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DETERMINATION EFFECTS OF PROCESS VARIABLES ON NITROGEN PRODUCTION PSA SYSTEM BY MATHEMATICAL MODELING

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Abstract

A dynamic model for a N2-PSA system is developed based on linearized mass transfer rate expressions and biocomponent langmuir isotherm. Constant pressure is assumed during adsorption and desorption but nonlinear relationship for pressure is considered during the pressurization and blow down steps. The mass transfer equations are considered and developed for all steps. After, the proposed model is validated using experimental data; the simulations studies are performed on investigate the effect of changing various process variables, such as duration of PSA steps, bed length and feed inlet velocity.

Keywords: Nitrogen; Pressure swing adsorption; Air; Process Variables

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1. Introduction

Traditionally, because of its simplicity and effectiveness, distillation is the dominant method by which chemical engineers perform large-scale separation tasks. However, the ease and costs of distillation depends on the nature of the chemicals, mainly, their relative volatility (α). As α decrease, the thermal efficiency (η), calculated as the ratio of the free energy of mixing to reboiler heat load at minimum reflux, falls rapidly [1]. Therefore, distillation of chemicals with a low α might require a large number of stages and extensive energy input, both of which would raise the cost of the process.

When distillation becomes too difficult or expensive, chemical engineers often use other methods that are more cost-effective, such as adsorption, membrane separation etc.

Adsorption can be defined as the preferential partitioning of substances from the gaseous or liquid phase on to the surface of solid substrate. In an industrial application, adsorption separation typically involve a column, packed with a suitable adsorbent, which a fluid stream containing specifically undesired adsorbents is passed in order to achieve separation. This process is usually fixed bed operations, but the moving bed process also exists. The fixed bed process essentially consists of two steps. The adsorption step and the desorption step. Desorption operation is usually performed either by raising the temperature or by reducing the total pressure. The former characterizes the thermal swing adsorption (TSA) process while the latter is applied in a pressure swing adsorption (PSA).

The pressure swing adsorption (PSA) process, which was originally developed by Skarstrom [2] has become a widely used unit operation for gas separation or purification. PSA is attractive, because it requires no separate desorption steps that need heat input, and because it runs continuously with automatic regeneration of the adsorbent. Also, it is capable of producing a very pure product [3].

Separation of a gas mixture by PSA is generally accomplished by either differences in amount of adsorption at equilibrium condition (equilibrium separation) or by differences in component gas diffusion rates in the sorbent (kinetic separation). One of the uses for PSA process is nitrogen or oxygen production from air. The process for nitrogen production uses carbon molecular sieve (CMS), which is kinetically selective for oxygen. In this material, oxygen is the faster diffusing species and is preferentially adsorbed, although at equilibrium, the affinities for oxygen and nitrogen are almost the same.

Some authors studied and modeled the PSA system for the nitrogen production from air. Raghavan et al [4] modeled the N_2-PSA system by using a linear driving force (LDF) approximation for intraparticle mass transfer and the linear equilibrium relationship for both oxygen and nitrogen. They also assumed isothermal behavior, negligible pressure drop, axial dispersed plug flow model, linear pressurization and blow down and frozen loading for all pressure changes steps. Hassan et.al [5] modeled the N_2-PSA system by using the Langmuir equilibrium relationships for both oxygen and nitrogen. This is the main difference between two pre mentioned models. Farooq et.al [6] and Shin et.al [7,8] have been considered the pore diffusion for intraparticle mass transfer instead of LDF, which is the most important difference with Raghavan model [4].

Ignoring adsorption/desorption during pressurization and depressurization steps through assumption of frozen solid phase may be erroneous, so in the present article we prepared the general model for PSA system by considering sorption during varied pressure steps. In this work, we have considered the mass transfer equations during the pressurization and blow down with a nonlinear relationship for pressure during these varied pressure steps. Thus in comparison with previous models, such as Hassan et.al [5] which is a frozen model for N_2-PSA.

