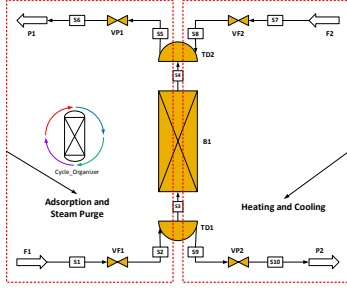


Figure 2. Flowsheet adsorption process in Aspen Plus [27]

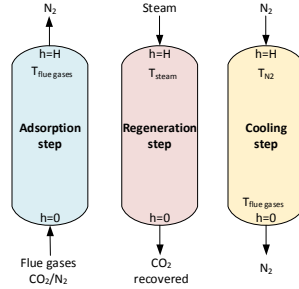


Figure 3. TSA cycle in 3 steps

Table II. Main parameters of adsorption process [20-22]

Column characteristics	Value for activated carbon	Value for silica gel with PEI
Column height, H, (mm)	100	100
Column wall thickness, δ (mm)	0.0254	0.0254
Column inside diameter, d _i , (mm)	9.5	9.5
Particle radius, r, (mm)	0.9	1
Void fraction, ε, (-)	0.32	0.39
Porosity, Φ, (-)	0.4	0.312
Tortuosity, τ, (-)	2.2	2.9
Flue gases and adsorbent characteristics	Value for activated carbon	Value for silica gel with PEI
Flue gases pressure, p _{flue_gases} , (bar)	1	1
Flue gases temperature, T _{flue_gases} , (°C)	95	95
Ambient temperature, T _{am} , (°C)	20	20
Column wall density, ρ _{wall} , (kg/m ³)	7850	7850
Flue gases dynamic viscosity, μ _{gases} , (kg/m·s)	0.0000215	0.0000215
Molecular diffusion, D _m , (m ² /s)	0.0000183	0.0000183
Specific heat flue gases, c _{p,gases} , (J/(kg·°C))	31.3	31.3
Specific heat adsorbent, c _{p,ad} , (J/(kg·°C))	1650	1230
Specific heat wall, c _{p,wall} , (J/(mole·°C))	500	500
Specific heat adsorption step, c _{p,ads} , (J/(mole·°C))	43.8	39.5

The flue gases are introduced into the packing bed at the bottom of the adsorption column (h=0) with a temperature of 95 °C and at atmospheric pressure. The temperature and pressure of flue gases are the initially conditions for the adsorption step. After the CO₂ is adsorbed, the packing bed is prepared for the regeneration step, the heating of packing bed

is accomplished by using steam. For increasing the bed temperature to 150 °C, the steam flow that comes in direct contact with the adsorbent is introduced in countercurrent with gases flow at the top of the column (h=H, H is the height of the column). At the bottom of the column is collected the CO₂ recovered (captured) from the packing bed. The final step of cycle consists of cooling the bed, for preparing the packing bed at the initially conditions for the adsorption step. The cooling process is performed by introducing in the adsorption column (h=H) the N₂ at 105 °C until the bed is cooled to 95 °C, the N₂ needs to be introduced at a temperature higher than 100 °C, in order to prevent the condensation of the steam in the bed. In Table III are presented the streams temperatures and the time set for each step of the temperature swing adsorption process.

Table III. TSA cycle conditions

TSA cycle 3 steps	Temperature stream	Time step
Adsorption step	T _{flue_gases} =95 °C	t _{ads} =0..110 s
Regeneration step	T _{steam} =150 °C	t _{reg} =250 s
Cooling step	T _{N2} =105 °C	t _{cool} =400 s

The purity of CO₂ was calculated as report between the total moles of CO₂ and the total moles of CO₂ and N₂ collected after the regeneration of the packing bed (Eq. 1). The total amount of the CO₂ recovered (CO₂ captured) is the ratio between the total moles of CO₂ after the bed regeneration and the total moles of CO₂ which enters in the column in the adsorption step (Eq. 2). To evaluate the capacity adsorption of CO₂ by the solid material it was calculate the productivity of CO₂. The productivity is the rapport between the total moles of CO₂ at the end of the adsorption step and the product between the mass of packing bed used and the time for complete TSA cycle (Eq. 3).

$$CO_2_{purity} = \frac{n_{CO_2}^{reg}}{n_{CO_2}^{reg} + n_{N_2}^{reg}} * 100(\%) \quad (1)$$

$$CO_2_{recovery} = \frac{n_{CO_2}^{reg}}{n_{CO_2}^{ads}} * 100(\%) \quad (2)$$

$$CO_2_{productivity} = \frac{n_{CO_2}^{reg}}{q_{ads} \cdot t_{cycle}} \text{ (mole/(g·s))} \quad (3)$$

$$t_{cycle} = t_{ads} + t_{reg} + t_{cool} \text{ (s)} \quad (4)$$

where: $n_{CO_2}^{reg}$ - the number of CO₂ moles after the regeneration step in the product (mole); $n_{N_2}^{reg}$ - the number of N₂ moles after the regeneration step in the product (mole); $n_{CO_2}^{ads}$ - the number of CO₂ moles in the initial composition of the flue gases (mole); q_{ads} - the mass of the adsorbent (g); t_{cycle} - is the total time for the TSA cycle (s); t_{ads} - is the time for the adsorption step (s); t_{reg} - is the time for the regeneration step (s); t_{cool} - is the time for cooling step (s).

