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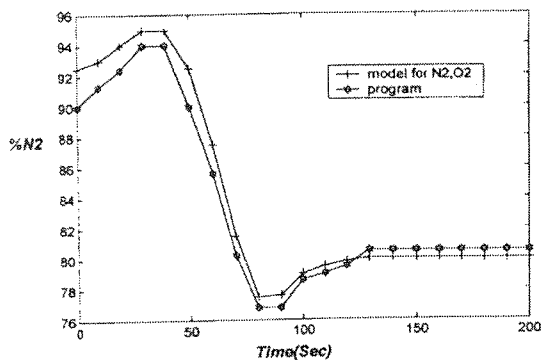
Figure (9) Comparison between program and a
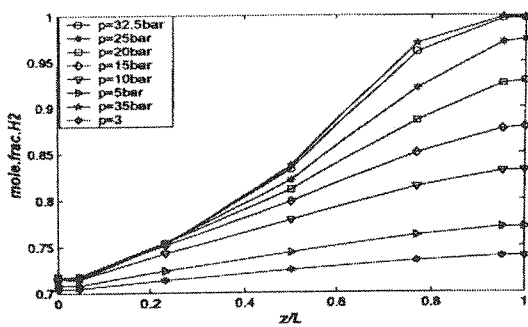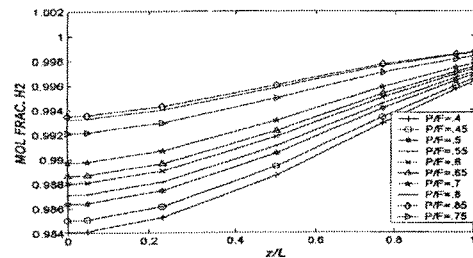theoretical model for separating O2 and N2.

Figure (11) Mole fraction of hydrogen with
bed length at different P/F ratios.

Figure (10) Variations of hydrogen mole
fraction with bed length in various pressures.

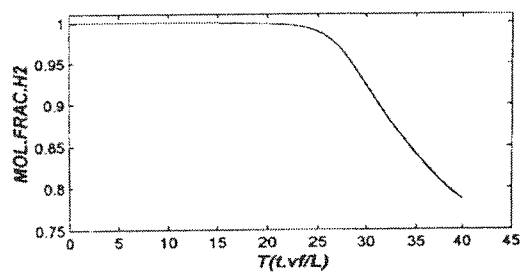

Figure (12) Variations of hydrogen mole fraction
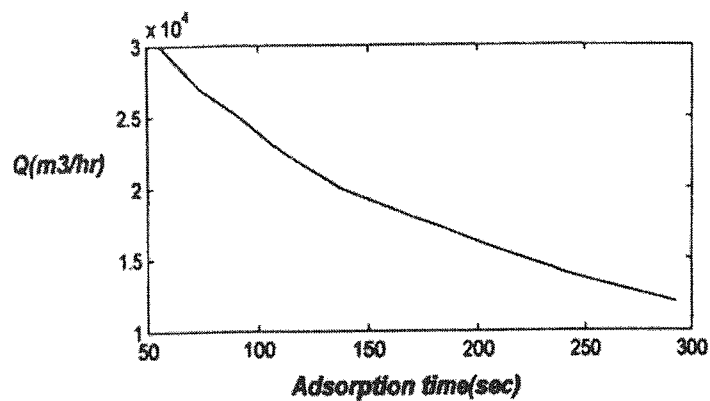with time in the bed in adsorption step.

Figure (13) Variations of flowrate versus time.

