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DESIGNING A COMMERCIAL SCALE PRESSURE SWING ADSORBER FOR HYDROGEN PURIFICATION

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Abstract

Since hydrogen is adsorbed much less than almost any other components, pressure swing adsorption (PSA) is the most relevant approach to produce pure hydrogen; therefore, developing a strategy to design and model such a plant is attractive from the industrial view point. In this research, a practical approach is proposed to estimate the breakthrough time of a commercial PSA process using 5A molecular sieve. According to the experimental data of adsorption isotherms and kinetic rates of adsorption in porous media, the mathematical model of PSA plant is solved using Aspen adsorption software; then, the calculated breakthrough time for the hydrogen purification is compared with the industrial data. Results indicate that the estimated time is close to the actual value obtained from the industrial plant, and it can guarantee a safe operation without bridging the breakthrough point corresponding to hydrogen purification using 5A molecular sieve.

Keywords: Pressure swing adsorption; Mathematical model; Molecular sieve 5A; Isotherm; Aspen adsorption; Hydrogen Purification.

1. Introduction

Pressure swing adsorption (PSA) process is a wide operating unit for separation and purification of gases that operates based on capability of solids adsorption and selective separation of gases [1]. This process is operative in most natural physical, biological and chemical systems and is widely used in industrial applications such as gas sweetening and purification [2]. The last few decades have seen a considerable increase in the applications of adsorptive gas separation PSA which is a versatile technology for separation and purification of gas mixtures [3]. In this process, bulk separation of a mixed gas is achieved by repeating adsorption at a higher pressure and desorption at a lower pressure. In this case, the step time for desorption is of the same order of magnitude as that of the adsorption (sometimes even smaller).

Production of pure hydrogen from a gas mixture containing 60–90 mol% hydrogen using PSA processes has become an interesting technology in the petrochemical industries. The PSA processes are designed to produce a dry hydrogen-rich product stream at the feed gas pressure containing 98–99.999 mol% H_2 with a H_2 recovery of 70–90% [4]. With extensive industry applications of pressure swing adsorption (PSA), there is significant interest for efficient modeling, simulation and optimization strategies [5]. However, the design and optimization of PSA systems still largely remain an experimental effort [6]. This is mainly because most practical PSA processes are fairly complex and are usually expensive and time-consuming to solve with the accuracy and reliability needed for industrial design [7-12].

In this study we present a method to estimate the breakthrough time of a commercial pressure swing adsorption process. According to the experimental adsorption isotherms and kinetic rates of adsorption in porous media, the isothermal mathematical model of PSA system

is solved using Aspen Adsorption software (AspenTech, 2011, Ver. 7.3); then, the calculated break through time for the hydrogen purification is compared with the actual data.

2. Process Description

Hydrogen stream with the molar flow rate of 562 kmol/h (CO=12.47mol% and CH_4=0.0799 mol%) is sent to the molecular sieve beds to produce pure hydrogen product (>99.99 mol%). Specifications of feed and product are presented in Table 1. The regeneration cycle are executed in following consecutive basic sub cycles:

- Equalization step
- Providing for purging step
- Dumping
- Purging
- Re-pressurization

Table 1. Feed and Product Specifications

Specifications	Unit	Feed	Product
Volume flow	m^3/h	373.7	230
Standard flow	sm^3/h	13291.7	7900.1
Mass flow	kg/h	2135.1	673.6
Mol flow	kmol/h	562.2	334.1
Vapour fraction	mol-fraction	1	1
Liquid fraction	mol-fraction	0	0
Solid fraction	mol-fraction	0	0
Specific heat	kJ/kmol.K	30.4	29.3
Temperature	°C	40	43
Dew point	°C	-130.5	<-220
Pressure	bar	40.01	39.31

Equalization step is considered in PSA processes to reduce compressor energy consumption and save the high pressure of the bed in adsorption mode during regeneration cycle. This step prevents loss of large amount of pure hydrogen gas via pressure balance between the vessels in progress and consequently the percent of hydrogen recovery increases. Providing purge is the second depressurizing step by that the pressure is reduced co-currently with feed stream, and then gas is released to the bed to purge out impurities from adsorbents. The last depressurization is known as dumping step. During this step adsorbed impurities begin to desorption. The next step is purging. Pure gas which released in providing purging step is used for purge out desorbed impurities in this step. Final step of regeneration cycle is re-pressurization. At this step vessel pressurizes using slip stream of pure hydrogen product. A simplified schematic of the described steps are shown in Figure 1. Moreover, the specifications of adsorbent and adsorption bed are presented in Table 2 and 3, respectively.