2. Theory

2.1. Process Description

The process consider here utilizes two identical columns packed with adsorbent. These are connected and operated in a four-step cycle as shown in figure .1

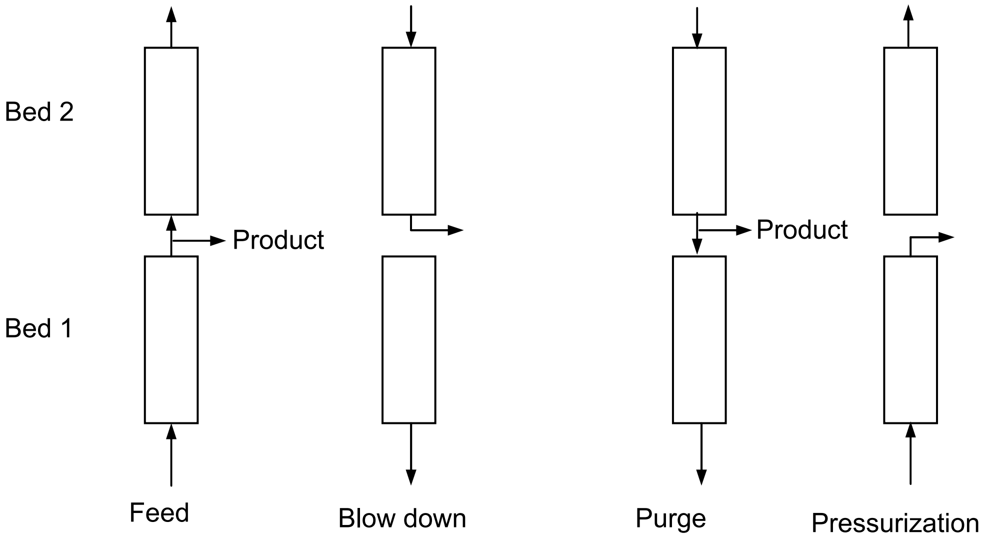


Figure 1. Step involved in PSA Cycle

During step 1 feed is supplied at high pressure to bed 1, where adsorption of the faster diffusing or higher affinity component occurs. The other component is removed as a relatively pure product. A portion of this product is throttled to low pressure for purging bed 2. In step 2, bed 1 undergoes blow down through the feed end, and bed 2 is pressurized with feed. These steps are repeated in step 3 and 4 expect that the points of feed introduction, purge, and blow down are reversed with respect to beds 1 and 2. Figure 2 shows the pressure changes in bed 1 during one cycle time.

A number of minor modifications of this cycle are possible. One that is also considered here is pressurization with product rather than feed. Also, a variety of conditions maybe used, giving rise to terminology such as vacuum swing adsorption.

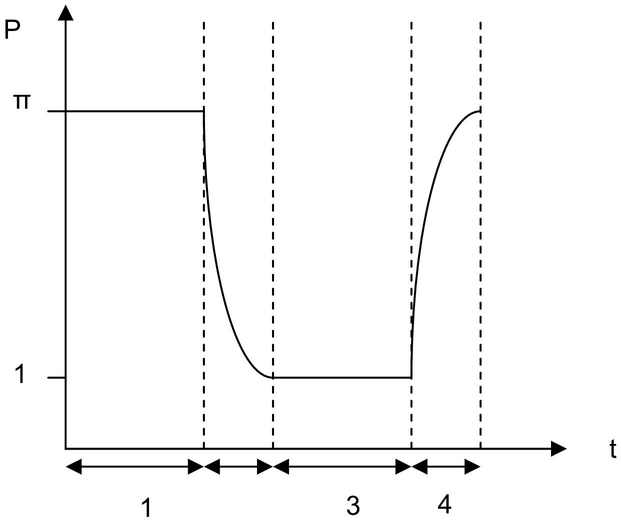


Figure 2. Pressure changes during one cycle of PSA system

2.2. Mathematical Model

In order to develop a mathematical model for this system the following assumptions are introduced:

1- The system is considered isothermal with total pressure remaining constant through the bed during high-pressure and low-pressure flow operations.
2- The equilibrium relationship is nonlinear described by Langmuir isotherm.
3- Plug flow prevails in the bed with axial dispersion.
4- The mass transfer rate is represented by a linear driving force (LDF) expression.
5- The pressure drop through the adsorbent bed is negligible.
6- The fluid velocity within the bed during adsorption and desorption varies along the length of the column, as determined by the mass balance.
7- The ideal-gas law applies.
8- During pressurization and blow down, the total pressure in the bed changes non-linearly with time and the adsorption/desorption occur.