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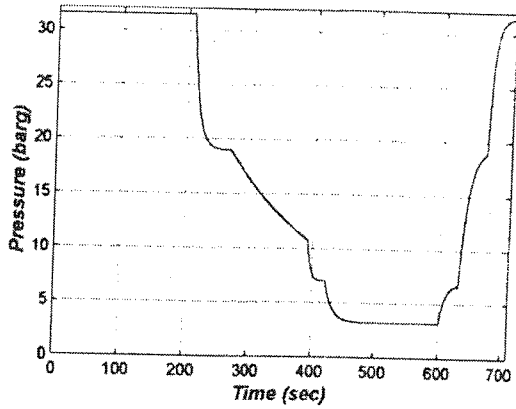
Figure (3) Variations of pressure
with time for a PSA cycle in a bed.
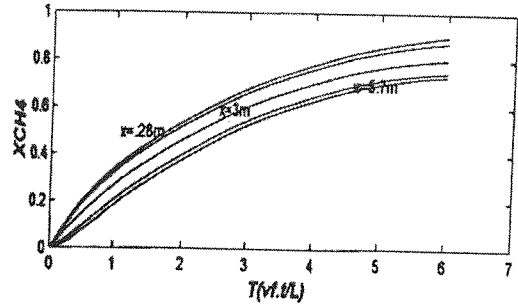
Figure (6) Variations of methane concentration
in gas phase with time in blow-down
step at different bed length.
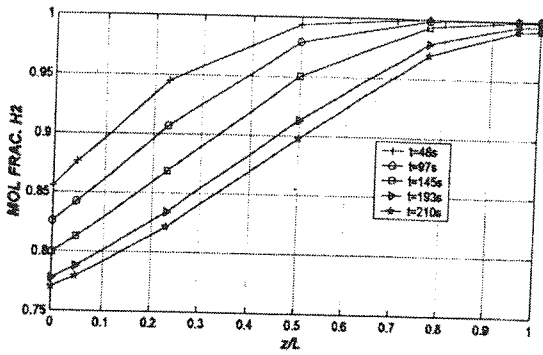
Figure (4) Variations of hydrogen
mole fraction with bed length
during adsorption step at different process times.
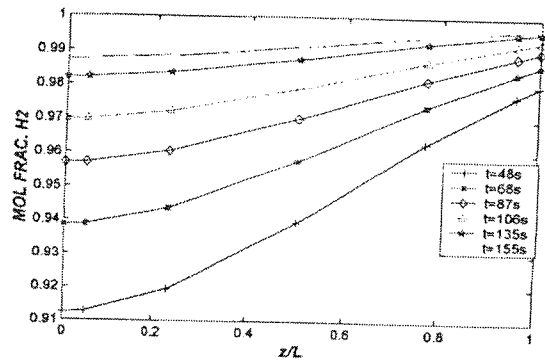
Figure (7) Variations of hydrogen
concentration with bed length
during purge step at different times.
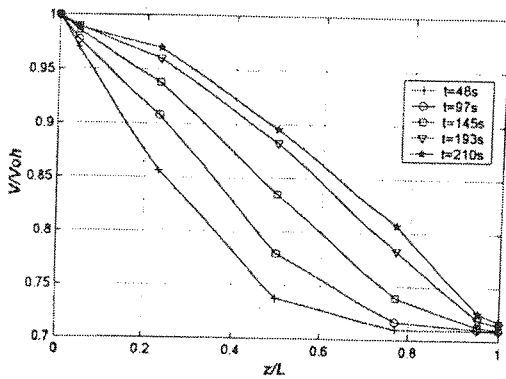
Figure (5) Variations of velocity with bed length
during adsorption step at different process times.
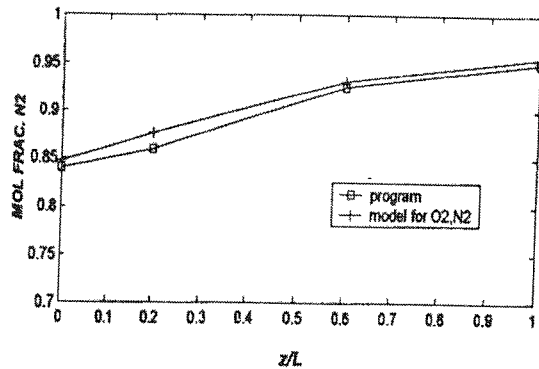
Figure (8) Comparison of present model with a
previous one for prediction of nitrogen
concentration changes with bed length
for separation of N2 and O2.