Table 2 Adsorbent specification

Specifications	Unit	value
Adsorbent	--	Molecular Sieve 5A
Shape	--	Beads
Crush Strength	N	40 min.
Diameter	mm	1.6-2.5
Bulk Density	g/ml	0.74 min.
Particle Density	g/ml	1.13
Attrition	Wt.%	0.3 max.

Table 3 Molecular sieve adsorption bed specification

Specifications	Unit	value
Bed Height	mm	2900
Bed ID	mm	1800
Bed Void Fraction	--	0.35

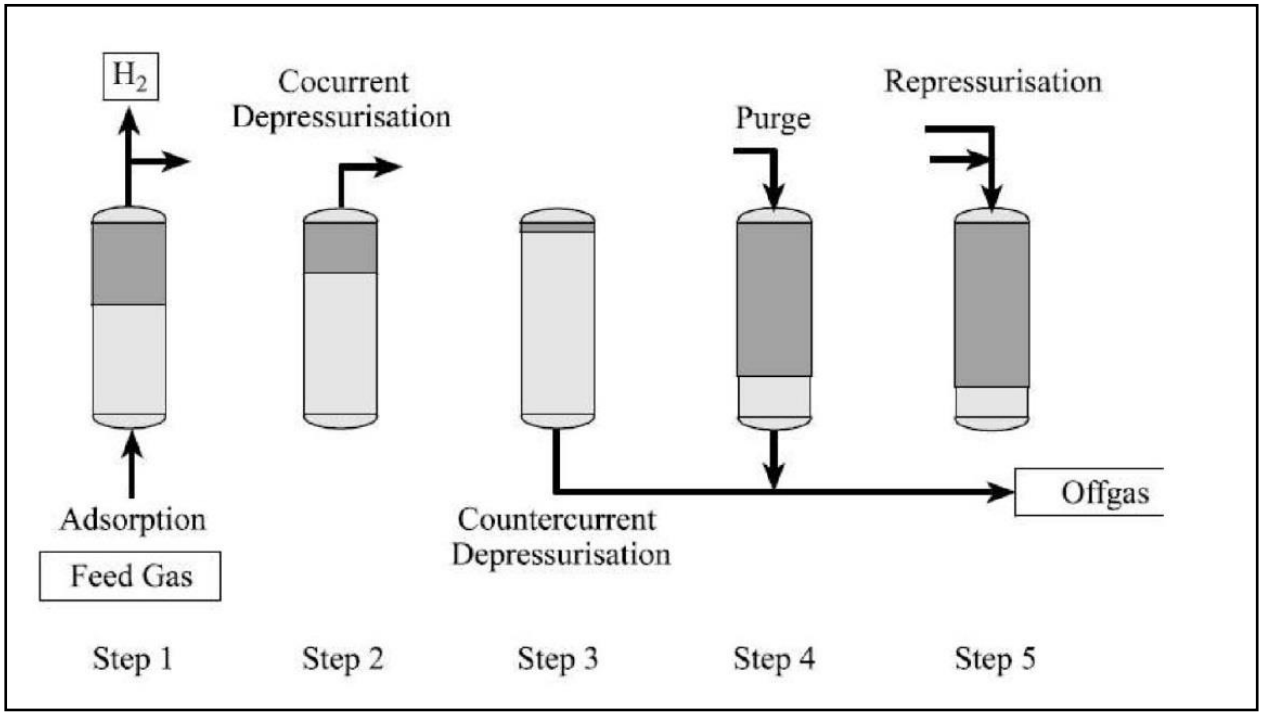

Figure 1. Simplified schematic of process sub cycles [12]

3. Model Development

The following model is used to simulate a hydrogen PSA unit using Aspen adsorption software V7.3 (AspenTech, 2011). 5A Molecular sieve is selected to remove methane and carbon monoxide from hydrogen stream and produce high purity hydrogen products. The following assumptions are considered for executing proposed dynamic simulation:

- The gas phase is ideal.
- The bed works in adiabatic and isothermal conditions without any heat transfer between solid and gas phase.
- The bed void is initially filled with hydrogen.
- Only axial mass dispersion is assumed.
- Pressure gradient is related to superficial velocity based on Ergun equation.
- Mass transfer coefficients consist of film resistance and macro pore diffusion coefficient.
- Ideal adsorbed solution (IAS) is considered for deviation of pure and mixture components involved in adsorption isotherm.

Based on the mentioned assumptions, the general and particular equations are as follows.

