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

Zaid A. Abdel-Rahman [1] ,   **Abdulbasit H. Mhdi** [2] ,   **Heba S. Auob**[3]
[1]*Chemical Eng. Department, Tikrit University, Salahaldeen, Iraq*
E-mail: zaid572010@yahoo.com
[2]*Chemical Eng. Department, Tikrit University, Salahaldeen, Iraq*
E-mail: Abdulbasit1979@yahoo.com
[3]*Chemical Eng. Department, Tikrit University, Salahaldeen, Iraq*
E-mail: hebah_alyobi@yahoo.com

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 للجزيئات

الخلاصة

تم دراسة فصل الهواء بواسطة الكاربون المنخلي للجزيئات (CMS) لمدى ضغط امتزاز من 2 الى 8 بار. بينت النتائج من دراسة منحني الاختراق، انه لا يوجد تأثير ملحوظ للضغط على نقاوة الناتج وعلى سعة المادة المازة عند ضغط أعلى من 4 بار. أعلى نقاوة كانت بحدود 98% حتى 60 ثانية من وقت الامتزاز. وسعة المادة المازة كانت متوافقة مع منحني توازن لانكمور متعدد المكونات حتى 4 بار. ظهرت اعلى سعة ثابتة بحدود (0.1 mol O₂/kg CMS) عند ضغط اعلى من 4 بار.

بالنسبة لطريقة الامتزاز بتغير الضغط (PSA) تتكون من عمودين وست خطوات تشغيل ، بينت النتائج بعدم وجود تأثير ملحوظ للضغط أعلى من 4 بار على النقاوة. لوحظ زيادة النقاوة عند نقصان الانتاجية. وكانت أعلى نقاوة بحدود 97.6% عند انتاجية   (156 lit/kg CMS.hr) وعند زمن دورة 100 ثانية ومعدل تنشيط 1لتر/دقيقة. وكانت الانتاجية بحدود (606 lit/kg CMS.hr) عند نقاوة 94% وزمن دورة 60 ثانية ومعدل تنشيط 4 لتر/دقيقة.

الكلمات الدالة: الامتزاز، الاختراق، فصل النيتروجين، الامتزاز بتغير الضغط.

Nomenclature

a   External surface area per unit particle volume m^2/m^3

b   Sips equation constant bar^{-1}

D   Bed inside diameter, cm

d_p Adsorbent particle diameter, mm

k   Adsorption rate constant s^{-1}

L   Bed length, mm

m_t Gas uptake at time t

m_{inf} Gas uptake at equilibrium

P_E Equalization pressure, bar

P_H Adsorption high pressure, bar

P_L Desorption low pressure, bar

Q_{prod} Product gas flow rate, lit/min

Q_{purg} Purge gas flow rate, lit/min

q_i Adsorption capacity of component i , mol/kg

q_s Saturation adsorption capacity, mol/kg

t   time, s

t_{eq} Equalization time, s

w   Adsorbent weight, kg

y_{O2} Oxygen gas purity

y_{N2} Nitrogen gas purity

Greek Symbols

ρ_B 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 Ao [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 O_2 is faster than that of N_2 by a factor of approximately $2.5*10^2$ and is due to large diffusion coefficient of O_2 into CMS in comparison with N_2. 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]:

$$m_t/m_{inf} = 1 - e^{-kt} \quad \text{…………...…………………(1)}$$

The plot of $\ln(1 - m_t/m_{inf})$ vs t should be a straight line with slope equal to k that is essentially comparable to d_p^2/a^2 in the Fickian diffusion model for spherical particles where $m_t/m_{inf} > 0.5$ [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 N_2 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 the 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).
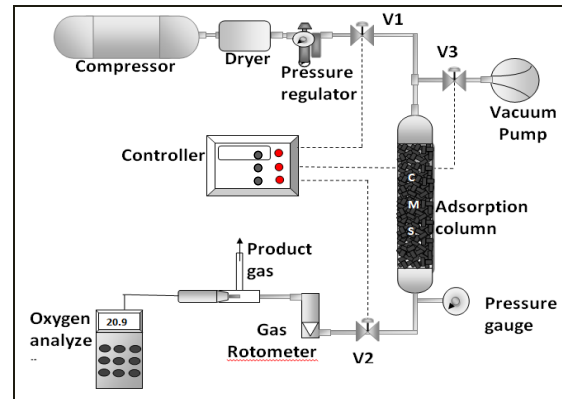