68
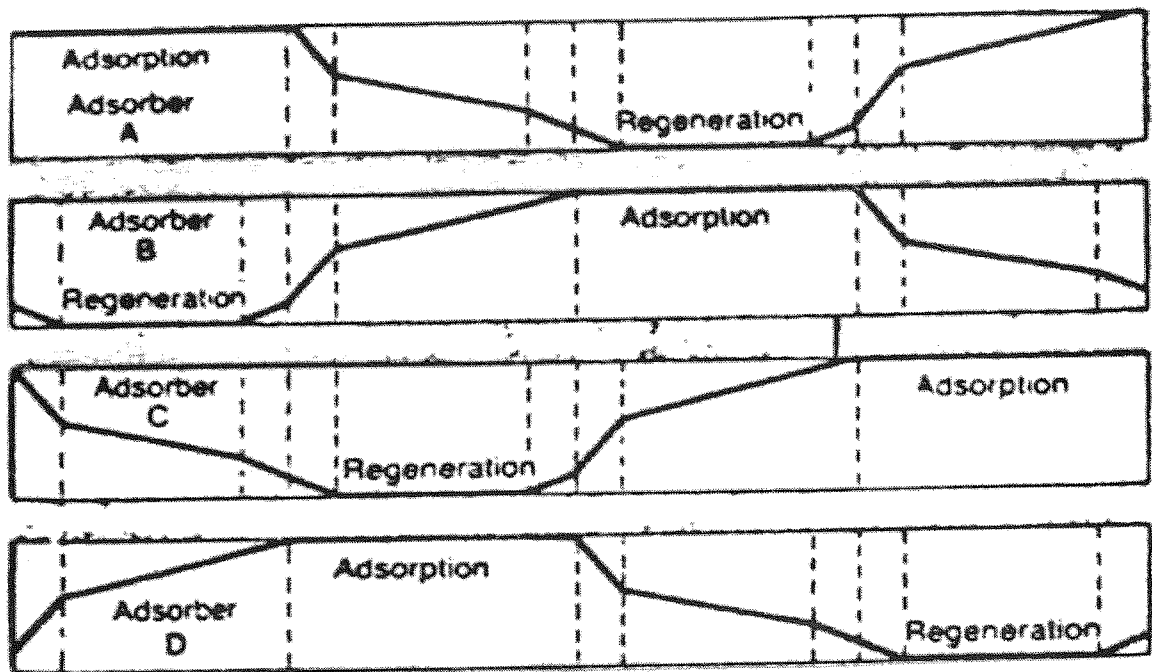
Figure (1) Pressure-time history for a 4-bed PSA system.

High Pressure   Pressure Equalization 1   Hold   Pressure Equalization 2   Purge
Adsorption   (Provide)   (Provide)   (Provide)

Blowdown   Purge   Pressure Equalization 2   Pressure Equalization 1   Repressurize
            (Receive)   (Receive)   (Receive)

Figure (2) Flow direction for a bed in various steps of a PSA cycle.

Figure (12), the hydrogen mole decreases because the adsorbent become more saturated and the impurities exit with product as process goes on.

It is desirable to have a short time step, because the amount and costs of adsorbent and the size and costs of the adsorbers become minimum in these conditions. For separation of feed with a flow rate equal to $15628 m^3/h$ the suitable adsorption time is between 190 to 210sec.

As shown in Figure (13), the adsorbtion time step decreases with increasing the inlet flow rate due to increased load of impurities on the adsorbent .

Based on these results, the optimal operating condition for PSA unit at Arak Petrochemical Company is as follows:

Adsorption pressure: 30-32(bar)

P/F ratio: 0.75 or 0.8

Adsorption time: 190-210(sec)