3.1 General Equations

3.1.1 Momentum balance

In this study, bed dimensions and particle diameter are constant; therefore, based on Ergun's equation, the superficial velocity can be related to the total pressure gradient as follows [13]:

$$\frac{\partial p}{\partial z} = -\left(\frac{1.5\times10^{-3}\,(1-\varepsilon)^2}{\left(2r_p\psi\right)^2\,\varepsilon^3}\mu v_g + 1.75\times10^{-5}M\rho_g\frac{(1-\varepsilon)}{2r_p\psi\,\varepsilon^3}{v_g}^2\right) \qquad (1)$$

Ergun equation considers laminar and turbulent flow conditions to calculate the pressure drop across the bed.

3.1.2 Material balance

The mass balance in the gas phase depends on the effect of axial dispersion, convection term, gas phase accumulation and rate of fluid to the adsorbent as the following [14-15]:

$$-\varepsilon D_{ax}\frac{\partial^2 c_i}{\partial z^2}+\upsilon_g\frac{\partial(c_i)}{\partial z}+\frac{\partial c_i}{\partial t}+\frac{1-\varepsilon}{\varepsilon}\frac{\partial \bar{q}_i}{\partial t}=0 \quad (2)$$

The dispersion coefficient in Eq.2 is calculated from the following correlation [13,16]:

$$D_{ax}=0.73D_{mi}+\frac{\upsilon_g r_p}{\varepsilon(1+9.49\frac{\varepsilon D_{mi}}{2\upsilon_g r_p})} \quad (3)$$

Moreover, to calculate binary molecular diffusivity (D_{AB}), Fuller, Schettler and Giddings equation is used. This equation includes empirical constants and keeps the form of Chapman- Enskog kinetic theory [17].

$$D_{AB}=\frac{0.00143T^{1.75}}{PM_{AB}^{1/2}[(\Sigma_v)_A^{1/3}+(\Sigma_v)_B^{1/3}]^2} \quad (4)$$

From Eq.4, binary molecular diffusivity can be calculated; hence, for estimating multi-component molecular diffusivity, the following equation is applied [18]:

$$D_{mi}=\frac{1}{\sum_{i=B}^{n}\frac{y_i'}{D_{A,i}}} \quad (5)$$

3.2 Particular Equations

3.2.1 Kinetic model

Mass transfer driving force is assumed to be a linear function of solid phase loading with transport mechanism from fluid to solid. Therefore, it consists of two terms as follows [13-19]:

- Extra-particle transport mechanisms
- Intra-particle transport mechanisms

The overall mass transfer coefficient can be calculated as follows:

$$\frac{1}{k_{MTC_i}}=\frac{r_p\bar{K}_{ki}}{3k_{fi}}+\frac{r_p^2\bar{K}_{ki}}{15\varepsilon_p D_{pi}} \quad (6)$$

In extra-particle transport term the film resistance is estimated from Sherwood number and wakao-funazkri correlation as the following [13-19]:

$$k_{fi}=sh_i\frac{D_{mi}}{2r_p} \quad (7)$$

$$sh_i=2.0+1.1Sc_i^{1/3}Re^{0.6} \quad (8)$$

Above correlation is reliable in the Reynolds number between 3 and 10^4 [12].

For the intra-particle transport term, the macro pore diffusion for molecular sieve has both molecular and Knudsen diffusions obtained from the Bosanquet equation as follows [20]:

$$\frac{1}{D_{pi}}=Tort(\frac{1}{D_{ki}}+\frac{1}{D_{mi}}) \quad (9)$$

$$D_{ki}=97r_{pore}(\frac{T}{M_i})^{0.5} \quad (10)$$

3.2.2 Isotherm model

The relation between loading of molecular sieve and the partial pressure or concentration of adsorbate is known as isotherm curve. The Langmuir-type isotherm is the most relevant model for practical applications. The Langmuir isotherm for pure component adsorption is defined as follows:

$$\theta\,(\frac{q}{q_m})=\frac{BP}{1+BP} \quad (11)$$

$$B = \frac{\alpha}{\beta\,(2\pi\, mkT)^{1/2}}\, e^{Q/RT} \quad (12)$$

In Eq.12, α is the sticking probability or accommodation coefficient for adsorption (upon a collision on the surface), and β is the rate constant for desorption. It is supposed that B (Langmuir isotherm constant) is not dependent to the pressure; therefore, estimated constant can be applied in the industrial condition (P=40.01 bara).

