

NUMERICAL SIMULATION OF A H₂-PSA. CASE STUDY: THE JAM PETROCHEMICAL INDUSTRIAL PLANT IN THE SOUTHERN PARS ZONE

Ehsan Javadi Shokroo, Mohammad Shahcheraghi, Mehdi Farniaei

*The Parthia Chemistry Company, Campus of Knowledge Based Companies, Martyr
Fahmideh Talent Foundation, Shiraz, Iran, Email Address: ejavadi@nsf-partshimico.tk*

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Abstract

The Jam H₂-PSA industrial plant, a five-bed PSA, is studied numerically by mathematical modeling and numerical simulation. The model includes energy, mass and momentum balances. The coupled partial differential equations are solved using fully implicit fourth order Runge-Kutta scheme in the simulation. In general, the PSA process performance strongly influenced by the design parameters and operational variables. So, this could be achieves a maximum possible performance relate to an optimum amount of process variables. Therefore it is important that the behavior of the PSA operating variables were under take a review to knowing the optimum operating conditions. The Jam H₂-PSA plant has been designed by the UOP co., so the design parameters is not being considered for review in this study. Since there are large feed temperature variations in the H₂-PSA, in this work we are dealing with the feed temperature and investigation of its effect on the H₂ purity and recovery known as a operating variable. Finally, the results of simulations show that the feed temperature near to range of 32-38 °c is well suited to H₂ production in terms of its purity and recovery. In addition, as the feed temperature increases H₂ productivity decreases.

Keywords: *Pressure Swing Adsorption; Industrial Plant, H₂ Purification, Numerical Simulation.*

1. Introduction

The demand of hydrogen grew as world's consumption of refinery products increased by the ever growing industrialization. Hydrogen can be recovered from steam reformers, dry-reformers, tri-reformers, thermal crackers, catalytic crackers, ethylene plants and etc. to satisfy the demand [1,2]. In general, three commercial methods are available for hydrogen purification, namely cryogenic, membrane technologies and pressure swing adsorption (PSA). PSA process is a wide operating unit to separation and purification of gases that operates based on capability of solids adsorption and selective separation of gases. The important operational parameter in this system is the pressure, and most industrial units operate at\or vicinity of the surrounding temperature. Today, the PSA process completely is 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 [3-5]. The hydrogen purification by pressure swing adsorption (H₂-PSA) system is well suited to rapid cycling, in contrast to other cyclic adsorption separation processes, and this has the advantage of minimizing the absorbent inventory and therefore the capital costs of the system [5].

Use of PSA process to gas separation took for the first time in 1958 by Skarstrom. He provided his recommended PSA cycles to enrich oxygen and nitrogen in air under subject of heatless drier [6]. Therefore, Skarstrom invented a two-bed PSA cycle with equalization step for oxygen production from air using zeolite 13X adsorbent in 1966 [7]. The main reasons for the success of this technology are many reforms that achieved in this field and also is the new design and configuration for the cycles and devices [8-11].

In a H₂-PSA when a gas mixture containing hydrogen enters the adsorbent bed at high pressure, heavy components are adsorbed to the adsorbent surface and bound to the adsorbent while the lighter components, such as hydrogen, are not trapped by adsorbent surface and pass through adsorbent bed without any significant interaction. Thereby impurities are reduced due to the process, so pure hydrogen is achieved.

In general, the PSA process performance strongly influenced by design parameters (such as: bed size, adsorbent physical properties, configuration and number of beds) and

operational variables (such as: pressurization time, production time, purge time, feed flow rate, purge flow rate, production flow rate, **temperature** and/or pressure variations). Therefore it is important that the behavior of the PSA operating variables were under take a review to knowing the optimum operating conditions.

The Jam petrochemical, the biggest ethylene producer in worldwide, is one of the most important industries of Iran. In the first step of the petrochemical, feedstock of its olefin unit after passing through a series of cracking furnaces, is cooled in a cold box then fed into a series of flash drums to separate cracked components in order to supply other units feed. Separated 86 % hydrogen after passing through a heat exchanger to set desired temperature is fed to a H₂-PSA system to purify hydrogen about 99.99 %. Since hydrogen purity and recovery serve significant role in unit production, the H₂-PSA system renowned as a heart of the olefin unit. Figure 1 shows schematic diagram of the Jam H₂-PSA industrial plant. Also the sequence time table in the plant is shown in figure 2. As we know, adsorption is an exothermic and desorption is an endothermic phenomenon inherently, so knowing optimum temperature is very necessary to achieve maximum H₂-PSA performance and efficiency. Therefore this paper focused on effects of the Jam petrochemical's H₂-PSA feed temperature variation using a numerical simulation.

