Abstract

A two-bed pressure swing adsorption system on a commercial type of zeolite 13X adsorbent has been studied numerically over a wide range of operating conditions to helium separation from gaseous mixture. The model includes energy, mass and momentum balances. The coupled partial differential equations are solved using fully implicit forth order Rung-Kutta scheme in the simulation. The effects of adsorption step pressure, adsorption step time and feed flow rate on the helium purity and recovery were investigated. Results shown that as the adsorption step pressure increases the helium purity will be increased. In addition, the helium recovery increases, and the helium purity decreases when the feed flow rate increases. Finally, the simulation results indicated a very good agreement with some current literature experimental work.

Keywords: Pressure Swing Adsorption; Helium Recovery; Mathematical Modeling; Numerical Simulation; Zeolite 13X

1. Introduction

Helium is a chemical element with symbol He and atomic number 2. It is a colorless, odorless, tasteless, non-toxic, inert and monatomic gas, which is the first in the noble gas group in the periodic table. The boiling and melting points of He are the lowest among all the elements.

Helium is the second lightest element and is the second most abundant element in the observable universe, being present at about 24% of the total elemental mass, which is more than 12 times the mass of all the heavier elements combined. Helium was first detected as an unknown yellow spectral line signature in sunlight during a solar eclipse in 1868 by French astronomer Jules Janssen. In 1903, large reserves of helium were found in natural gas fields in parts of the United States, which is by far the largest supplier of the gas today.

Liquid helium is used in cryogenics (its largest single use, absorbing about a quarter of production), particularly in the cooling of superconducting magnets, with the main commercial application being in MRI scanners. Helium’s other industrial uses — as a pressurizing and purge gas, as a protective atmosphere for arc welding and in processes such as growing crystals to make silicon wafers, account for half of the gas produced. A well-known but minor use is as a lifting gas in balloons and airships. On the Earth, it is relatively rare 5.2 ppm by volume in the atmosphere.

Pressure swing adsorption (PSA) process is a wide operating unit to separate and purify the gases that operates based on capability of solids ad-
sorption and selective separation of gases. The important operational parameter in this system is the pressure, and most industrial units operate at or very close to the surrounding temperature. Today, the PSA process is completely known in a wide region of the processes, and this process was preferred in contrast to other conventional separation methods, especially for lower capacity and higher purity.

Linde Group developed the world’s first air separation plant for the production of oxygen in 1902 and the first production facility was set up as early as 1903. Since then, it is one of the world’s largest helium suppliers and since 1994 Linde has been the sole provider of helium and helium separators by the method of swing adsorption. Bhushan[2] purified helium by gas adsorption method in 2011. The purifier was designed to purify up to 40% impurity to give 4.5 grade or 99.995% pure helium by high pressure and low temperature cryosorption process. Activated carbons have been used for a long time at low temperature for cryogenic applications. The pore geometry and size can be used to optimize the carbon structure for a specific application. In 1978, Stoll et al.[3] commissioned a fully automatic large capacity helium purifier which included operation, regeneration, re-cooling and re-pressurization time. In 2007, E. Van Cleve et al.[4] developed a cryogenic pulsed laser deposition (PLD) system to deposit lithium films onto a quartz crystal microbalance (QCM) and adsorption isotherms of 4 He on lithium were measured. PLD system was used to form lithium substrates and the first helium adsorption measurements on this surface were reported. In 2008, Nisith Kr. Das[5] employed a technique known as pressure swing adsorption to concentrate a lean amount of helium present in natural gas through selective physical elimination of N₂, CO₂, CH₄ and heavier hydrocarbons in a stepwise cycle sequence at present time intervals. In 2011, D. Martins et al.[6] reported on the low temperature adsorption properties of He, H₂, and N₂, using three activated carbons with different pore size distributions. In 2012, R. Majidia et al.[6] used the molecular dynamics simulation to study the helium adsorption on the CNCs with a declination angle of 240° and 300°. The results indicated that the adsorption capacity of the CNCs became considerable by decreasing the declination angle. In the same year, Nisith Kr. Das et al.[7] developed a helium purification system using a three-bed seven-step pressure swing adsorption (PSA). It removed impurities like N₂ and O₂ from a ternary mixture leaving out high-purity helium from the gas mixture. The PSA system operated successfully resulting in high-purity helium (>99.9%) with a yield of around 89%. The adsorption capability of carbon dioxide on 5A molecular sieve (5AMS) was investigated in a fixed-bed apparatus with two-road gas mixing system by dynamic column breakthrough method with helium as the carrier gas for helium purification system of high-temperature gas-cooled reactor (HTGR) in 2013 by Chang Hua et al.[8]