The Langmuir isotherm for pure-component adsorption can readily be extended to an n-component mixture, known as the extended Langmuir isotherm: [21]

$$q_i = \frac{q_{mi} B_i P_i}{1+\sum_{j=1}^{n} B_j P_j} \quad (13)$$

In this research, the linear isotherm is also compared with Langmuir type. To compare the estimated values and measured values, average absolute deviation (AAD%) and mean squared error (MSE) were applied as follows:

$$AAD\ \% = 100 \times \frac{\Sigma \sqrt{\frac{(Y_{Actual} - Y_{Modle})^2}{Y_{Actual}^{\,2}}}}{Number\ of\ tests} \quad (14)$$

$$MSE = \frac{\Sigma (Y_{Actual} - Y_{Modle})^2}{Number\ of\ tests} \quad (15)$$

Furthermore, to correlate the constants of Langmuir and linear isotherms from experimental data, estimation module of Aspen Adsorption software V7.3 is utilized.

4. Result and Discussion

Loading of CH_4, CO and H_2 on 5A Molecular Sieve was measured using a Quantachrome pore size distribution analyzer in different pressures. These experiments were carried out at standard conditions (atmospheric pressures and temperature of 25°C). For each experiment, the weight sample was approximately 1g. In Figures 2 to 4, the volume of adsorbed materials in standard condition is sketched versus the pressure. The apparatus reported the amount of adsorbed materials on the molecular sieve sample in volume basis at standard condition. As it was expected, by increasing the pressure, the amount of uptake increased.

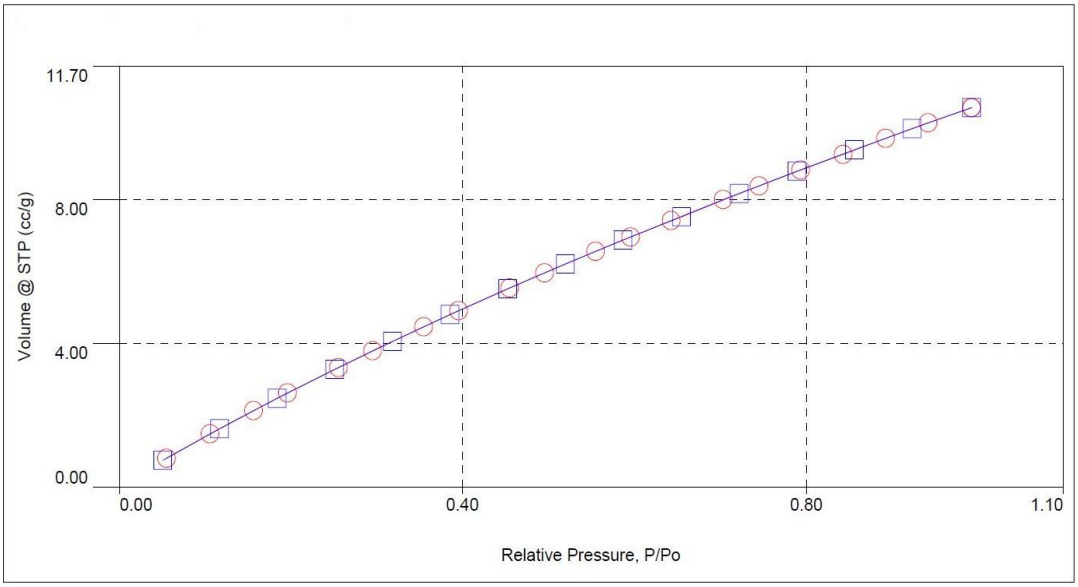

Fig. 2. Loading of H_2 on 5A MS using Quantachrome analyzer (○ Adsorption step; □ Desorption step)