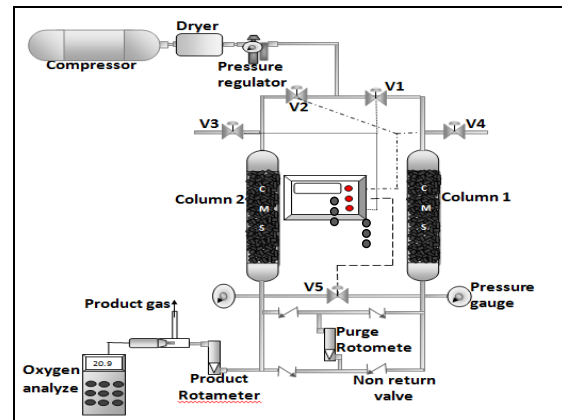**Fig. 1.** Experimental setup of single column process

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_{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_{purg}= 1 to 4 l/min
- Product flow rate, Q_{prod}=0.5 to 1 l/min
- Equalization step time, t_{eq}= 0 to 15 sec

The binary adsorption isotherm employed is the multicomponent Langmuir isotherm (Sips equation):

$$\frac{q_i}{q_{si}} = \frac{b_i P_i}{1 + \sum b_i P_i} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots(2)$$

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

Table 1. Adsorption column and adsorbent properties

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

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. Adjust the effluent flowrate by gas rotameter to desired value.
4. Record the product purity (O_2%) with time and calculate the N_2% by (N_2%=100-O_2%).
5. Calculation of the capacity of the CMS according the following equation for single column process:

$$q = (Q_{prod} / 22.4w) \sum (0.21 - y_{O_2}) \Delta t \quad \dots\dots\dots\dots..(3)$$

The experimental procedures for the two columns PSA process is:
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:

$$PRODACTIVITY = Q_{prod} * y_{N_2} / w \quad \dots\dots\dots..(4)$$

Table 2. Solenoid valves operation for 6-steps cycle

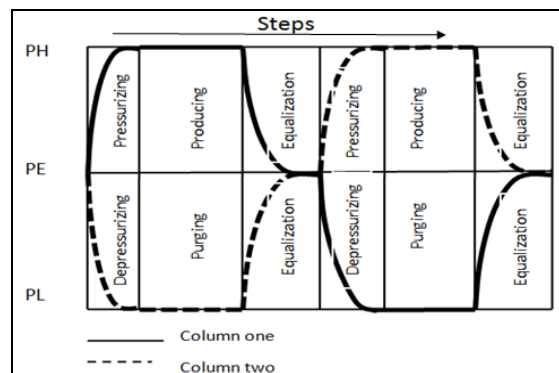| Half cycle	Column steps		Valve Position				
	Column 1	Column 2	V1	V2	V3	V4	V5
1st half cycle	Pressurizing	Depressurizing	O	C	O	C	C
	Producing	Purging	O	C	O	C	C
	Equalization	Equalization	C	C	C	C	O
2nd half cycle	Depressurizing	Pressurizing	C	O	C	O	C
	Purging	Producing	C	O	C	O	C
	Equalization	Equalization	C	C	C	C	O

*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 to1 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.
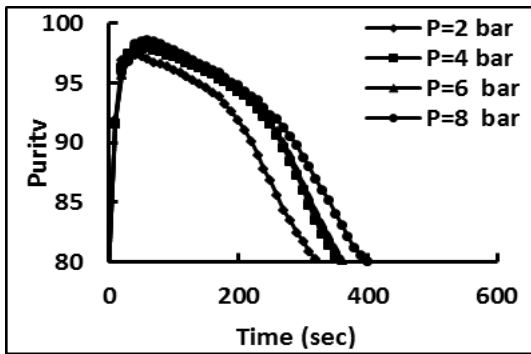

