Parametric Study for Nitrogen Separation from Air by Pressure Swing Adsorption Using Carbon Molecular Sieve

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Abstract

The separation of air by carbon molecular sieve (CMS) adsorption was studied in this work over a range of adsorption pressure of (2–8) bar. Breakthrough curves showed no significant effect of the pressure on product nitrogen purity and adsorbent capacity above 4 bar. Maximum purity of about 98% is observed for time up to 60 s. Adsorbent capacity obtained is in agreement with multicomponent Langmuir isotherm up to 4 bar. Maximum constant adsorbent capacity of about 0.1 mol O2/kg CMS is obtained for pressure above 4 bar.

For PSA two columns 6-steps process, no significant effect of the pressure on the product purity above 4 bar. The purity increases with decreasing the productivity. Maximum purity of 97.6% is obtained at productivity of 156 lit/kg CMS.hr, cycle time of 100 s, and purge flowrate of 1 lit/min. The productivity of 606 lit/kg CMS.hr is obtained at purity of 94%, cycle time of 60s, and purge flowrate of 4 lit/min.

Keywords: Adsorption, Breakthrough, Nitrogen separation, PSA.

دراسة العوامل المؤثرة على فصل النيتروجين من الهواء بطريقة الامتزاز بتغير الضغط باستعمال الكاربون المنخلي

الخلاصة

تم دراسة فصل الهواء بواسطة الكاربون المنخلي للجزيئات (CMS) ل مدى ضغط امتزاز من 2 إلى 8 بار. بينت النتائج من دراسة منحنى الاختراق أنه لا يوجد تأثير ملحوظ للضغط على نقاوة الناتج و على سعة المادة المازة عند ضغط أعلى من 4 بار. أعلى نقاوة كانت بحدود 98% حتى 60 ثانية من وقت الامتزاز. و سعة المادة المازة كانت متوافقة مع منحنى توازن لانكمور متعدد المكونات حتى 4 بار. ظهرت أعلى سعة ثابتة بحدود (0.1 mol O2/kg CMS) عند ضغط أعلى من 4 بار. بالنسبة لطريقة الامتزاز بتغير الضغط (PSA) تتكون من عمودين و ست خطوات تشغيل، بينت النتائج بعدد وجود تأثير ملحوظ للضغط أعلى من 4 بار على النفاوة. لوحظ زيادة النفاوة عند نقصان الإنتاجية. وكانت أعلى نقاوة بحدود 97.6% عند انتاجية (156 lit/kg CMS.hr) و عند زمن دورة 100 ثانية و معدل تشيش ي 4 لتر/ث. وكانت الانتاجية بحدود (606 lit/kg CMS.hr) عند نفاوة 94% و زمن دورة 60 ثانية و معدل تشيش ي 4 لتر/ث. و تتميز الانتاجية: الامتزاز، الاختراق، فصل النيتروجين، الامتزاز بتغير الضغط.
**Nomenclature**

- a: External surface area per unit particle volume m²/m³
- b: Sips equation constant bar⁻¹
- D: Bed inside diameter, cm
- dₚ: Adsorbent particle diameter, mm
- k: Adsorption rate constant s⁻¹
- L: Bed length, mm
- mₜ: Gas uptake at time t
- mₑq: Gas uptake at equilibrium
- Pₑ: Equalization pressure, bar
- Pₜₚ: Adsorption high pressure, bar
- Pₜₜ: Desorption low pressure, bar
- Qₚₚ: Product gas flow rate, lit/min
- Qₚₑq: Purge gas flow rate, lit/min
- qᵢ: Adsorption capacity of component i, mol/kg
- qₑq: Saturation adsorption capacity, mol/kg
- t: Time, s
- tₑq: Equalization time, s
- w: Adsorbent weight, kg
- yₒ₂: Oxygen gas purity
- yₙ₂: Nitrogen gas purity

**Greek Symbols**

- ρₒ: Bulk density, g/L
- ε: Bed porosity
- Δt: Time increment for breakthrough curve, s

**Introduction**

In 1964, PSA process was used to separate oxygen from air [1]. Pressure swing adsorption (PSA) processes, has become a subject of interest in gas separations and widely used in industries for air and other gas separations. Oxygen and nitrogen are produced from atmospheric air by either of two methods depending upon the volume of production. For high volume production, cryogenic distillation of liquefied air is employed, whereas, for low to medium volume production, air separations by methods such as pressure swing adsorption are found to be more economical, because of its low energy and cost requirement [2, 3, 4].