Conclusion
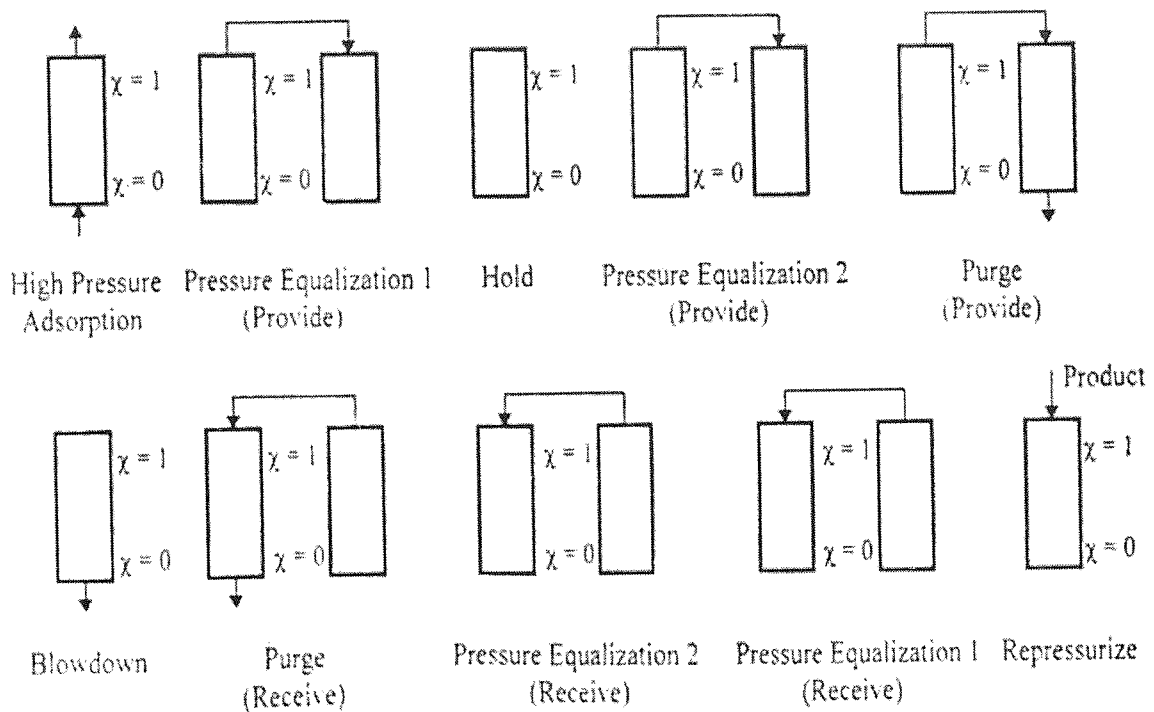
In this study, a model developed which simulates properly the performance of a pressure swing adsorption unit for purification of hydrogen in a gas stream containing methane and carbon monoxide. Predictions of the proposed model indicate that hydrogen recovery with high purity (>99.99%) is possible for an operating unit at Arak Petrochemical Company.

Using this model a hydrogen recovery equal to 72.6% is obtained for this unit which is closed to the experimental value of 70%. The results of the present model is comparable with those of the previous model for separation of N_2 and O_2 in a PSA unit. The optimal operating condition for hydrogen recovery in the PSA unit is determined. as: pressure : 30-32(bar); adsorption time : 190-210(sec);P/F ratio : 0.75.

Notations

A : the cross sectional area

$A\Delta z$: the void volume in the length Δz

b_0 : the parameters in Langmuir relation

C: concentration

D_L : axial dispersion coefficient

K: mass transfer coefficient

L: bed length

n: the number of adsorbent partiselc

N: mass rate

P: pressure

$-p'_c$: constant in pressure relation

Pe: Peclet number

q: solid concentration

q^*: equilibrium concentration

q_s : saturated concentration in solid phase

R: particle radius

S: the adsorbed amount tnebrosda yb

Sc : Schmit number

t : time

u: interstitial velocity

v: velocity

V: volume, dimensionless velocity

v_{0H} : velocity in adsorption step (maximum velocity)

v_{0L} : velocity in the end of adsorption step

x: dimensionless length

X: dimensionless gas phase concentration

y : mole fraction in gas phase

Y: dimensionless solid phase concentration

z: axial direction

ΔH_A : the adsorption heat in Langmuir relation

Greek letters

ε:noitcarf diov deb

τ : nemidṣemit sselnoi

α : dimensionless mass transfer coefficient

γ,ψ: dimensionless parameters in the collocation method

Π: erusserp

μ: viscosity

ρ: density

stpircsbuS

i: component

t : total amount

f: feed

p: particle, amount in purge

Results and Discussion

The results, predicted by the proposed model, for concentration changes in gas and solid phase, variation of pressure and velocity in different steps, hydrogen recovery and also optimal for operational condition an operating PSA unit, is presented in this section. Figure (3), gives the variations of pressure with time during a cycle for one bed. In this figure, the constant pressure corresponds to adsorption and purge steps.