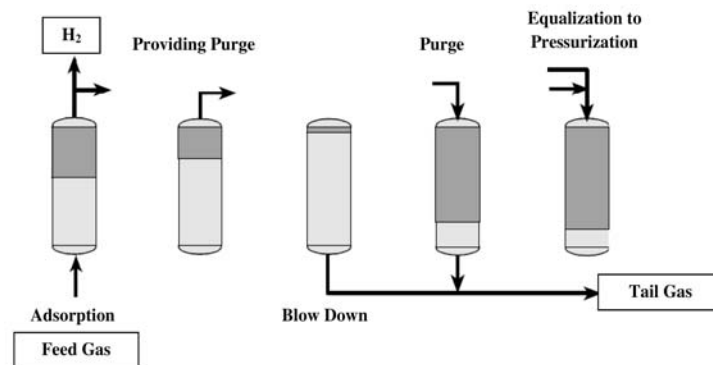


Figure 1 Schematic diagram of the Jam H₂-PSA industrial plant [15]

Step	Time (s)	Adsorber				
		A	B	C	D	E
1	10		EP	ID	BD	ED
2	10					
3	10	AD				
4	10		PR	PG2	PG1	PP
5	10					
6	10					
7	10	ED		EP	ID	BD
8	10		AD			
9	10			PR	PG2	PG1
10	10	PP				
11	10					PG1
12	10					
13	10	BD	ED		EP	ID
14	10					
15	10		PP	AD	PR	PG2
16	10	PG1				
17	10					
18	10					
19	10	ID	BD	ED		EP
20	10					
21	10				AD	
22	10	PG2	PG1	PP		PR
23	10					
24	10					
25	10					
26	10	EP	ID	BD	ED	
27	10					AD
28	10	PR	PG2	PG1	PP	
29	10					
30	10					

Figure 2 Steps sequence time table used in the plant [15]

2. Mathematical Model

In order to develop a mathematical model for a PSA system the main assumptions that have been applied include:

- Gas behaves an ideal gas
- The flow pattern is described by the axially dispersed plug-flow model
- Adsorbing properties throughout the tower would remain constant and unchanged
- Radial gradient is to be negligible

- e) Equilibrium equations for the components of feed (H₂, CH₄, CO) can be expressed by three-component Langmuir-Freundlich isotherm
- f) Mass transfer rate is expressed by a linear driving force equation
- g) Thermal equilibrium between gas and solid phases is assumed
- h) Pressure drop along the bed is calculated by the Ergun's equation.

The model equations for the bulk phase in the adsorption bed are written in Table 1. For the coupled PDEs problem, the well-known Danckwerts boundary conditions are applied [12-14]. The adsorption isotherm parameters and diffusion rate constant of H₂, CH₄ and CO over zeolite 5A is shown in Table 2. In Table 3 the characteristics of adsorbent and adsorption bed are indicated.

Table 1 Model equations [3-5].

