THE IRANIAN JAM PETROCHEMICAL'S H$_2$-PSA ENHANCEMENT USING A NEW STEPS SEQUENCE TABLE

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Abstract

The Jam H$_2$-PSA industrial plant, located in the southern pars zone of Iran, was studied numerically by mathematical modeling and numerical simulation. The major disadvantage of the steps sequence table of the Jam H$_2$-PSA plant is the existence of a time-delay between two purge (PG) steps. In addition, the time of adsorption (AD) step does not equal to PG step. The existence of the time-delay in PG step and inequally in times of the pressurizing (PR) and depressurizing (BD) steps can be influenced on the process performance (mainly H$_2$ recovery). In this work, therefore, a steps sequence table is designed in a way to take the same time for AD and PG steps and also same time for BD and PR steps. The two other characteristics of the designed sequence table are the continuity of the PG step and purging of a bed by two other beds effluent, in contrast to plant sequence table that two beds are regenerated by a bed effluent. Furthermore, the results of simulations show that the H$_2$ recovery is improved with the proposed steps sequence table in this work. In addition, results of simulation indicated a very good agreement with plant data.

Keywords: Pressure Swing Adsorption; Industrial Plant; H$_2$ Purification; Numerical Simulation; Zeolite 5A.

1. Introduction

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.

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 H$_2$-PSA system to purify hydrogen about 99.99 %. Since hydrogen purity and recovery serve significant role in unit production, the H$_2$-PSA system renowned as a heart of the olefin unit. Figure 1 shows schematic diagram of the Jam H$_2$-PSA industrial plant.
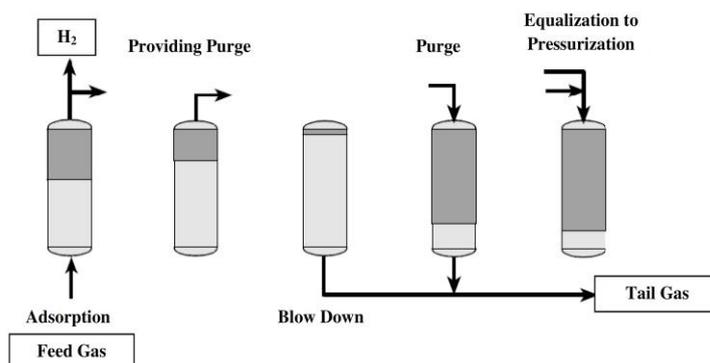

Figure 1 Schematic diagram of the Jam H$_2$-PSA industrial plant [15]

In this work, the Jam H_2-PSA industrial plant was studied by mathematical modeling. Furthermore, a new steps sequence table is suggested for improving the performance of the plant.

2. Mathematical Model

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

a) Gas behaves an ideal gas

b) The flow pattern is described by the axially dispersed plug-flow model

c) Adsorbing properties throughout the tower would remain constant and unchanged

d) Radial gradient is to be negligible

e) Equilibrium equations for the components of feed (H_2, CH_4, 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.

Table 1 Model equations [1-3].

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

For the coupled PDEs problem, the well-known Danckwerts boundary conditions are applied [1-3]. The adsorption isotherm parameters and diffusion rate constant of H_2, CH_4 and CO over zeolite 5A is shown in Table 2. In Table 3 the characteristics of adsorbent and adsorption bed are indicated.

Table 2 Equilibrium\Rate parameters and heat of adsorption of H_2, CH_4 and CO on zeolite 5A

Parameter	Component		
	H_2	CH_4	CO
$k_1 \times 10^3$ (mol/g),[4]	4.31	4.89	5.05
$k_2 \times 10^3$ (mol/g.k),[4]	-0.01060	-0.00896	-0.00905
$k_3 \times 10^4$ (1/atm),[4]	25.15	5.34	11.37
k_4 (k),[4]	458.2	1795.9	1617
k_5 (--),[4]	0.9860	0.396	0.5245
k_6 (k),[4]	46.03	187.4	256.5
Heat of adsorption, $-\Delta H_i$ (cal/mol),[5]	2800	5600	5400