The variation of hydrogen mole fraction in gas phase with bed length at different process times in adsorption step is shown in Figure (4). This figure indicates that hydrogen mole fraction approaches to one at the bed exit and it also decreases with increasing process time due to the reduction of adsorption capacity of the bed.

Figure (5) shows the velocity changes with bed length at different process times during adsorption step. The velocity of gas phase decreases due to the adsorption of impurities along the bed as expected. In Figure (6), the variation of methane concentration in gas phase for blow down step is shown which indicating that with increasing process time, the concentration of impurity is increased, because adsorbent capacity reduces as separation proceeds.

In Figure (7), the variation of hydrogen concentration with bed length during purge step, with a countercurrent direction, is shown. The Concentration of hydrogen decreases as going down from top to the bottom of the bed due to desorption of impurities, but increases with process time because more impurities or removed as process proceeds.

The production of the present model for separation of O2 and N2 with those of a previous model developed by (Pakseresht, 1994) is compared in Figure (8) which indicates small differences between them. To verify the validity of the proposed model, the operational parameters of a PSA unit of Arak Petrochemical Company were used to predict hydrogen recovery. The predicted hydrogen recovery was 72.6% in comparison with 70% of industrial results, indicating that present model is very suitable for simulation of experimental conditions.

The effect of process variables on the performance of a PSA system are also examined to obtain optimal conditions.

The adsorption step is the main step in the cycle, because the product is taken from this step and the change in some parameters including pressure can be very effective on purity and recovery of the product. The variation of hydrogen mole fraction with bed length in various pressures is shown in Figure (10).

By increasing the pressure, the purity is increased until a distinct limit, and further increased of pressure doesn't have any effect on purity of the product, while the cost of separation increases which is not favorable .

These results suggest that the optimum pressure in this case is between 30-32 bar. Meanwhile at high adsoption pressure Π_F according to the following relation the lower amount of purge is required. Decreasing the amount of purge results in increasing recovery of hydrogen and followed by the size reduction of the bed.

$$P/F = (\Pi_p/\Pi_F) - y_{iF} \tag{32}$$

The P/F ratio is the amount of hydrogen in a one purge step to the amount of hydrogen in the feed in a one adsorbtion step. By increasing the ratio, the purity of hydrogen in the product is increased [see Fig.(11)].

The length of the process time is an important factor from economical point of view. When the inlet flow rate is remained constant, and the adsorption time takes a longer time, according to

Length(m)	6
Diameter(m)	3
Temperature(^{0}C)	20
Total bed void fraction	0.7
Bulk density(Kg/m^3)	600

Adsorbent type	Carbon molecular sieve
Particle diameter(mm)	3.2
Particle density(Kg/m^3)	1200
Particle void fraction	0.58
De$_{ave}$(m^2/s),Malek(1997)	0.0232

Table (3) Feed Specifications.

Components	H_2,CH_4,CO
Inlet flowrate(m^3/h)	15628
Compositions(mole%)	H_2(70.6),CH_4(29),CO(0.004)
Pressure(bar)	32.5

Table(4) Equilibrium parameters(Batta,1979;Malek,1997).

	b_0(atm)	$-\Delta H_A$(j/mol)	q_s(mmol/g)
CH_4	$9.38 * 10^{-5}$	$26.44 * 10^3$	1.51
CO	$5 * 10^{-4}$	$20 * 10^3$	2

For calculating the mass trancfer coefficient, the following relation was used(Malek, 1997)

$$Ki = \left(\frac{15\varepsilon_p . De,ave}{R_p^2} \right) \left(\frac{C_{if}}{\rho_p . q_i^*} \right)$$

(27)

For calculating the axial dispersion coefficient, the following relation was used (Yang, 1998):

$$\frac{D_L}{2uRp} = \frac{20}{Re.Sc} + 0.5$$

(28)

For calculating the pressure loss in the bed, Ergun's equation was used as follows:

$$-\frac{dP}{dZ} = a\mu u + b\rho u^2$$

(29)

$$a = \frac{150}{4R_p^2} \frac{\varepsilon(1-\varepsilon)^2}{\varepsilon^3}$$

(30)

$$b = 1.75 \frac{(1-\varepsilon)}{2Rp.\varepsilon^3}$$

(31)

The calculated pressure loss in the bed is about 0.6atm which is assummed to be negligible.