III. RESULTS AND DISCUSSIONS

The time set for the adsorption step influences the purity and the recovery of CO₂. In this study, the adsorption time was varied in the range 0..110 s, and the adsorption column was initial filled with nitrogen. In Fig. 4, the results obtained for the purity and the recovery of CO₂ for silica gel impregnated with PEI are shown. The purity of CO₂ increases with the adsorption time due to higher amount of CO₂ in the exhaust gases. On the other hand, as the CO₂ is adsorbed in the bed the nitrogen is released from the adsorption column, thus, more moles of carbon dioxide are found in the bed. The recovery of CO₂ decreases as the adsorption time is increased due to lower amount of the carbon dioxide absorbed along of the bed during the process.

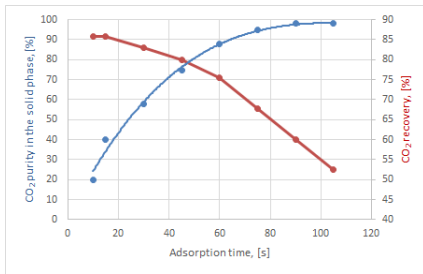


Figure 4. CO₂ purity and recovery variation for silica gel with PEI

As we noticed, no major difference between the CO₂ purity variations in the activated carbon case compared to silica gel with PEI (Fig. 5). The maximal purity was attained after the same period of time due to the same composition of the exhaust flue gases and the same initial conditions in the adsorption column. We can conclude, that the adsorption time chosen for CO₂ adsorption was optimal of 100 s.

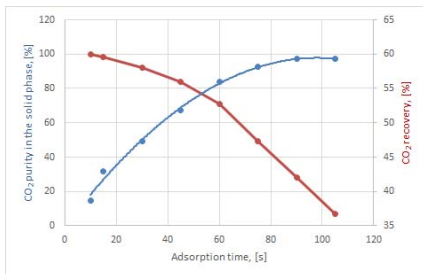


Figure 5. CO₂ purity and recovery variation for activated carbon

For establishing the bed characteristics influence on the CO₂ molar variation along to the bed length, six variations for different adsorption time were presented in Figures 6-7 for both adsorbents. Thus, no large variations of the CO₂ concentration along to the bed in the solid phase were observed, irrespective the adsorption time exposure. However, the presence of the amine in the silica gel structure has a positive influence of the CO₂ attraction. In the future works, it will be interesting to analyze the amount of thermal energy required for the adsorbent regeneration.

As we expected, as the adsorption time increases a faster saturation of the adsorbents was obtained. For highlighting the conclusion mentioned above, a comparison between the two adsorbents was realized in Fig. 8. The CO₂ concentration at the adsorption column inlet was higher in the silica gel

with PEI case compared with the activated carbon case due to the amine presence. The difference between the cases is maintained irrespective the adsorption time.

For establishing the CO₂ adsorption capacity of the adsorbents, the CO₂ productivity (Fig. 9) was determined for each one taking into account the mass of the adsorbents and the total time of the complete cycle (see the Eq. 3).

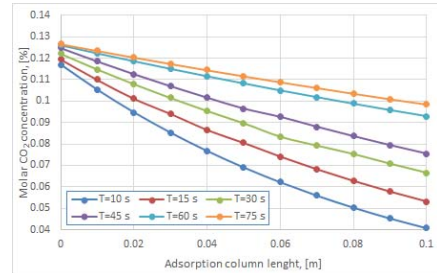


Figure 6. CO₂ concentration in the solid phase for silica gel with PEI

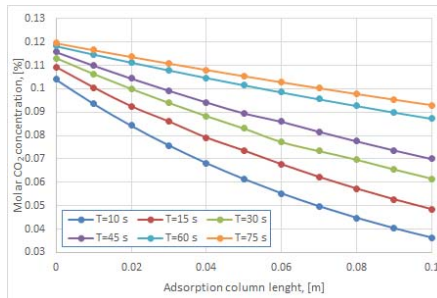


Figure 7. CO₂ concentration in the solid phase for activated carbon

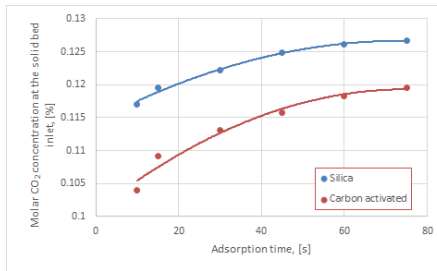


Figure 8. CO₂ concentration at the solid bed inlet

Due to the fact that for a low adsorption time a higher amount of carbon dioxide is adsorbed by the silica with PEI compared to activated carbon, and the activated carbon is defined by a higher density (2100 compared to 1216 kg/m³), the CO₂ productivity is higher for the first adsorbent.

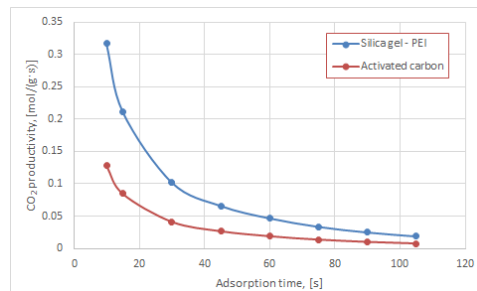


Figure 9. CO₂ productivity according to the adsorption time

CONCLUSIONS

In this paper a study concerning the adsorption of the carbon dioxide was conducted using the Aspen Plus V9 software. Thus, two adsorbents like silica gel with PEI impregnated and activated carbon as benchmark case were analyzed. We consider that the adsorption time is a key factor for dimensioning the adsorption column and for choosing the optimal adsorbent. However, if the silica gel with PEI impregnated will be used for CO₂ separation, a lower investment will be required for retrofitting a power plant or an industry technology. This technology could be integrated both in energetic or industrial sector. For industrial sector two research directions are followed: glass and cement factories.

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