Activated carbon shows very little selectivity in the adsorption of molecules of different size. Special activation procedure of micropore size is used for carbon to behave as molecular sieve. The diameter of CMS micropore of about 4 to 9 Åo [5]. Carbon molecular sieve (CMS) is a carbonaceous material which has the pores of molecular dimensions that provide the relatively high adsorption capacity and kinetic selectivity for various molecules. Selectivity for gas uptake by CMS is controlled by the relative rates of diffusion of the adsorbing gaseous species that allows them to discriminate molecules on the basis of their size and shape [6]. Carbon molecular sieves (CMS) have become an increasingly important class of adsorbents for application in the separation of gas molecules that vary in size and shape [7].

Air separation can be achieved by the Pressure Swing Adsorption (PSA) process. This is a commercially important process allowing the separation of a mixture of gases into its components. The adsorbent used in PSA is a carbon molecular sieve (CMS), which utilizes kinetic differences in the adsorption of nitrogen and oxygen [8]. The CMS does not show a significant difference in equilibrium adsorption capacities between oxygen and nitrogen. However, oxygen is adsorbed faster than nitrogen, leading to a kinetic selectivity, which allows achieving nitrogen purities as high as 99.999%. The process, using carbon molecular sieves, was first developed by Bergbau Porschung GmbH and produces nitrogen of 97 to 99.9% vol. Separation principle is based on the difference between Oxygen and Nitrogen adsorption speed on CMS. [9] Oxygen, having a smaller diameter of kinetic molecule, and diffuses much faster on CMS than Nitrogen, therefore the rate of adsorption of O₂ is faster than that of N₂ by a factor of approximately 2.5*10⁻² and is due to large diffusion coefficient of O₂ into CMS in comparison with N₂. Consequently, we get enriched Nitrogen at adsorbent layer exit. PSA air separation systems with CMS are mainly used as Nitrogen generators, as Oxygen concentration in the desorbed gas (enriched Oxygen) is of only (30-45) % vol, due to the high partial pressure of Nitrogen in the air[9,10,11].

The transport process controlling the uptake rate of a gas seems to obey two different mechanisms, either diffusional molecular transport within the bulk of the micropores—Fickian sieves—or surface barrier at the micropore entrances— non-Fickian sieves. Different equations have been
proposed in the literature to describe the uptake of oxygen and nitrogen [11].

A Linear Driving Force Mass Transfer Model (LDF) has been used to evaluate the adsorption/desorption dynamics of pure gases and vapors on activated carbons, carbon molecular sieves. The LDF model can be described by the equation [8]:

\[ \frac{m_t}{m_{\text{inf}}} = 1 - e^{-kt} \] ...........................................(1)

The plot of ln(1 - \( m_t/m_{\text{inf}} \)) vs t should be a straight line with slope equal to k that is essentially comparable to \( d^2/a^2 \) in the Fickian diffusion model for spherical particles where \( m_t/m_{\text{inf}} > 0.5 \) [12]. The linear driving force (LDF) model, which was originally proposed, by Gleuckauf and Coates [13], for adsorption chromatography, is frequently used for this purpose because it is analytical, simple, and physically consistent [14].

In the present work, the characteristics of air separation by the single column adsorber packed with CMS are to be investigated for several adsorption pressure via breakthrough curves. Two column PSA unit is constructed to study the effect of operation conditions such as adsorption pressure, cycle time, equalization time, and gas purge flowrate on the product N₂ purity and productivity.