In 2014, Bartolomei et al.[9] performed quantum dynamical simulations on reliable new force fields in order to assess the graphdiyne capability for helium chemical and isotopic separation.

In this work, a semi-industrial PSA unit for helium recovery from gaseous mixture was simulated. In this process, the effect of some operating variables such as adsorption time, feed flow rate, and adsorption pressure on process performance was investigated. The simulated PSA process is a six-step process with the following sequence (Figure 1): (I) co-current feed pressurization (PR); (II) high-pressure adsorption (AD) step; (III) counter-current depressurizing pressure equalization (ED) step; (IV) counter-current blow down (BD) step; (V) counter-current purge with a light product (PG) step; (VI) co-current pressurizing pressure equalization (EP) step. The sequence time table of the PSA process was also depicted in Table 1.
Table 1. Step sequence of the PSA process

| No. | 1   | 2   | 3   | 4   | 5   | 6   |
|-----|-----|-----|-----|-----|-----|-----|
| Time (sec.) | 25  | 60  | 10  | 25  | 60  | 10  |
| Column 1   | PR  | AD  | ED  | BD  | PG  | EP  |
| Column 2   | BD  | PG  | EP  | PR  | AD  | ED  |

SV1: on on off on on off
SV2: off off on off off off
SV3: off off off off off off
SV4: on on off on off on
SV5: on on off on on on
SV6: on on off on on on
SV7: off off off off off off
SV8: off off off off off off
SV9: off off off off off off
SV10: off off off off off off
SV11: off off off off off off
SV12: off off off off off off
SV13: off off off on off off

Figure 1. Schematic diagram of He-PSA.

2. Mathematical model

In order to develop a mathematical model for an adsorption bed, the following assumptions were made:

1- Gas behaves as an ideal gas;
2- The flow pattern is axially assumed as plug-flow model;
3- Equilibrium equations for air are expressed as multi-component Langmuir-Freudlich isotherm;
4- Rate of mass transfer is presented by linear driving force (LDF) relations;
5- Bed is clean at initial state and there is no gas flow in it;

According to these assumptions, dynamic behavior of system in terms of mass, energy and momentum balances can be expressed as follows:

Dimensionless partial mass balance for gas phase in the adsorption bed is \([9-12]\):

$$\left(\frac{1}{\hat{P}}\right) \frac{\partial \hat{P}}{\partial \hat{\tau}} + \frac{\partial \hat{u}}{\partial \hat{z}} + \frac{\partial \hat{u}}{\partial \hat{z}} - \left(\frac{\hat{P}}{\hat{P}_0}\right) \frac{\partial \hat{P}}{\partial \hat{z}} = \left(\frac{1}{\hat{P}}\right) \frac{\partial \hat{P}}{\partial \hat{\tau}} + \frac{\partial \hat{u}}{\partial \hat{z}} + \frac{\partial \hat{u}}{\partial \hat{z}} + \frac{\partial \hat{u}}{\partial \hat{z}} + \left(\frac{\hat{P}}{\hat{P}_0}\right) \frac{\partial \hat{P}}{\partial \hat{z}} = \frac{\partial \hat{q}_{m,i}}{\partial \hat{\tau}} \frac{\partial \hat{q}_{m,i}}{\partial \hat{\tau}} = 0 \tag{1}$$