Table 3 The characteristics of adsorbent and adsorption bed

Adsorbent [4]		Adsorption bed	
Adsorbent	Zeolite 5A	Length, L (cm), [6]	339
Type	Sphere	Inside radius, $R_{B,i}$ (cm), [6]	100
Average pellet radius, R_p (cm)	0.157	Outside radius, $R_{B,o}$ (cm), [6]	100.50
Particle density, ρ_p (g/cm^3)	1.16	Heat capacity of column, Cp_w (cal/g.k), [3]	0.12
Bulk density, ρ_B (g/cm^3)	0.795	Density of column, ρ_w (g/cm^3), [4]	7.83
Heat capacity, Cp_s (cal/g.k)	0.22	Internal heat transfer coefficient, h_i (cal/cm^2.k.s), [4]	9.2×10^{-4}
Particle porosity, α	0.36	External heat transfer coefficient, h_o (cal/cm^2.k.s), [4]	3.4×10^{-4}

3. Results and discussion

The fourth order Rung-Kutta scheme is used to solve a mathematical model that considered of coupled partial differential equations. The plant operating conditions data supplied by [6] can be found in Table 4. It was 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 H_2, CO and CH_4. Figure 1 shows the H_2-PSA industrial plant process. The current sequence table in the plant (a) together with the presented in this work sequence table (b) are shown in figure 2. As indicated in figure 2-a, the purge step is occurred at two time sections with a delay as ID. In addition, the time of adsorption (AD) step is not equal to desorption (PG_1+PG_2) step.

Table 4 Industrial H_2-PSA operating condition [6]

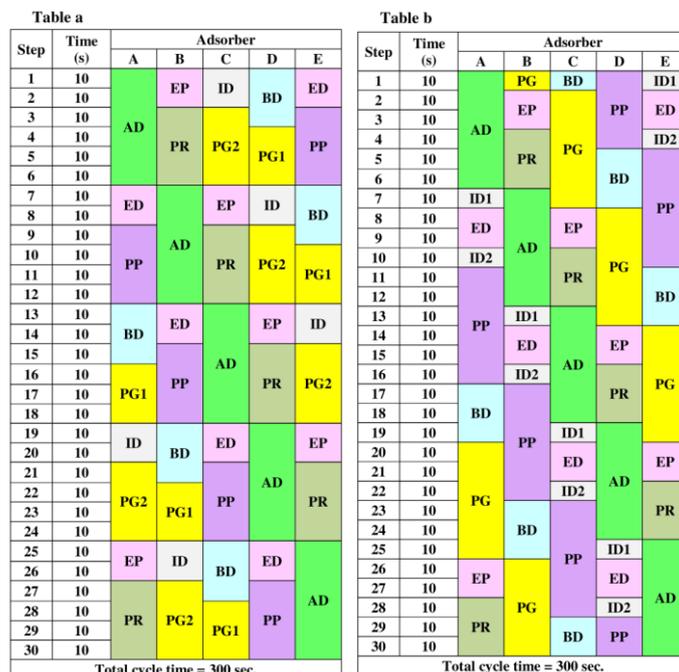| Composition, Mol (%)	Feed	Product	Tail
H_2	94.84	99.99	82.15
N_2	0.01	Balance	0.02
CO	0.29	0.03 ppm	1.00
CO_2	10 ppm	Balance	0.00
CH_4	4.86	Balance	16.93
C_2H_6	10 ppm	Balance	0.00
C_2H_4	10 ppm	Balance	0.00
Unit Recovery (%)	---	75	---
Pressure (bar)	32.30	31.60	4.60
Flow Rate (N.m^3/h)	37186.00	26453.05	10732.95