**Experimental Work**

The experimental work in this study was divided into two sections, Single column breakthrough characteristic, and two columns PSA Processes. Schematic diagram of single column, and two column PSA apparatus are shown in Figure (1), and Figure (2) respectively. The adsorption column is galvanized steel of diameter (D) of 25mm, and length (L) of 900mm. The pressure is controlled by a regulator installed on the feed line. The product and purge flowrates are controlled by two gas rotameter. Two pressure gauge at the top and the bottom of each column is used. Input and output connections are of 12mm tubing, fittings and solenoid valves. A programmed timer used to controller the operating time of the solenoid valves. The concentration of the effluent is measured by the oxygen analyzer (Model: DO-5510HA, lutron Company). The adsorbent used in this work is CMS. The adsorbent and adsorption column properties are listed in Table (1).

**Fig. 1.** Experimental setup of single column process

**Fig. 2.** Experimental setup of the two columns PSA process

The operating parameters considered in the two sections of the present work are:

**Single column characteristic process**
- Adsorption pressure, \( P_H = 2 \) to 8 bar.
- Effluent flowrate, \( Q_{\text{prod}} = 1 \) lit/min

**Two column PSA process**
- The original Skarstrom cycle with equalization step adopted in the present work.
- Cycle time = 40 to 120 s
- Adsorption pressure, \( P_H = 2 \) to 8 bar
- Purge flow rate, \( Q_{\text{pur}} = 1 \) to 4 l/min
- Product flow rate, \( Q_{\text{prod}} = 0.5 \) to 1 l/min
- Equalization step time, \( t_{\text{eq}} = 0 \) to 15 sec
The binary adsorption isotherm employed is the multicomponent Langmuir isotherm (Sips equation):

\[ \frac{q_i}{q_{si}} = \frac{b_i P_i}{1 + \sum b_i P_i} \] ..................................................(2)

The isotherm parameters for the pure components are shown in Table (1) [15].

**Table 1. Adsorption column and adsorbent properties**

<table>
<thead>
<tr>
<th>Adsorbent properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>CMS</td>
</tr>
<tr>
<td>Company</td>
<td>Pingxiang XingFeng</td>
</tr>
<tr>
<td>Shape</td>
<td>Granular</td>
</tr>
<tr>
<td>Particle diameter (d_p)</td>
<td>1.7 - 1.8</td>
</tr>
<tr>
<td>Bulk density (\rho_b) (g/L)</td>
<td>680-700</td>
</tr>
<tr>
<td>Bed porosity</td>
<td>0.37</td>
</tr>
<tr>
<td>Adsorption column</td>
<td></td>
</tr>
<tr>
<td>Length (m)</td>
<td>0.95</td>
</tr>
<tr>
<td>Inside diameter</td>
<td>25</td>
</tr>
<tr>
<td>Sips equation</td>
<td></td>
</tr>
<tr>
<td>Oxygen parameter</td>
<td></td>
</tr>
<tr>
<td>(q_s) (mol/kg)</td>
<td>1.513</td>
</tr>
<tr>
<td>(b) (1/bar)</td>
<td>0.121</td>
</tr>
<tr>
<td>Nitrogen parameter</td>
<td></td>
</tr>
<tr>
<td>(q_s) (mol/kg)</td>
<td>1.126</td>
</tr>
<tr>
<td>(b) (1/bar)</td>
<td>0.113</td>
</tr>
</tbody>
</table>

The experimental procedures for the single column characteristics are:
1. Preparation of the system using vacuum pump to remove tracer of oxygen.
2. Adjust the feed pressure by pressure regulator.
3. Control operation time (on/off) of the valves by controller, the operation time of the valves and steps of the procedure of two column PSA process, are shown in Table (2), and Figure (3) respectively.
4. Adjust the product flowrate and the purge flowrate by gas rotameters to desired values.
5. Record the product purity (O\(_2\)% at steady state time of about one hour and calculate the N\(_2\)% by (N\(_2\)%=100-O\(_2\)%).
6. Calculate the productivity by the following equation:

\[ \text{PRODUCTIVITY} = Q_{\text{prod}} \times \frac{y_{N_2}}{w} \] ............(4)