Subject to these assumptions, the dynamic behavior of the system may be described by the following set of equations for each bed.

Step 1: high-pressure adsorption in bed 2 (purge step in bed 1)

a) Material balance in gas phase

$$\frac{\partial C_{A2}}{\partial t} - D_{L2}\frac{\partial^2 C_{A2}}{\partial z^2} + V_2\frac{\partial C_{A2}}{\partial z} + C_{A2}\frac{\partial V_2}{\partial z} + \left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial q_{A2}}{\partial t} = 0 \quad (1)$$

$$\frac{\partial C_{B2}}{\partial t} - D_{L2}\frac{\partial^2 C_{B2}}{\partial z^2} + V_2\frac{\partial C_{B2}}{\partial z} + C_{B2}\frac{\partial V_2}{\partial z} + \left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial q_{B2}}{\partial t} = 0 \quad (2)$$

b) Continuity

$$C_{A2} + C_{B2} = C_t = C_{HP}(Cons\tan t) \quad (3)$$

c) Overall material balance

$$C_{HP}\frac{\partial V_2}{\partial z} + \frac{1-\varepsilon}{\varepsilon}\left(\frac{\partial q_{A2}}{\partial t} + \frac{\partial q_{B2}}{\partial t}\right) = 0 \quad (4)$$

d) Mass transfer rates:

$$\frac{\partial q_{A2}}{\partial t} = k_{A2}(q_{A2}^* - q_{A2}) \qquad \frac{\partial q_{B2}}{\partial t} = k_{B2}(q_{B2}^* - q_{B2}) \quad (5)$$

Adsorption equilibrium:

$$\frac{q_{A2}^*}{q_{As}} = \frac{b_A C_{A2}}{1 + b_A C_{A2} + b_B C_{B2}} \qquad \frac{q_{B2}^*}{q_{Bs}} = \frac{b_B C_{B2}}{1 + b_A C_{A2} + b_B C_{B2}} \tag{6}$$

Boundary conditions:

$$D_L \frac{\partial C_{A2}}{\partial z}\Big|_{z=0} = -V_{0H}\,(C_{A2}\big|_{z=0^-} - C_{A2}\big|_{z=0}) \tag{7}$$

$$\frac{\partial C_{A2}}{\partial z}\Big|_{z=L} = 0 \tag{8}$$

$$\frac{\partial V_2}{\partial z}\Big|_{z=L} = 0 \tag{9}$$

$$V_2\big|_{z=0} = V_{0H} \tag{10}$$

Step 2: Blow down of bed 2 (Pressurization in bed 1)

In this step, total concentration varies with time, so except the followings; the other equations remain without changing:

$$C_{A2} + C_{B2} = C_2 = f(t) \tag{11}$$

Overall material balance:

$$C_2 \frac{\partial V_2}{\partial z} + \frac{\partial C_2}{\partial t} + (\frac{1-\varepsilon}{\varepsilon})\left(\frac{\partial q_{A2}}{\partial t} + \frac{\partial q_{B2}}{\partial t}\right) = 0 \tag{12}$$

Boundary conditions:

$$D_{L2} \frac{\partial C_{A2}}{\partial z}\Big|_{z=0} = 0 \tag{13}$$

$$\frac{\partial C_{A2}}{\partial z}\Big|_{z=L} = 0 \tag{14}$$

$$V_2\big|_{z=L} = 0 \tag{15}$$

$$\frac{\partial V_2}{\partial z}\Big|_{z=0} = 0 \tag{16}$$

Step 3: Purge of bed 2 (High pressure adsorption in bed 1)