Dimensionless equilibrium loading of \(i\) th component for solid phase in the adsorption bed is:

$$\frac{\partial \hat{q}_{m,i}}{\partial \hat{\tau}} = \frac{\partial \hat{q}_{m,i}}{\partial \hat{\tau}} \frac{\partial \hat{q}_{m,i}}{\partial \hat{\tau}} = k_{2,i}T_0 \frac{\partial \hat{q}_{m,i}}{\partial \hat{\tau}} \tag{2}$$

Dimensionless loading of \(i\) th component for solid phase in the adsorption bed is (LDF relation):

$$\frac{\partial \hat{q}_{i}}{\partial \hat{\tau}} = \alpha_i \left( \frac{\beta_i y_i n_i}{1 + \sum_{j=1}^{N} \beta_j y_j n_j} - \frac{\hat{q}_{i}}{\hat{q}_{m,i} \frac{\partial \hat{q}_{m,i}}{\partial \hat{\tau}}} \right) - \left(\frac{\hat{q}_{i}}{\hat{q}_{m,i} \frac{\partial \hat{q}_{m,i}}{\partial \hat{\tau}}} \right) \tag{3}$$

According to equation (3), the LDF relation depends on various parameters such as: equilibrium parameter for the Langmuir model, mole fraction of species \(i\) in the gas phase, average amount adsorbed and equilibrium parameter for the Langmuir model.

The equilibrium of triple Langmuir-Freudlich isotherm is as follows:

$$\hat{q}_{i} = \frac{\beta_i y_i n_i}{1 + \sum_{j=1}^{N} \beta_j y_j n_j} \tag{4}$$

where \(\beta, n, q_m\) are as follows:

$$q_{m,i} = k_1 + k_2 T_0 \hat{P} \tag{5}$$

$$\beta_i = k_3 \exp \left(\frac{k_4}{T_0}\right) \tag{6}$$

$$n = k_5 + \frac{k_6}{T_0} \tag{7}$$

Overall dimensionless mass balance for gas phase in the adsorption bed is\([13-16]\):

$$\left(\frac{1}{\hat{P}}\right) \frac{\partial \hat{P}}{\partial \hat{\tau}} + \frac{\partial \hat{u}}{\partial \hat{z}} + \frac{\partial \hat{u}}{\partial \hat{z}} - \left(\frac{\hat{P}}{\hat{P}_0}\right) \frac{\partial \hat{P}}{\partial \hat{z}} = \left(\frac{1}{\hat{P}}\right) \frac{\partial \hat{P}}{\partial \hat{\tau}} + \frac{\partial \hat{u}}{\partial \hat{z}} + \frac{\partial \hat{u}}{\partial \hat{z}} + \frac{\partial \hat{u}}{\partial \hat{z}} + \left(\frac{\hat{P}}{\hat{P}_0}\right) \frac{\partial \hat{P}}{\partial \hat{z}} = 0 \tag{8}$$
Dimensionless energy balance for gas phase in the adsorption bed is\(^{(17-21)}\):

\[
- \left( \frac{1}{\rho_a} \right) \frac{\partial T}{\partial z} + \varepsilon \left( \frac{\partial T}{\partial r} + \frac{T}{\rho_a C_p} \right) + \left( \frac{\partial u}{\partial t} + \frac{\partial \rho_a C_p}{\partial z} \right) \frac{\partial T}{\partial r} = \frac{\rho_a C_p}{\rho_a C_p} \left( \frac{\partial h}{\partial r} \right) + \frac{\rho_a C_p}{\rho_a C_p} \frac{\partial h}{\partial t} + \frac{\rho_a C_p}{\rho_a C_p} \left( \frac{\partial h}{\partial t} \right) = 0
\]