**Table 2. Solenoid valves operation for 6-steps cycle**

<table>
<thead>
<tr>
<th>Half cycle</th>
<th>Column 1 steps</th>
<th>Column 2 steps</th>
<th>Valve Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st half</td>
<td>Pressurizing</td>
<td>Depressurizing</td>
<td>O C O C C</td>
</tr>
<tr>
<td>1st</td>
<td>Producing</td>
<td>Purging</td>
<td>O C O C C</td>
</tr>
<tr>
<td>2nd half</td>
<td>Equalization</td>
<td>Equalization</td>
<td>C C C C O</td>
</tr>
<tr>
<td>2nd</td>
<td>Equalization</td>
<td>Equalization</td>
<td>C C C C O</td>
</tr>
</tbody>
</table>

*O: open   C: closed

**Fig. 3. Pressure history of the beds during the 6-steps cycle**

**Results and Discussion**

**Single Column Characteristics**

Figure (4) shows the single column performance as a breakthrough curve by air pressurizing at different adsorption pressure, the effluent flowrate is adjusted to 1 lit/min, the
purity of the nitrogen product is in the range of 96.5% to 97.8% up to 60 seconds, and then decreases, due to the effect of axial dispersion that made the shape of the mass transfer zone (MTZ) very wide, the desired shape of the MTZ when closer from steeper shape (Shock Wave), this may be attributed by abundantly flow of the air during pressurizing time, and penetrate the bed before full depletion of the CMS. No significant effect of the adsorption pressure on the effluent purity.

Figure (4) shows that the capacity of the adsorbent (uptake) increased with increases of the pressure up to 4 bar, and no significant of the pressure above 4 bar. The experimental equilibrium curve is in agreement with multicomponent lamgmuire isotherm up to 4 bar. Maximum constant adsorbent capacity of about 0.1 mol O₂/kg CMS is obtained for pressure above 4 bar.

Figure (6) refers to adsorption rate constant for oxygen for air pressurizing single column packed with CMS, which depends on the kinetic differences in the adsorption of nitrogen and oxygen, and evaluate adsorption rate constant up to breakthrough point by Equation (1). The adsorption rate constant (k) of about 0.005 s⁻¹ is obtained and it is constant with increasing the adsorption pressure up to 8 bar, as shown in the Figure (7), this may be attributed to use atmospheric air instead of pure gas. This result disagrees with that of noticed by Bae et al., that adsorption rate constants of all the adsorbates on the CMS showed strong pressure dependence, in the case of pure gas pressurizing [6].

Two Columns PSA Process

Figure (8) shows the effect of the adsorption pressure on the product nitrogen purity at product flowrate of 0.5 lit/min and different purge flowrates. The purity increases...
with increasing adsorption pressure from 2 to 6 bar, and no significant effect of the adsorption pressure above 6 bar. Maximum purity observed at the pressure of 6 bar. Same trend is observed with other purge flowrates. The increase in the purity with increases of the adsorption pressure is attributed to increase the capacity of the CMS with the pressure up to 4 bar. No significant effect of the adsorption pressure on the product purity above 4 bar. This result confirmed with that of breakthrough experiments which show no significant effect of the adsorption pressure on the capacity of CMS above 4 bar as shown in Figure (5).

Figure (8) also shows the effect of purge flowrate on the product nitrogen purity. The product nitrogen purity increases with increasing the purge flowrate up to 3 lit/min, and then the purity decreases above 3 lit/min. Same trend is observed at different adsorption pressure. This result is in agreement with that found by Mostamand et al. 2011 [4].

Figure (9) shows the effect of the cycle time on the product nitrogen purity at different purge flow rates. For short cycle time, and low purge flow rate, low product purity is observed, and the purity increases with increasing the cycle time up to 100 seconds at purge flow rate at 1 lit/min. This may be attributed to increase amount of the purge gas requirement to remove tracer of the oxygen per cycle (regenerate the CMS), and then the purity decreased at the cycle time of 120 seconds, due to approaching the system to the equilibrium state. Increasing of the purge flowrate from 1 to 4 lit/min at the low cycle time leads to increase the purity of the product. Whereas opposite behavior observed at long cycle time, the purity decreased with increases of the purge flowrate. The performance of the system at the long cycle time with low purge is better than the short cycle time with high purge flowrate. The optimum cycle time and purge flowrate are 100 s and 1 lit/min respectively.