The equations for step 1 also remain unchanged in step 3 with the following changes in boundary conditions:

$$D_{L2} \frac{\partial C_{A2}}{\partial z}\Big|_{z=0} = -V_{OL}(C_{A2}\big|_{z=0^-} - C_{A2}\big|_{z=0}) \tag{17}$$

$$C_{A1}\big|_{z=L} = \left(\frac{P_L}{P_H}\right) C_{A2}\big|_{z=L} \tag{18}$$

$$\frac{\partial V_2}{\partial z}\Big|_{z=0} = 0 \tag{19}$$

$$V_2\big|_{z=L} = V_{0L} \tag{20}$$

Step 4: Pressurization of bed 2 (Blow down in bed 1)

With the following changes in boundary conditions we can use the equations of step 2 for step 4

$$D_L \frac{\partial C_{A2}}{\partial z}\Big|_{z=0} = -V_{0H}\,(C_{A2}\big|_{z=0^-} - C_{A2}\big|_{z=0}) \tag{21}$$

$$\frac{\partial C_{A2}}{\partial z}\Big|_{z=L} = 0 \tag{22}$$

$$V_2\big|_{z=L} = 0 \qquad (23)$$

$$\frac{\partial V_2}{\partial z}\Big|_{z=0} = 0 \qquad (24)$$

The valid initial conditions for the start-up of the cyclic operation with two clean beds are the following sets of equations:

$$C_{A2}(z,0)=0 \qquad C_{B2}(z,0)=0$$
$$q_{A2}(z,0)=0 \qquad q_{B2}(z,0)=0$$
$$C_{A1}(z,0)=0 \qquad C_{B1}(z,0)=0$$
$$q_{A1}(z,0)=0 \qquad q_{B1}(z,0)=0 \qquad (25)$$

2.3. Solution Technique

In order to solve the above set of second and first order coupled partial differential equations, they dimensionalized and discretized in space using the orthogonal collocation method. The set of equations contains 2m unknowns, m-1 mole fractions in bulk stream (dimensionless form of concentration in gas phase), m adsorbed phase concentration in the adsorbent, and the flow velocity of the stream in the column. The resulting linear equations (The overall material balance upon discrimination, yielded a set of algebraic equations) and ordinary differential equations were solved by LU decomposition and Runge-Kutta order 4.

3. Results and Discussion

3.1. N_2-PSA System

The used parameters in simulating our experimental runs for N_2-PSA system are summarized in Tab.1. The predictions of the theoretical model have been compared with the experimental results. The experimental and model results in the adsorption step are shown in figure 3.

Table 1. Used parameters in simulation of N_2-PSA system

Feed composition	21.8% Oxygen, 78.2% Nitrogen
Adsorbent	CMS
L(m)	1.0
r_i(m)	0.0125
ε	0.4
T_0(°C)	30.0
Blow down pressure (atm)	1.0 atm.
Pressurization pressure (atm)	8.0
Axial Dispersion coefficient (m^2/s)	$4.876e^{-4}$
Equilibrium constant for Oxygen (K_A)	9.25
Equilibrium constant for Nitrogen (K_B)	8.9
LDF constant for Oxygen (k_A)(s^{-1})	$44.71e^{-3}$
LDF constant for Nitrogen (k_B)(s^{-1})	$7.62e^{-3}$
Saturation constant for Oxygen (q_{AS})(mol/m^3)	$2.64e^{3}$
Saturation constant for Nitrogen (q_{BS})(mol/m^3)	$2.64e^{3}$