(9)

Dimensionless energy balance for the wall of adsorption bed is:

\[
\frac{\partial \theta}{\partial t} = \left( \frac{2\pi R_{B,0} h_w L}{\rho_w C_p A_w U_0} \right) \left( \frac{T_w}{T_0} - \frac{T_a}{T_0} \right)
\]

(10)

Cross-sectional area of adsorption bed wall is:

\[A_w = \pi \left( R_{B,0}^2 - R_{B,i}^2 \right)\]

(11)

Ergun equation is utilized in order to investigate the pressure drop across the adsorption bed\(^{(22,23)}\):

\[-\frac{dP}{dz} = [a \mu U_0 \bar{u} + b \rho \bar{u}^2 \bar{u}, \bar{u}] \left( \frac{L}{P_0} \right)\]

(12)

\[a = \frac{150}{4R_p} \left( \frac{1-\epsilon}{\epsilon^2} \right)^2; \quad b = 1.75 \left( \frac{1-\epsilon}{2R_p \bar{u}} \right)
\]

(13)

Physical properties of adsorbents and characteristics of adsorption bed are depicted in Tables 2 and 3, respectively.

**Table 2. Physical properties of bed and adsorbent**\(^{(24)}\)

| Characteristic          | Zeolite 13X |
|-------------------------|-------------|
| Type                    | Sphere      |
| Average pellet size, R_p (cm) | 0.07        |
| Pellet density, \(\rho_p\) (g/cm\(^3\)) | 1.17        |
| Heat capacity, \(C_p\) (cal/g.K) | 0.32        |
| Bed porosity, \(\varepsilon\) | 0.391       |
| Bed density, \(\rho_b\) (g/cm\(^3\)) | 0.713       |

**Table 3. Adsorption bed properties**\(^{(25)}\)

| Characteristic          | Zeolite 13X |
|-------------------------|-------------|
| Length, L (cm)          | 76          |
| Inside radius, \(R_{i0}\) (cm) | 2.138       |
| Outside radius, \(R_{o0}\) (cm) | 2.415       |
| Heat capacity of the column, \(C_{pv}\) (cal/g.K) | 0.12        |
| Density of column, \(\rho_c\) (g/cm\(^3\)) | 7.83        |
| Internal heat-transfer coefficient, \(h_i\) (cal/cm\(^2\).K.s) | \(9.2 \times 10^{-4}\) |
| External heat-transfer coefficient, \(h_o\) (cal/cm\(^2\).K.s) | \(3.4 \times 10^{-4}\) |
| Axial thermal conductivity, \(K_i\) (cal/cm.s.K) | \(6.2 \times 10^{-5}\) |
| Axial dispersion coefficient, \(D_i\) (cm\(^2\)/s) | \(1 \times 10^{-5}\) |

3. Results and discussion

The fourth order Runge-Kutta Gill scheme was used to solve a mathematical model considered as coupled partial differential equations. The experimental data obtained from literatures has been simulated in order to validate the simulation results in this study\(^{(10,22,26)}\). An experimental and simulation study of a PSA unit which is running a traditional Skarstrom cycle and a Skarstrom cycle with co-current equalization owing to separate oxygen from air using a 5A zeolite has been proposed by Mendes et al.\(^{(11)}\) in 2001. Moreover, a small-scale two-bed six-step PSA process using zeolite 13X was performed by Jee et al.\(^{(27-30)}\) in order to provide oxygen-enriched air. They showed that there is a strong effect of feed flow rate on \(O_2\) purity. The effects of adsorption and desorption on zeolite 5A and CMS beds were investigated in a mixture of \(N_2/O_2\) by Jee et al.\(^{(31)}\) in 2004. A non-isothermal mathematical model was applied in order to simulate the adsorption dynamics in their studies\(^{(26)}\).