Fig. 4. Single column performance for nitrogen separation from air

Figure (5) 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 O_2/kg CMS is obtained for pressure above 4 bar.
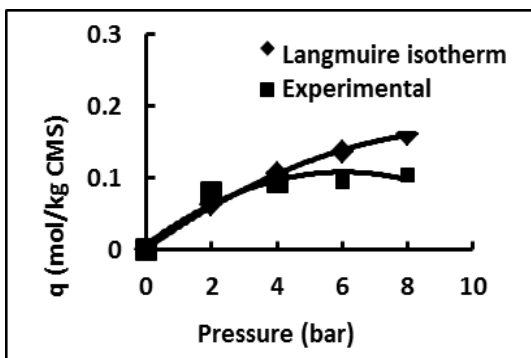

Fig. 5. Adsorption equilbrium for oxygen by CMS with air pressurizing

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].
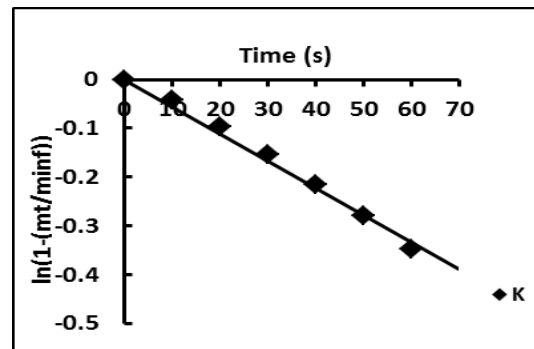

Fig. 6. Adsorption rate constant of the oxygen during air pressurizing upto break through point P= 2 bar
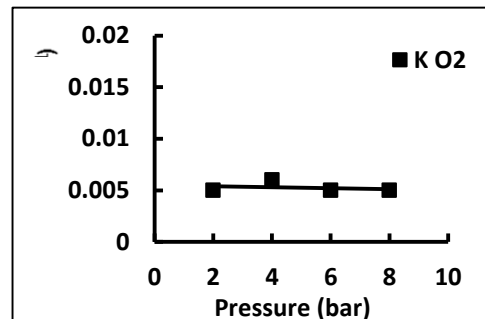

Fig. 7. Effect of adsorption pressure on the adsorption rate (k) of the Oxygen

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 1lit/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 flowrate 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 flowrate 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]
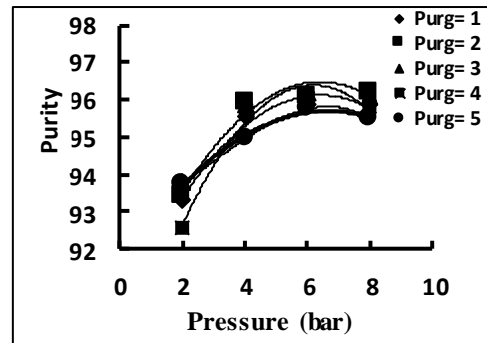

Fig. 8. Effect of adsorption pressure on the effluent purity, product flowrate = 0.5 lit/min, equalization time = 10s
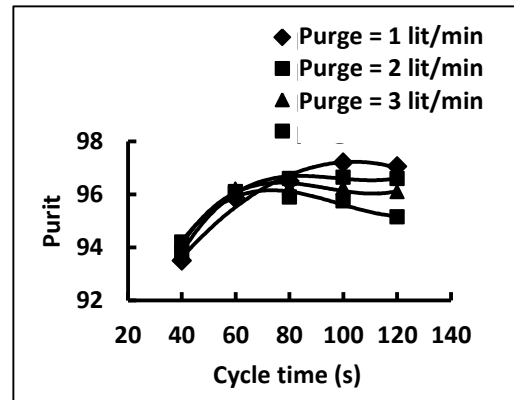

Fig. 9. Effect of cycle time on the effluent purity, product flowrate = 1 lit/min, equalization time = 10s