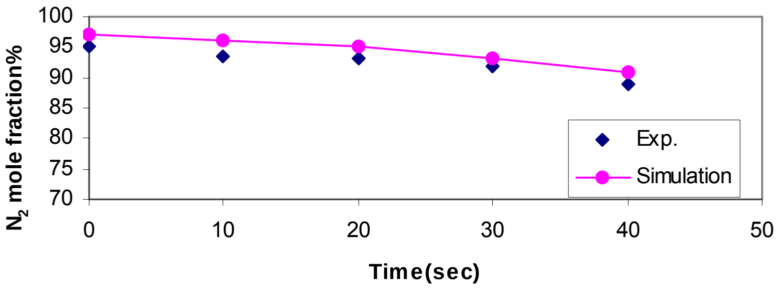
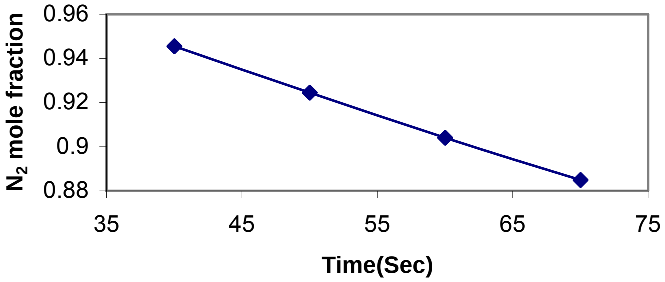


Figure 3. Comparison of simulation and experimental product purity results at high-pressure (adsorption) step as a function of adsorption time

According figure 3 a good agreement between the experiments and the simulation is observed. In order to better understanding of the N_2-PSA process, the effect of process variables on the nitrogen purity obtained by simulation studies.

3.1.1. Effect of Duration of High Pressure Feed, Blow Down and Pressurization Steps

The effect of duration of high-pressure feed step is shown in figure 4. The increase of duration, results in greater oxygen contamination for the product, but increasing quantities of product.



t_2=10 sec t_3=40 sec t_4=10 sec Bed length=1.0m V_L=0.1 m/sec V_H=0.16 m/sec P_H=8.0 atm P_L=1.0 atm

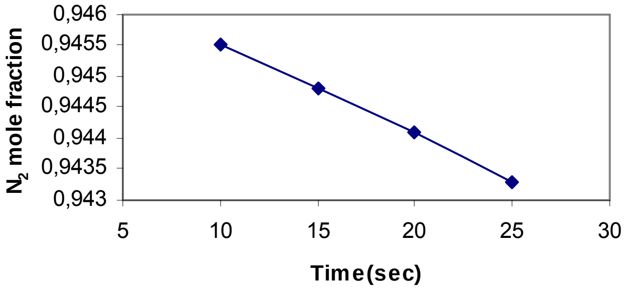
Figure 4. Effect of duration of high pressure step on N2-PSA system

Since the adsorbed impurity, oxygen diffuses out of the adsorbent during the blow down step, a longer blow down time results in a cleaner bed. The effect of blow down time on product purity is given in Tab.2.

Table 2. Effect of Duration of blow down step on N_2-PSA system

t_2(sec)	Y(N_2)
10	0.9455
15	0.9485
20	0.9511
25	0.9534
t_1=t_3=40sec t_4= 10sec Bed length=1.0 m, V_l=0.1 m/sec V_H=0.16 m/sec P_H=8.0atm, P_L=1.0 atm	

According of Tab.2 we can find that the blow down time has a good effect on the product purity. The results for various durations of the pressurization step at cyclic steady state are given in figure 5. The results show that as the duration increases, the purity decreases

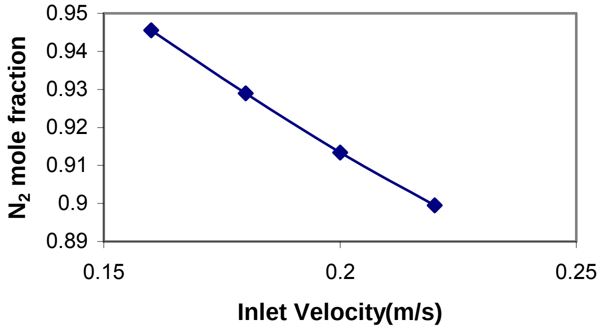


t_1=40 sec t_2=10 sec t_3=40 sec Bed length=1.0 m V_L=0.1m/sec V_H=0.16 m/sec P_H=8.0 atm P_L=1.0 atm

Figure 5. Effect of duration of pressurization step on N2-PSA system

3.1.2. Effect of Inlet Velocity

The inlet velocity is directly related to the purity of product, this effect has been shown in figure 6.