$\frac{\partial C_i}{\partial t} - D_L \frac{\partial^2 C_i}{\partial z^2} + \frac{\partial(C_i \cdot u)}{\partial z} + \rho_p \cdot \left(\frac{1-\varepsilon}{\varepsilon}\right) \cdot \frac{\partial \bar{q}_i}{\partial t} = 0$	(1)
$\frac{\partial C}{\partial t} - D_L \frac{\partial^2 C}{\partial z^2} + \frac{\partial(C \cdot u)}{\partial z} + \rho_p \cdot \left(\frac{1-\varepsilon}{\varepsilon}\right) \cdot \sum_{i=1}^N \frac{\partial \bar{q}_i}{\partial t} = 0$	(2)
$-K_l \frac{\partial^2 T}{\partial z^2} + \varepsilon \cdot \rho_g \cdot c_{p,g} \cdot \left(u \frac{\partial T}{\partial z} + T \frac{\partial u}{\partial z}\right) + (\varepsilon_t \cdot \rho_g \cdot c_{p,g} + \rho_B \cdot c_{p,s}) \cdot \frac{\partial T}{\partial t} - \rho_B \cdot \sum_{i=1}^N \left(\frac{\partial \bar{q}_i}{\partial t} \cdot (-\Delta \bar{H}_i)\right) + \frac{2h_i}{R_{B,i}} (T - T_w) = 0$	(3)
$\rho_w \cdot c_{p,w} \cdot A_w \frac{\partial T_w}{\partial t} = 2\pi R_{B,i} h_i (T - T_w) - 2\pi R_{B,o} h_o (T_w - T_{amb}); A_w = \pi (R_{B,o}^2 - R_{B,i}^2)$	(4)
$P(t) = a \cdot t^2 + b \cdot t + c$	(5)
$-\frac{dP}{dz} = a \cdot \mu \cdot u + b \cdot \rho \cdot u \cdot u ; a = \frac{150}{4R_p^2} \cdot \frac{(1-\varepsilon)^2}{\varepsilon^2}; b = 1.75 \frac{(1-\varepsilon)}{2R_p \varepsilon}$	(6)
$q_i = \frac{q_{m,i} \cdot B_i \cdot P_i}{1 + \sum_{j=1}^s B_j \cdot P_j}; q_{m,i} = k_1 + k_2 \cdot T; B_i = k_3 \cdot \exp\left(\frac{k_4}{T}\right)$	(7)
$\frac{\partial \bar{q}_i}{\partial t} = \omega_i \cdot (q_i - \bar{q}_i); \omega_i = \frac{15D_{ei}}{r_c^2}; \frac{15D_{ei}}{r_c^2} = C_i \cdot P_r^{0.5} \cdot (1 + B_i \cdot P_i)^2$	(8)
$\text{Recovery}_{H_2} = \frac{\text{Hydrogen}^{\text{product}}}{\text{Hydrogen}^{\text{feed}}}$	(9)

Table 2 Equilibrium/Rate parameters and heat of adsorption of H₂, CH₄ and CO on zeolite 5A.

Parameter	Component		
	H ₂	CH ₄	CO
k ₁ × 10 ³ (mol/gr), [16]	4.31	4.89	5.05
k ₂ × 10 ³ (mol/gr.k), [16]	-0.01060	-0.00896	-0.00905
k ₃ × 10 ⁴ (1/atm), [16]	25.15	5.34	11.37
k ₄ (k), [16]	458.2	1795.9	1617
k ₅ (--), [16]	0.9860	0.396	0.5245
k ₆ (k), [16]	46.03	187.4	256.5
Heat of adsorption, -Δ H _i (cal/mol), [17]	2800	5600	5400

Table 3 The characteristics of adsorbent and adsorption bed.

	Adsorbent, [16]	Adsorption bed	
Adsorbent	Zeolite 5A	Length, L (cm), [15]	339
Type	Sphere	Inside radius, R _{B,i} (cm), [15]	100
Average pellet radius, R _p (cm)	0.157	Outside radius, R _{B,o} (cm), [15]	100.50
Particle density, ρ _p (gr/cm ³)	1.16	Heat capacity of column, C _{p,w} (cal/gr.k), [5]	0.12
Bulk density, ρ _B (g/cm ³)	0.795	Density of column, ρ _w (gr/cm ³), [16]	7.83
Heat capacity, C _{p,s} (cal/g.k)	0.22	Internal heat transfer coefficient, h _i (cal/cm ² .k.s), [16]	9.2 × 10 ⁻⁴
Particle porosity, α	0.36	External heat transfer coefficient, h _o (cal/cm ² .k.s), [16]	3.4 × 10 ⁻⁴

3. Results and discussion

The fourth order Rung-Kutta scheme was used to solve a mathematical model which is considered of coupled partial differential equations. The plant operating conditions data supplied by the Jam petrochemical co. can be found in Table 4 [15]. It is evident from this Table that the plant is a purification process because the impurities in the feed flow are less than 10 percent. In this simulation study, the feed components assumed to be H₂, CO and CH₄.