By choosing the points which are the zeros of the orthogonal polynomial, the accuracy of the method increases too much (Villadsen,1978). The collocation method contains two approaches, the first is Villadsen method and the second is Finlayson method. Here the second method (Finlayson,1972 and 1980) was used.

To discrete the equations, they were first converted to dimensionless equations. The mass transfer equation for the component i in dimensionless form is given by:

$$\frac{\partial X_k}{\partial \tau} = \frac{1}{Pe}\left(\frac{\partial^2 X_k}{\partial x^2}\right) - V\frac{\partial X_k}{\partial x} - \left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{q_{ks}}{C_t}\times\rho\frac{dY_k}{d\tau} + \left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{q_{AS}}{Ct}\times\rho X_k\sum_{i=1}^{2}\frac{q_{si}^*}{q_{s1}}\frac{dY_i}{d\tau} \tag{24}$$

The LDF equation in dimensionless form is :

$$\frac{dY_k}{d\tau} = \alpha_k\left\{\frac{\beta_k.X_k}{1+\sum\limits_{i=1}^{2}\beta i.Xi} - Y_k\right\} \tag{25}$$

To discrete the equations in collocation method the first and second derivative matrices, A and B were used. Meanwhile, all of the boundary condition equations must be discretisized. For doing so Eq. (24) is converted to :

$$\frac{\partial X_k(j)}{\partial \tau} = \frac{1}{Pe}\sum_{i=1}^{N+2}B(j,i).X_k(i) - V(j)\sum_{i=1}^{N+2}A(j,i).X_k(i) - \psi\left[\frac{dY_k(j)}{d\tau} - X_k(j)\sum\gamma_i\frac{dY_i(j)}{d\tau}\right] \tag{26}$$

in which N is the number of collocation points.

By finding the A and B matrices and discreting all of the boundary conditions, the differential equations were obtained and then solved with a fourth order Range-Kutta method.

At first, the differential equations of solid concentration and then the differential equations in gas phase for the internal points were used. Then the equation of boundary points were solved and after that, the velocity equations were solved.

For writing the simulation program the MATLAB software were used. Plotting the profiles parallel to give the data from program is the major advantage of this software.

Input Data

The specifications of the bed and adsorbent and also the inlet feed to PSA system for an operating uint at Arak petrochemical company are given below. Otherwise the name of the references are written near the parameters.

$$P_1 - P_2 = (P_{10} - P_{20}).\exp(-2P_c'.t)$$

(16)

in which P_{10} and P_{20} are the initial pressures in bed 1 and bed 2, respectively. Substituting Eq.(16) into Eq.(14) and integration of the resulting equation give:

$$P_1 = \frac{(P_{10} + P_{20})}{2} + \frac{(P_{10} - P_{20})}{2}.\exp(-2P_c'.t)$$

(17)

Equations (14)-(17) were used to calculate pressure variations in all steps except adsorption and desorption steps.

For the adsorption, blow-down and purge steps with variable concentration and velocity, Eqs.(2),(8),(11),(12) and (13) were used by considering that their boundary and initial conditions differ from each other.Initial condition in each step is the final condition from the previous step. The boundary conditions of adsorption step are described in relations (5),(6),(9) and(10).

In blowdown step the bed end is closed and the other side is open. The boundary conditions in this case are as follows:

$$\text{B.C.1}: (v)_{z=L} = 0$$

(18)

$$\text{B.C.2}: \left(\frac{\partial v}{\partial z}\right)_{z=0} = 0$$

(19)

In purge step, the pressure is costant and the boundary conditions are:

$$\text{B.C.1}: (v)_{z=L} = v_{0L}$$

(20)

$$\text{B.C.2}: \left(\frac{\partial v}{\partial z}\right)_{z=0} = 0$$

(21)

$$\text{B.C.3}: \left(\frac{\partial C_A}{\partial z}\right)_{z=0} = 0$$

(22)

$$\text{B.C.4}: D_L \left(\frac{\partial C_A}{\partial z}\right)_{z=L} = -v\left((C_A)_{z=L^+} - (C_A)_{z=\bar{L}}\right)$$