Figure (10) Refers to the effect of the equalization time on the product purity at adsorption pressure of 6 bars, cycle time of 80 seconds, and different purge flowrate. The purity increases with increasing equalization time from 0 to 5 second, and then the purity decreases slightly with increasing equalization time above 15 seconds.
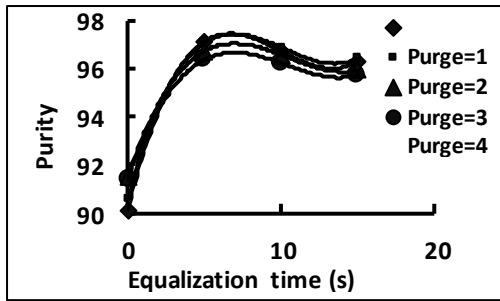
Fig. 10. Effect of equalization time on the effluent purity, product flowrate = 1 lit/min, P=6bar.

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.
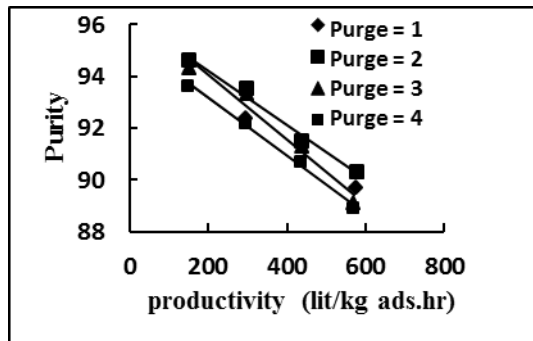

Fig. 11. Effect of purge flowrate on the effluent purity and productivity

Figure (12) shows the effect of the productivity on the product nitrogen purity at adsorption pressure of 8 bar, and at different cycle time. High purity with low productivity observed at cycle time of 100 seconds with low purge flow rate of 1 lit/min. This may be due to there is enough time to remove tracer of oxygen in spite of low purge flowrate. The productivity decreases slightly with increasing of the cycle time from 60 to 80 seconds with

constant purge flowrate, due to the decrease of the product purity with increasing cycle time at the purge flow rate of 2 lit/min.

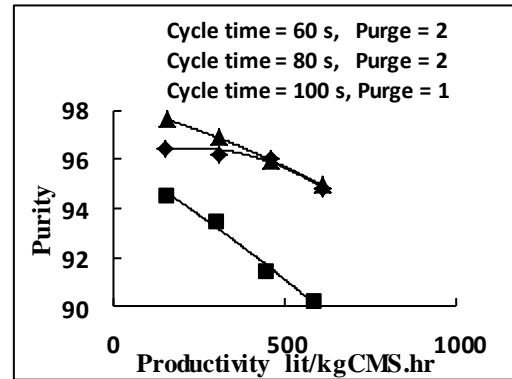Lemcoff et al. observed that the specific product decreases as the cycle time increases[3].

Fig. 12. Effect of cycle time on the purity and the productivity

Figure (13) shows the effect of adsorption pressure and purge flowrate on the process productivity, the productivity increases slightly with increasing purge flowrate up to 3 lit/min at different adsorption pressure and then decreases, due to the increase of the purity with increasing the purge flowrate. The maximum productivity observed at the purge flowrate of 3 lit/min. 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 adosprtion 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 (14) 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.
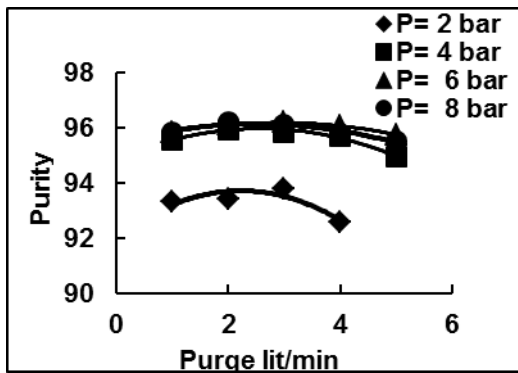
Fig. 13. Effect of purge flowrate on the productivity, product flowrate = 1 lit/min
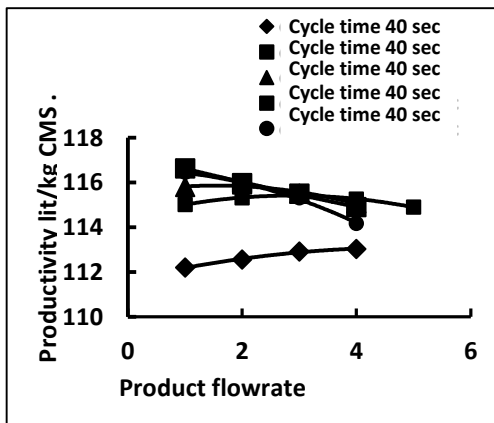