Figures 2(a) and (b) indicate the effect of product flow rate and P/F on the purity and recovery of oxygen during PSA process, respectively. The impact of temperature variations in gas phase during adsorption as a function of time is illustrated in Figure 2(c). It is obviously seen that there is a relatively high accuracy in the simulation of experimental data\(^{(27)}\).
Figure 2c. Numerical simulation of experimental data in this work\[26\].

Figure 3 shows the effects of feed flow rate on helium purity and recovery at adsorption pressure of 8.5 bar and adsorption time of 20 sec. In this figure it can be seen that the increase in feed leads to a decrease in the helium purity while helium recovery has increased. The feed flow will rise at a constant purge flow in these simulations, which the P/F decreases and subsequently helium purity decreases. At a certain purge flow rate when the feed amount increases therefore, the P/F ratio is reduced and finally, the product purity decreases. In the other word, dead space of the bed in the adsorption step will rise with the feed flow rate. Thus, purging the bed in the purge step requires more purgative flow. In these simulations, a constant purge flow rate causes a reduction in the helium purity with the feed flow rate.

The variations of helium purity and recovery in terms of adsorption step time at pressure of 5.5 bar and P/F of 0.1 are shown in Figure 4. It is clear from this figure that increase of adsorption time leads to reduction in helium purity. It is due to the well-known breakthrough time of the adsorption beds. Thus, the adsorption time should be near to the breakthrough time in order to achieve the maximum process performance in terms of adsorption time. In fact, the adsorption time is a required time for occurring breakthrough time. After this time, the product purity is decreased while the entire capacity of the bed has not utilized before this time. Therefore, the adsorption time must be close to the breakthrough time in order that the best process performance in terms of adsorption time is achieved\[10\]. With referring to this figure, the best time for adsorption is 25 sec. Furthermore, it should be noted that, the helium recovery is in reverse order with its purity at all points. It was evident that the recovery reduces as the gas volume of the feed increases through increasing the adsorption time. Figure 5 shows the effect of adsorption step pressure on the process performance. It is apparent from this figure that the higher adsorption pressure improves the PSA unit performance. As the adsorption pressure increases, the amount of adsorbed heavy species on the adsorbent will be increased and therefore, the helium purity increases. For the favorable isotherm systems, if the pressure is increased, the highly adsorbed species are more adsorbed and the product purity will be increased. This result was seen in the literature\[10-12,15,16,21,26,31,32\]. Helium concentration profile curves are depicted in Figure 6. It is obvious from this figure that the helium purity has a minimum and maximum quantity in the blow down step because of depressurized bed and the pressurization step as result of the cleansed bed, respectively.
Helium separation from gaseous mixture in a two-bed pressure swing adsorption setup on a commercial type of zeolite 13X adsorbent has been studied numerically over a wide range of operating conditions. The influences of adsorption step pressure, adsorption step time and feed flow rate on the process performance were investigated. Results showed that as the adsorption step pressure increases, the helium purity will be increased. The time of the adsorption step is clearly defined through the physical properties of the bed such as length, diameter, adsorbent type as well as the feed flow rate. Furthermore, the helium recovery increases, and the helium purity decreases when the feed flow rate increases. Finally, a considerable agreement was found between the experimental data and the simulation results for various operating variables.

4. Conclusions

Helium separation from gaseous mixture in a two-bed pressure swing adsorption setup on a commercial type of zeolite 13X adsorbent has been studied numerically over a wide range of operating conditions. The influences of adsorption step pressure, adsorption step time and feed flow rate on the process performance were investigated. Results showed that as the adsorption step pressure increases, the helium purity will be increased. The time of the adsorption step is clearly defined through the physical properties of the bed such as length, diameter, adsorbent type as well as the feed flow rate. Furthermore, the helium recovery increases, and the helium purity decreases when the feed flow rate increases. Finally, a considerable agreement was found between the experimental data and the simulation results for various operating variables.

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