(23)

Numerical Solution

For solving the equations of the proposed model the Orthogonal Collocation method were used, in which the partial differential equation is converted to ordinary differential equations. In this method with high accuracy, it is tried to minimize the residual of the selective points (collocation points) in differential equations.

where z=0⁻ is the situation in a point before entering the bed.
Summation of mass transfer equations for three components and the assumption of constant total concentration, (C_t) yield:

$$C_t \frac{\partial v}{\partial z} + \left(\frac{1-\varepsilon}{\varepsilon}\right)\left(\frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} + \frac{\partial q_C}{\partial t}\right) = 0 \qquad (8)$$

which gives the boundary conditions for equation (8) are as follows:

$$B.C.3: (v)_{z=0} = v_{OH} \qquad (9)$$

$$B.C.4: \left(\frac{\partial v}{\partial z}\right)_{z=L} = 0 \qquad (10)$$

For the solid phase concentration of methane and CO as it is described in the introduction, the LDF assumption is used;

$$\frac{\partial q_i}{\partial t} = K_i (q_i^* - q_i) \qquad (11)$$

The Langmuir equilibrium isotherm for adsorption of these components on the solid adsorbent is given by :

$$q_i^* = \frac{q_{is} \cdot b_{oi} \cdot \exp(-\Delta H A)_i p_i}{1 + b_{oi} \cdot \exp(-\Delta H A)_i \cdot p_i} \qquad (12)$$

$$p_i = y_i \cdot P_t \qquad (13)$$

The linear differential equation for pressure changes with time ,[Eq.(1)], gives:

$$\frac{dP_1}{dt} = -P'c (P_1 - P_2) \qquad (14)$$

$$\frac{dP_2}{dt} = +P'c (P_1 - P_2) \qquad (15)$$

Combination of Eqs. (14) and (15) followed by integration of the resulting equation yield:

1. The flow is represented with oxial dispersion play flow model with hegligible redial gradient.

2.The gas phase is ideal.

3.The system is isotherm and the temperature gradient between particles and the fluid is neglected.

4. The tw. Adserbent are only Methane and CO.

5.The extended Langmuir model is adopted for computing the adsorption equilibria (Malek and Farooq, 1996).

6.The linear driving force is used for the particle transport (Malek and Farooq,1997)

7.The interbed pressure dynamics for the variable pressure steps are estimated using the linear dynamic pressure differential equation as follows:

$$\frac{d P_1}{d t} = -P'c \, (P_1 - P_2) \tag{1}$$

in which P1 and P2 are the pressures in bed 1 and bed 2,respectively and they varry with time. In simulation model the pressure in high pressure adsoption and the pressure in desorption are required while the other pressure is calculated from Eq.(1).

The mass transfer equation for each component (i=A,B and C) is given by:

$$\frac{\partial C_i}{\partial t} - D_L \frac{\partial^2 C_i}{\partial z^2} + v \frac{\partial C_i}{\partial z} + C_i \frac{\partial v}{\partial z} + \left(\frac{1-\varepsilon}{\varepsilon}\right) \frac{\partial q_i}{\partial t} = 0 \tag{2}$$

The initial conditions for the above equation are :

$$\left(q_A\right)_{t=0} = \left(q_B\right)_{t=0} = \left(q_C\right)_{t=0} = 0 \tag{3}$$

and

$$\left(C_A\right)_{t=0} = \left(C_B\right)_{t=0} = \left(C_C\right)_{t=0} \tag{4}$$

The boundary conditions are as follows :

$$\text{B.C. 1}: D_L \left(\frac{\partial C_i}{\partial z}\right)_{z=0} = -(v)_{z=0} \left((C_i)_{z=\bar{0}} - (C_i)_{z=0}\right) \tag{5}$$

$$B.C.2 : \left(\frac{\partial C_i}{\partial z}\right)_{z=L} = 0 \tag{6}$$

The first boundary condition is named as Danckwert condition and for obtaining it, it is assumed that there is no back mining before entering the bed, i.e.;

$$\left(D_L\right)_{z=\bar{0}} = 0 \tag{7}$$

used for the adsorption equilibrium. The proposed model for an isothermal and bulk PSA process is based on the linear driving force (LDF) approximation for the rate of adsorption and the use of extended Langmuir isotherm for adsorption equilibrium.