Table 4: Industrial H₂-PSA operating condition [15]

Composition, mol (%)	Feed	Product	Tail
H ₂	94.84	99.99	82.15
N ₂	0.01	Balance	0.02
CO	0.29	0.03 ppm	1.00
CO ₂	10 ppm	Balance	0.00
CH ₄	4.86	Balance	16.93
C ₂ H ₆	10 ppm	Balance	0.00
C ₂ H ₄	10 ppm	Balance	0.00
Unit Recovery (%)	---	75	---
Pressure (bar)	32.30	31.60	4.60
Flow Rate (N.m ³ /h)	37186.00	26453.05	10732.95

In order to validate the simulation results, the results of this work first were compared with the plant data. Figure 3 shows the simulated H₂ purity as a function of feed flow rate, together with H₂-PSA industrial plant data. This figure shows as the feed flow rate increases the hydrogen purity decreases, which is correspondence with other PSA simulations results [16]. In addition, as obvious in this figure, the simulation and presented model in this work predicts the results of the plant data with a relatively high accuracy. The effect of feed temperature on H₂ purity and recovery is indicated in figure 4.

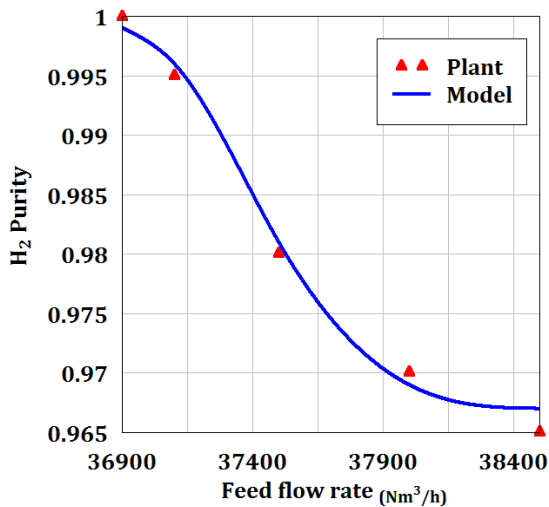


Fig. 3 Simulated purity and plant data of H₂-PSA industrial process as a function of feed flow rate

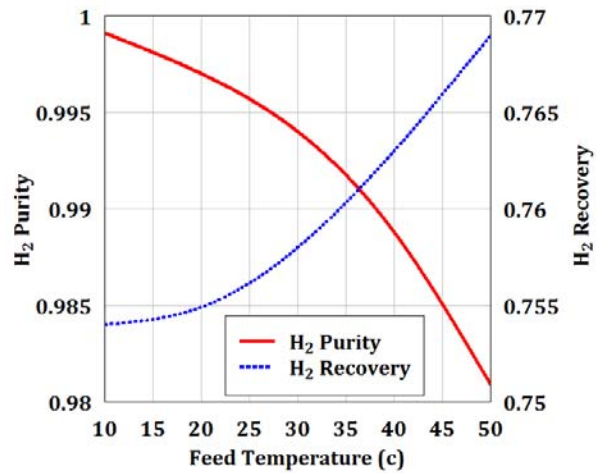


Fig. 4 H₂ purity and recovery as a function of feed temperature.

It can be seen from this figure that the increasing of the feed temperature is leading cause of a reduction in the H₂ purity and an increment in the H₂ recovery. The adsorption is an inherently exothermic phenomena, so the decreasing of the H₂ purity with the feed temperature is occurred in the normal way. In other hand, the incremental behavior of the H₂ recovery through the increasing of the feed temperature is due to gaseous molar volume expansion in the adsorption (AD) step, which is leading cause of the increasing of the H₂ molar flow in the product stream. Adsorption of all compounds in the bed decreases as the feed temperature increases, in which case molar flow of all components increases in the product stream. In addition, it is evident that as the hydrogen molar flow in the product stream increases the hydrogen recovery also will be increased. From the other point of view, impurities increase rapidly in the product stream as the hydrogen molar flow increases. Subsequently, hydrogen purity will decrease. This figure shows the feed temperature near to 35°C is well suited to H₂ production in terms of its purity and recovery. Figure 5 depicts H₂ productivity decreases as the feed temperature increases. Productivity is defined as the ratio of mole of H₂ in the product stream to kg of the adsorbent per cycle time. The

H₂ productivity decreases when the H₂ purity decreases. The cyclic partial concentration of H₂ at the top of the bed during a whole cycle is shown in figure 6. Since the H₂ mole fraction should be in highest level in AD step and it should be in lowest level in PG step, according to figure 6, it is obvious that the process performance (H₂ purity) is modified correspond to medium feed temperature in range of 32-38°C.