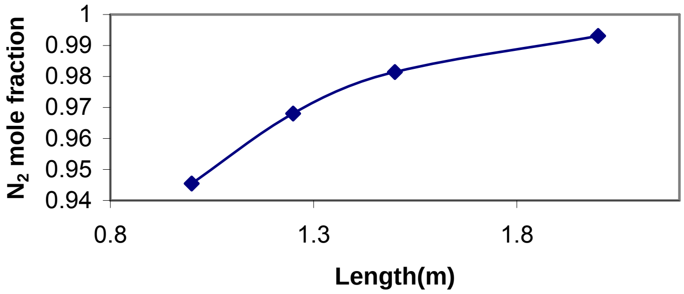


Cycle Time=100 sec t1,t3=0.4*Cycle time t2,t4=0.1*Cycle time
Bed length=1.0 m V_L=0.1m/sec P_H=8.0 atm P_L=1.0 atm

Figure 6. Effect of inlet velocity on N2-PSA system

3.1.3. Effect of Bed Length

The effect of varying the bed length is illustrated in figure 7. It shows that with a longer bed, higher purity of product is achievable.



Cycle Time=100 sec t_1,t_3=0.4*Cycle time t_2,t_4=0.1*Cycle time
V_H=0.16 m/sec V_L=0.1 m/sec P_H=8.0 atm P_L=1.0 atm

Figure 7. Effect of bed length on N2-PSA system

3.1.4. Cycle Time

The effect of cycle time on the product purity is shown in Tab.3. It is show that the product purity increase when cycle time decrease.

Table 3.Effect of Cycle Time on N_2-PSA system

Cycle time(sec)	$Y(N_2)$
50	0.951
100	0.9455
150	0.9251
200	0.8965
250	0.8659
300	0.8416
t_1,t_3=0.4*Cycle time t_2,t_4=0.1*Cycle time Bed Length=1.0 m V_H=0.16 m/sec V_l=0.1 m/sec P_H=8.0 atm P_L=1.0 atm	

4. Conclusions

In this work the general dynamic model developed with modification in pressure changes relationship and consideration of mass transfer in all steps.

The developed model applied to N_2-PSA system and a good agreement between the experiments simulation results are observed. The effects of duration of PSA steps, cycle time, inlet feed velocity and bed length on product purity is also studied. The results shows that the products (N_2) purity increases when the duration of blow down step or bed length increase but with increase of another process variables such as cycle time, inlet velocity, duration of high pressure step and duration of pressurization step, products purity will be decreases.

The cycle used here is the simple two-bed Skarstrom cycle but there is no reason to prevent the application of the same model to the more complex multi-bed systems, which are commonly used in large-scale units.

Notations

b_A, b_B: langmuir constant for component A and B
C_{A2}, C_{B2}: concentration of components A and B in gas phase in bed 2
C_2: total gas phase concentration at blow down step
C_H :total gas phase concentration at high- pressure step
d_P: particle diameter
D_L: axial dispersion coefficient
k_A, k_B: effective mass transfer coefficient for components of A and B
K_A, K_B: adsorption equilibrium constant for components A and B
L: bed length
P_H, P_L: column pressure at high-pressure step and low-pressure step
q_{A1}, q_{A2}, q_{B1}, q_{B2}: concentration of components of A and B in solid phase in bed 1 and bed 2
q_{AS}, q_{BS}: saturation constants for component A and B
q^*_{A1}, q^*_{A2}: value of q_{A1},and q_{A2} in equilibrium with C_{A1} and C_{A2}
q^*_{B1}, q^*_{B2}: value of q_{B1},and q_{B2} in equilibrium with C_{B1} and C_{B2}
r_i: inner diameter of column
t_1: duration of high-pressure step
t_2: duration of blow down step
t_3: duration of purge step
t_4: duration of pressurization step
T_0: ambient temperature
V_2: velocity in bed 2
V_{0H}, V_{0L}: inlet velocity during high-pressure step and purge step
z: axial distance from column inlet
ε: bed Voidage

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