A linear pressure differential equation for the variable pressure steps and mass transfer during blow-down are also considered in this model.

Process Description

In the pressure swing adsorption process, feed gas passes from the bed and by increasing the pressure the impurities are adsorbed and the product exits from the other side of the bed. In next steps, by decreasing the pressure the impurities desorbe from the adsorber and the bed is prepared for the next cycle of adsorption.

The pure product can be used for cleaning of the bed and these steps repeat in a cyclic manner. Different processes are used for hydrogen recovery, such as cryogenic separation, selective diffusion by polymer membranes and PSA from which PSA has the following advantages;

1. Giving high purity hydrogen to decrease the cost of the processes which use hydrogen.
2. The feed doesn't need any process before entering the separation unit.
3. Long life for the selective adsorber (over 20 years).

Each bed has the following steps for the cycle:

1. Adsorption in high pressure
2. The first step of pressure equalization
3. Isolation
4. Provide purge
5. The second step of pressure equalization
6. Counter- current depressurising
7. Purge
8. Repressurization during the second pressure equalization
9. Repressurising during the first pressure equalization
10. Repressurising during the first pressure equalization from the other bed

When a bed is in adsorption state, remaining beds are in the different steps of reviving the bed. Adsorption takes place in the highest operating pressure while desorption occures in the lowest operating pressure. The pressure-time profile for a four bed PSA system is shown in Figure(1).

Mathematical Model

The proposed model in this study, predicts the changes in pressure, concentration and velocity for a bed during a 10 steps cycle.

Most of the previous works were based on the simulation of a two bed PSA system which don't use any pressure equalization. In the present study, it is assumed that pressure is constant during the adsorption and desorption steps and it varries with time in the other steps.

In this model the change in velocity is taken into account because of the adsorption and desorption. Meanwhile the change in concentration in gas and solid phases during blow down step is considered here while in many models the frozen solid theory that considers no change in concentration during this step, was used.

In Figure (2), the flow direction is shown for a bed during a 10 steps PSA cycle.

The model assumptions are summarized as follows:

Simulation and Sensitivity Analysis of a Pressure Swing Adsorption (PSA) Unit for Purification of Hydrogen

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Abstract

A mathematical model for hydrogen recovery from a feed gas using a four-bed , ten step PSA system, is proposed. Methane and Carbon Monoxide is the impurities of the feed gas from which hydrogen is recovered. The numerical solution of the proposed model resulted in pressure, concentration and velocity profiles within the beds. Finally, the effect of some important parameters such as adsorption pressure, cycle time, etc. are discussed and the optimum operational condition for this separation process is suggested .

Key Words
Separation , Adsorption, PSA system

Introduction

The ability of pressure swing adsorption (PSA) to separate efficiently and economically the components of a mixed gas stream has made it the preferred separation process for many applications. This is especially the case if high-purity product is required. The PSA process has undergone significant modifications and improvements over the original design by Skarstrom (1960). In the initial design, a two-bed four- step system that contained :pressurization , adsorption, blow-down and purge was used to dry air.

One early modifications was the introduction of the pressure equalization step, (Marsh et al.,1964), that allows saving in the overall energy consumption. The other improvement was using of multiple beds that may reach up to 10 to 12 beds, (Fuderer,1976), which brings us a greater number of pressure-equalization steps, that results in the increase product recovery and also reduction in mechanical energy consumption.

The other modification is the use of multiple adsorbents, (Kumar, 1992). The recovery of purified hydrogen from various process gases constitutes the largest commercial application of PSA separation. These processes use 4-12 beds and sometimes a combination of different adsorbent types.

Extension of the simpler PSA models to develope a reliable model for a complex industrial process is a hard challenge. Modeling and simulation of a four-bed PSA process, using Carbon molecular sieve (CMS) as a single adsorbent, for the purification of hydrogen from the steam reformer gas is described here. The isothermal, bulk separation PSA model adopts the linear driving force approximation for the rate of adsorption and the extended Langmuir isotherm is