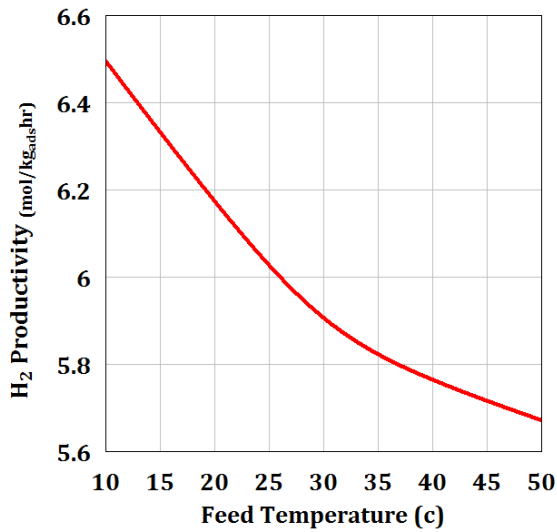


Fig. 5 Effect of feed temperature on the H₂ productivity

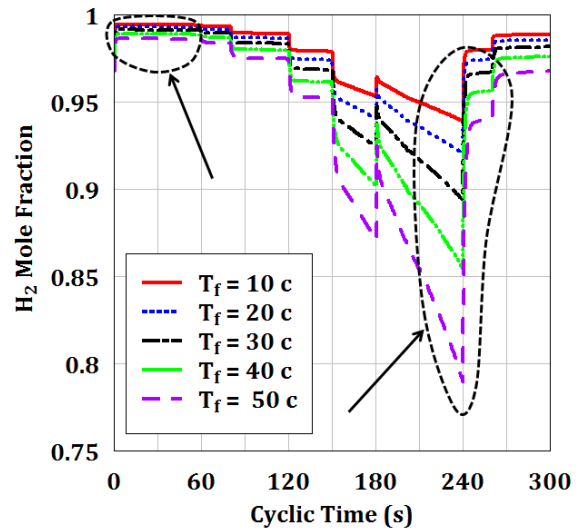


Fig. 6 Cyclic partial concentration profiles of H₂ during a whole cycle at the top the bed.

4. Conclusions

The Jam petrochemical olefin unit's H₂-PSA, located in the southern pars zone, have been simulated. In this simulation, the effect of feed temperature on the process performance is studied by a mathematical modeling. The mathematical model in the gas phase takes into account the balances in energy, mass and momentum. The coupled partial differential equations are solved using fully implicit fourth order Runge-Kutta scheme. Results show that the unit performance (in terms of H₂ purity and recovery) is in may well conditions when the feed temperature set in the range of 32-38 °C. Furthermore, H₂ productivity decreases as the feed temperature increases.

5. Acknowledgment

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Nomenclature

A _w	wall cross-sectional area (cm ²)	PP	providing purge step
AD	adsorption step	Pr	reduced pressure, (---)
B	L-F parameter (atm ⁻¹)	PG	purge step
BD	blow down step	PR	pressurization step
cp _g	gas heat capacities (cal/g.K)	q	amount adsorbed (mol/g)
cp _s	pellet heat capacities (cal/g.K)	q*	equilibrium amount adsorbed (mol/g)
cp _w	wall heat capacities (cal/g.K)	q _m	saturated amount adsorbed (mol/g)
D _L	axial dispersion coefficient (cm ² /s)	R	gas constant (cal/mol.K)
ED	equalization to depressurization step	R _p	radius of the pellet (cm)
EP	equalization to pressurization step	R _{Bi}	inside outside radius of the bed (cm)
h _i	internal heat-transfer coefficient (cal/cm ² .K.s)	R _{Bo}	outside outside radius of the bed (cm)
h _o	external heat-transfer coefficient (cal/cm ² .K.s)	t	time (s)
ΔH	average heat of adsorption (cal/mol)	T	gas phase temperature (k)
ID	idle step	T _{atm}	temperature of the atmosphere (K)
k	parameter for the LDF model	T _w	wall temperature (K)
K _L	axial thermal conductivity (cal/cm.s.K)	u	interstitial velocity (cm/s)
L	bed length (cm)	y _i	mole fraction of species <i>i</i> in gas phase
P	total pressure (atm)	Z	axial distance (cm)