For short cycle time and high purge flow rate the present results is in agreement with Mostamand et.al.[4]. High purity is achieved, because there is not enough time for nitrogen adsorption instead of oxygen.

For long cycle time and high purge flow rate the present results is in agreement with Shirily et. al. [10]. At long cycle times, the nitrogen adsorption competes with the oxygen adsorbed on the carbon molecular sieve, and low purity is observed.

Lemcoff et al. noticed that for short cycles the system behavior depends on the difference in adsorption kinetics. On the contrary for long cycles, the system is closer to equilibrium and its behavior depends on the difference in the adsorption isotherms. On the other hand, at short cycle times, the oxygen is not near equilibrium conditions, and a faster kinetics helps achieve higher nitrogen purity. [3]
Figure 10. Effect of equalization time on the effluent purity, product flowrate = 1 lit/min, \( P=6\)bar.

Figure (11) shows the relationship between the product purity and the productivity, at adsorption pressure of 8 bar, cycle time of 80 seconds, and at different purge flowrates. The purity decreases with increasing the productivity, the same trend observed for different purge flowrate. Since increasing the productivity is done by increasing the feed flowrate. The increase input to the system per one cycle, may cause to penetrate breakthrough point, and then decreases in the purity of the product.

Figure 11. Effect of purge flowrate on the effluent purity and productivity

Figure (12) shows the effect of cycle time on the purity and the productivity. The maximum productivity observed at the cycle time of 100 s. Also the productivity increases with increasing adsorption pressure up to 4 bar. No significant effect of adsorption pressure above 4 bar. This result confirmed with that of breakthrough experiments which show no significant effect of the adsorption pressure on the capacity of CMS above 4 bar. Also increasing adsorption pressure cause an increase of the axial dispersion during pressurizing step which has negative effect on the product purity.

Lemcoff et al. obtained that at a constant product purity, the specific product increases with increasing purge flowrate [3].

Figure (13) refers to the relation between the productivity and purge flowrate at different cycle time. At cycle time of 40 seconds the productivity increases with increasing of purge flow rate, due to the increase in the product purity by increasing the volume of the gas to remove tracer of the oxygen.
Shirily et al. found, at short cycle times, the amount of oxygen entering the bed during the feed step is small compared with the adsorption capacity of the adsorbent. The system is far from the equilibrium conditions, and the adsorption/desorption rate has a significant effect on the performance. On the other hand, for long cycle times, the system is close to equilibrium conditions, and the oxygen adsorption rate has a much smaller effect [10].

At cycle time of 60 and 80 seconds the maximum productivity is observed at the purge flowrate between of 3 and 4 lit/min. Whereas at cycle time greater than 80 seconds the maximum productivity observed at the purge flowrate of 1 lit/min, and the productivity slightly decreases with increasing of purge flowrate. This may be attributed to that the system approach equilibrium, enough time is exist to adsorb nitrogen as well as oxygen.

**Conclusion**

1. From breakthrough column performance results, the maximum product nitrogen purity obtained is about 98.6%, with no significant effect of the adsorption pressure.
2. Adsorbent capacity obtained is in agreement with multicomponent Langmuir isotherm up to 4 bar. No significant effect of the adsorption pressure on the adsorption capacity of the CMS above 4 bar. Maximum constant adsorbent capacity of about 0.1 mol O₂/kg CMS is obtained for pressure above 4 bar.
3. The adsorption rate constant (k) of about 0.005 s⁻¹ is obtained and it is independent on adsorption pressure up to 8 bar.
4. For two column PSA process results, the maximum purity obtained of about of 97.6% at the productivity of 156 lit/kg CMS.hr, at the pressure between 4 and 8 bar.
5. The productivity of 606 lit/kg CMS.hr obtained at purity of 94%, at cycle time of 60 second, and purge flowrate of 4 lit/min.
6. The optimum value of the equalization time is between 5 and 10 seconds.

**References**