Figure 2 Steps sequence tables, a) used in the plant, b) presented in this work

The time of BD step (dump) also is not equal to PR step. The existence of the time-delay in PG step and not equally in times of the pressurizing (PR) and depressurizing (BD) steps can be influenced on the process performance (mainly H_2 recovery), so the presented in this work sequence table (figure 2-b) is designed in a way to take the same time for AD and PG steps and also same time for BD and PR steps. The two other characteristics of the designed sequence table are the continuity of the PG step and purging of a bed by two other beds effluent (PP), in contrast to plant sequence table that two beds are regenerated by a bed effluent. Furthermore, the total cycle time of the designed sequence table is equal to the time of plant sequence table. The effect of the designed sequence table, therefore, can be found in the numerical simulation results. Figure 3 shows the simulated H_2 purity as a function of feed flow rate, together with H_2-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 [4].
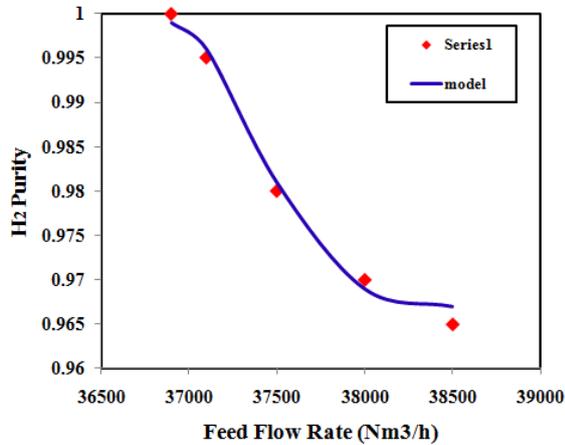

Fig. 3 Simulated purity and plant data of H_2-PSA industrial process as a function of feed flow rate
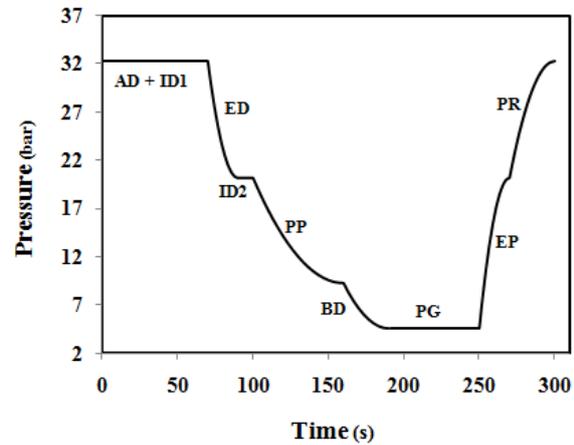

Fig. 4 The adsorption bed pressure versus cycle time

As obvious in this figure, the simulation and presented model in this work can predict the results of plant data with a relatively high accuracy. Figure 4 illustrates simulated values for the pressure history during a whole cycle with the designed sequence table. As indicated in this figure, the total pressure is a constant value in AD, ID and PG steps and it changes as a nonlinear function of time in other steps. Figure 5 depicts the cyclic partial concentration of H_2 for plant and designed steps sequence table at the top of the bed. It is obvious from this figure that the H_2 purity has an minimum and maximum quantity in the blow-down step because of depressurized bed and the pressurization step as result of cleansed bed, respectively. It was evident also from this figure that the H_2 purity is higher correspond to designed sequence table than the plant sequence table in all steps.
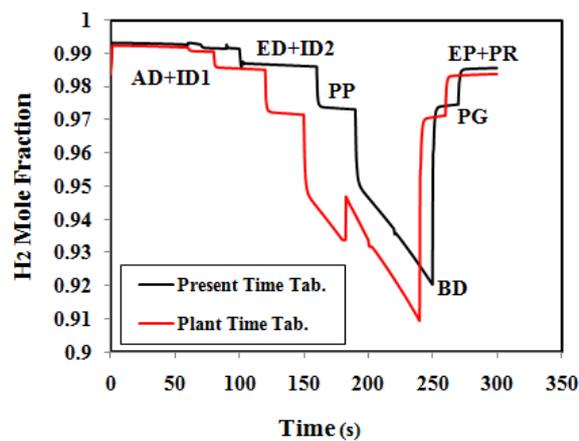

Fig. 5 Cyclic mole fraction of H_2 at the top of the bed during the whole cycle, the steps situations of the designed sequence table are indicated
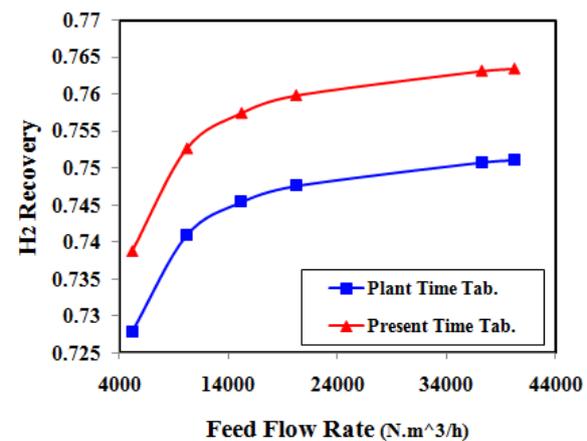

Fig. 7 H_2 recovery as a function of feed flow rate.