Fig. 14. The relation between purge flowrate and productivity at product flowrate= 1 lit/min, purity > 93%

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. Form 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 O_2/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

1- Mendes, A. M. M., Costa, C. A. V., Rodrigues, A. E., "Oxygen Separation from Air by PSA: Modeling and Experimental Results", Separation and Purification Technology, 24, 173-188, 2001.
2- Rege, S. U. and Yang, R. T., "Kinetic Separation of Oxygen and Argon Using Molecular Sieve Carbon", Adsorption 6, 15–22, 2000.
3- Lemcoff, N. O., and LaCava A. I., "Effect of Regeneration Pressure Level in Kinetically Controlled Pressure Swing Adsorption", Gas Separation & Purification Vol 6, No 1, 1992.
4- Mostamand, A., Mofarahi, M., "Simulation of a Single Bed Pressure Swing Adsorption for Producing Nitrogen", International Conference on Chemical, Biological and Environment Sciences (ICCEBS'2011) Bangkok Dec., 2011.
5- Ruthven, D. M., "Principles of Adsorption and Desorption Processes", John-Wiley and Sons, 1984.

6- Bae, Y.S., Lee, C. H., "Sorption Kinetics of Eight Gases on a Carbon Molecular Sieve at Elevated Pressure, Science Direct", Carbon 43 95–107, 2005.

7- Lizzio, A. A. and Rostam-Abadi, M., Production of Carbon Molecular Sieves from Illinois COAL", Fuel Processing Technology, 34, P 97-122, 1993.

8- Anson, R. S., Fletcher, A. J. and Thomas, K. M., "Adsorption Characteristics of Carbon Molecular Sieve: Deconvolution Competing Adsorption Processes", Conference Proceeding, Carbon 2004, providence, USA, 2004.

9- Vaduva, M., Stanciu, V., "Separation of Nitrogen From Air by Selective Adsorption of Carbon Molecular Sieves", U.P.B. Sci. Bull., Series A, Vol. 68, No. 2, 2006.

10- hiI-RIey, A. I. and Lemcoff, N. O., "Air Separation by Carbon Molecular Sieves", Adsorption 8: 147–155, 2002.

11- Crittenden, B., and Thomas, W. J., "Adsorption Technology and Design", Reed Ed., and Prof. Publishing Ltd 1998.

12- Nabais, J. M. V., Carrott, P. J. M., Carrott, M. M. L. R., Padre-Eterno, A. M., Mene´ndez, J. A., Dominguez, A., and Ortiz, A. L., "New Acrylic Monolithic Carbon Molecular Sieves for O2/N2 and CO_2/CH_4 Separations", Carbon 44 1158–1165, (2006).

13- Gleuckauf, E. and Coates, J. I., "The Influence of Incomplete Equilibrium on the Front Boundary of Chromatograms and the Effectiveness of Separation", J. Chem. Soc. 1947, cited in Ref.14.

14- Sircar Sand Hufton J. R., "Why Does the Linear Driving Force Model for Adsorption Kinetics Work?", Adsorption 6, 137–147, 2000.

15- Campo, M. C., Magalhães, F. D., Mendes, A., "Separation of Nitrogen from Air by Carbon Molecular Sieve Membranes", Journal of Membrane Science 350, 139–147, (2010).