Greek Letters

α	particle porosity
ε	voidage of the adsorbent bed
ε_t	total void fraction
ρ_g	gas density (g/cm ³)
ρ_p	pellet density (g/cm ³)
ρ_B	bulk density (g/cm ³)
ρ_w	wall density (g/cm ³)

Subscripts

B	bed
<i>i</i>	component <i>i</i>
p	pellet
g	gas phase
s	solid
w	wall

References

- [1] Vizcaino AJ, Carrero A, Calles JA. (2007). Hydrogen Production by Ethanol Steam Reforming Over Cu–Ni Supported Catalysts. *Int J Hydrogen Energy*, 32,1450–1461.
- [2] Haryanto A, Fernando S, Murali N, Adhikari S. (2005). Current Status of Hydrogen Production Techniques by Steam Reforming of Ethanol: a review. *Energy Fuels*, 19, 2098–2106.
- [3] Ruthven D. M., Farooq S., Knaebel K. S. (1994). *Pressure Swing Adsorption*. New York: VCH Publishers, Inc.
- [4] Yang R. T. (1987). *Gas Separation by Adsorption Processes*. London: Butterworth, Reprinted by Imperial College Press.
- [5] Ruthven D. M. (1984). *Principle of Adsorption and Adsorption Processes*. New York: John Wiley & Sons, Inc.
- [6] Skarstrom C. W. (1960). Method and Apparatus for Fractionating Gaseous Mixture by Adsorption. U. S. Patent, No. 2,944,627.
- [7] Skarstrom C. W. (1966). Oxygen Concentration Process. U. S. Patent, No. 3,237,377.
- [8] Fuderer A., Rudelstorfer E. (1976). Selective Adsorption Process. U.S. Patent 3,986,849.
- [9] Malek A., Farooq S. (1997). Study of a Six-Bed Pressure Swing Adsorption Process. *AIChE J.*, 43, 2509.
- [10] Malek A., Farooq S. (1998). Hydrogen Purification from Refinery Fuel Gas by Pressure Swing Adsorption. *AIChE J.*, 44, 1985.
- [11] Sircar S., Golden T. C. (2000). Purification of Hydrogen by Pressure Swing Adsorption. *Sep. Sci. Technol.*, 35, 667.
- [12] Jee J. G., Kim M. B., Lee C. H. (2005). Pressure Swing Adsorption to Purify Oxygen Using Carbon Molecular Sieve. *Chem. Eng. Sci.*, Vol. 60, 869-882.
- [13] Jee J. G., Park H. G., Haam S. J., Lee C. H. (2002). Effects of Nonisobaric Steps and Isobaric Steps on O₂ Pressure Swing Adsorption for an Aerator. *Ind. Eng. Chem. Res.*, 41, 4383-4392.
- [14] Cavenati S., Grande C. A., Rodrigues A. E. (2006). Separation of CH₄/CO₂/N₂ Mixtures by Layered Pressure Swing Adsorption for Upgrade of Natural Gas. *Chem. Eng. Sci.*, 61, 3893-3906.
- [15] National Petrochemical Co., Jam Petrochemical Co., H₂-PSA Plant, URL: <<http://www.jpcomplex.com/>>.
- [16] Yang J., Lee C-H. (1997). Separation of Hydrogen Mixtures by a Two-Bed Pressure Swing Adsorption Process Using Zeolite 5A. *Ind. Eng. Chem. Res.*, 36, 2789-2798.
- [17] Yang J., Park M-W., Chang J-W., Ko S-M., Lee C-H. (1998). Effect of Pressure Drop in a PSA Process. *Korean J. of Chem. Eng.*, (15) 2, 211-216.

* To whom correspondence should be addressed. E-mail: ejavadi@nsf-partshimico.tk, The Parthia Chemistry Company, Postcode: 71 888 41111, Fax: +98 7116362782.