In other word, it can be achieved the high pure H_2 (as the current purity in the plant) with using higher feed flow rates, which is leading cause of the increasing of H_2 recovery. The process performance (H_2 recovery), therefore, is improved with the designed sequence

table. H_2 mole fraction at the base of the bed vs. PG step time is shown in figure 6. It can be seen from this figure that the decline rate of H_2 mole fraction with PG step time is lesser correspond to designed sequence table than the plant sequence table. As expected, therefore, the adsorbent will be regenerated fairly well in PG step with the designed sequence table. Figure 7 shows the H_2 recovery as a function of feed flow rate. This figure also was announced that the designed sequence table is well suited to higher process performance (H_2 recovery). There is a reason for this, the equality of the time of AD and PG steps and also PR and BD steps will be cause to decrease the time of tail stream (PG & BD). Note that, ignoring the time delay in PG step (ID) can be led to the decrease the PG step time because of the PG step performs at once.
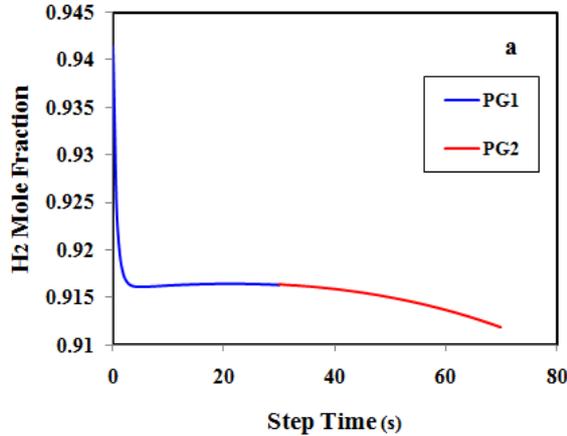

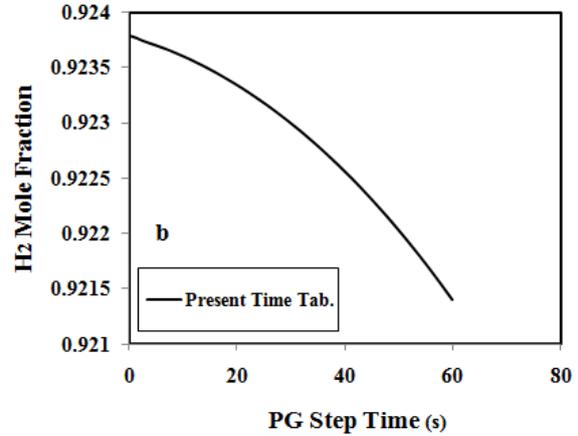Fig. 6-a H_2 mole fraction at the base of the bed Vs. PG step time, result with the plant sequence table.

Fig. 6-b mole fraction at the base of the bed Vs. PG step time, result with the designed sequence table

4. Conclusions

The Jam petrochemical olefin unit's H_2-PSA, located in the southern pars zone, have been simulated. In this simulation, a new steps sequence table is designed for improving the plant performance. The steps sequence table is designed in a way to take the same time for adsorption (AD) and purge (PG) steps and also same time for blow-down (BD) and pressurization (PR) steps. In addition, two other advantages of the designed sequence table are the continuity of the PG step and purging of a bed by two other beds effluent, in contrast to plant sequence table that two beds are regenerated by a bed effluent. Finally, the results of simulations show that the proposed steps sequence table in this work takes precedence over the sequence table in-use in the Jam petrochemical co.

Acknowledgment

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_q	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 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	component i
p	pellet
g	gas phase
s	solid
w	wall

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