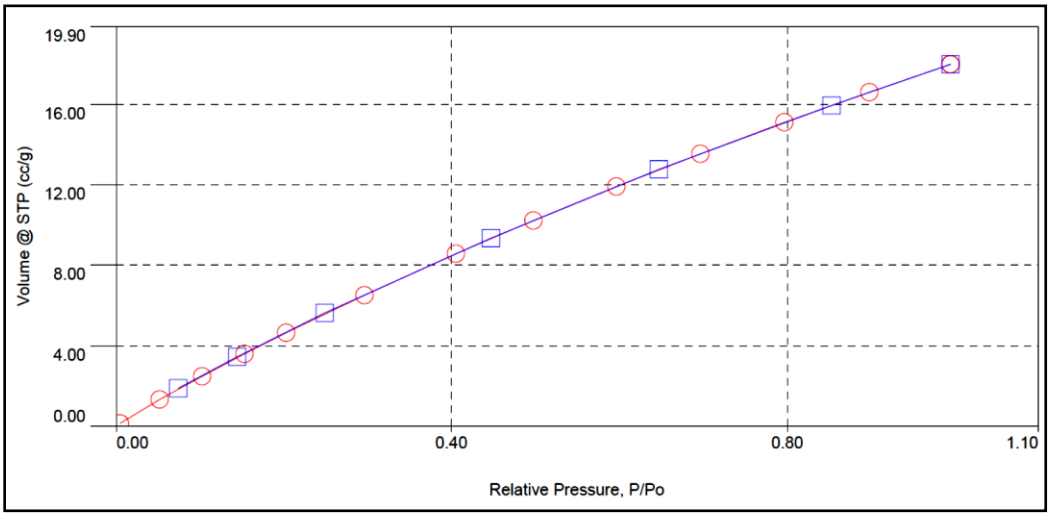

Figure 3 Loading of CH_4 on 5A MS using Quantachrome analyzer (○ Adsorption step; □ Desorption step)

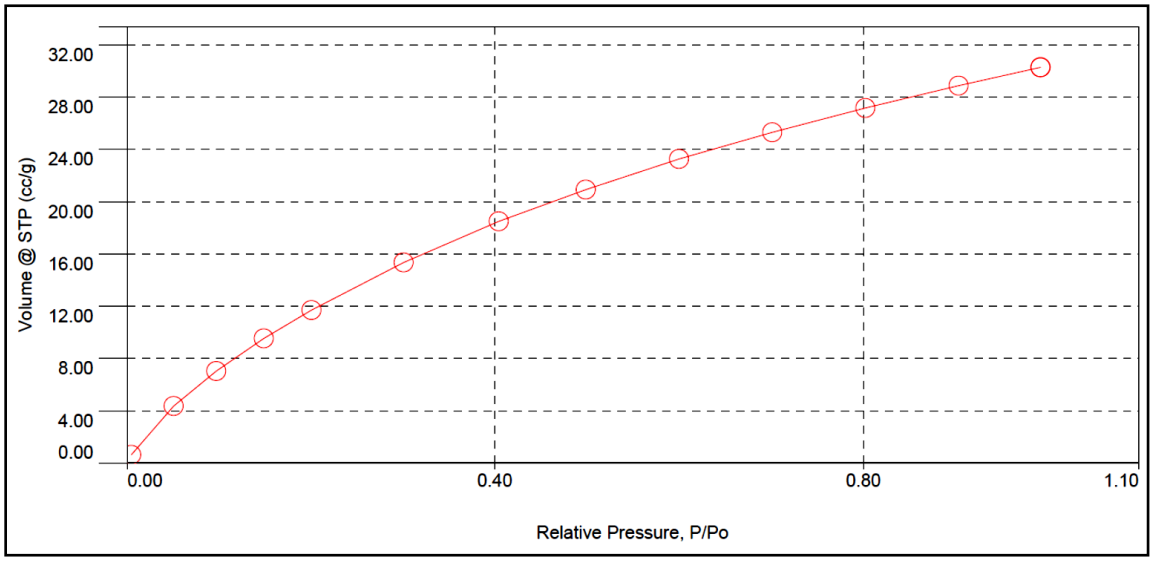

Figure 4 Loading of CO on 5A MS using Quantachrome analyzer (○ Adsorption step)

Now, to find the optimal isotherm parameters, estimation module of Aspen adsorption software was applied. The measured values were converted to the mole of adsorbed material on the unit mass of molecular sieve, and these data were applied to estimate the isotherm constants for both Langmuir and linear models.

In Table 4, the estimated isotherm constants, average absolute deviation (AAD%), and mean squared error (MSE%) of correlation for the mentioned isotherms are presented. Additionally, Figures 5 to 7 compare the actual adsorbed material against the simulated values. It can be seen that Langmuir isotherm is capable of simulating the absorbed material with the higher precision; therefore, in this work, it was chosen as the isotherm model for Aspen adsorption module.

Table 2 Estimated isotherm constants and calculated errors

Component	Linear				Langmuir			
	IP1	IP2	MSE %	AAD %	IP1	IP2	MSE %	AAD %
CO	0.00263	1.5E-09	3.84E-05	39.96	0.0033	1.509	3.32E-08	3.55
CH_4	8.05E-04	3.65E-05	2.08E-08	3.59	0.0011	0.35	7.26E-10	1.77
H_2	4.63E-04	2.77E-05	6.87E-09	4.315	6.26E-	0.33	1.74E-10	0.92

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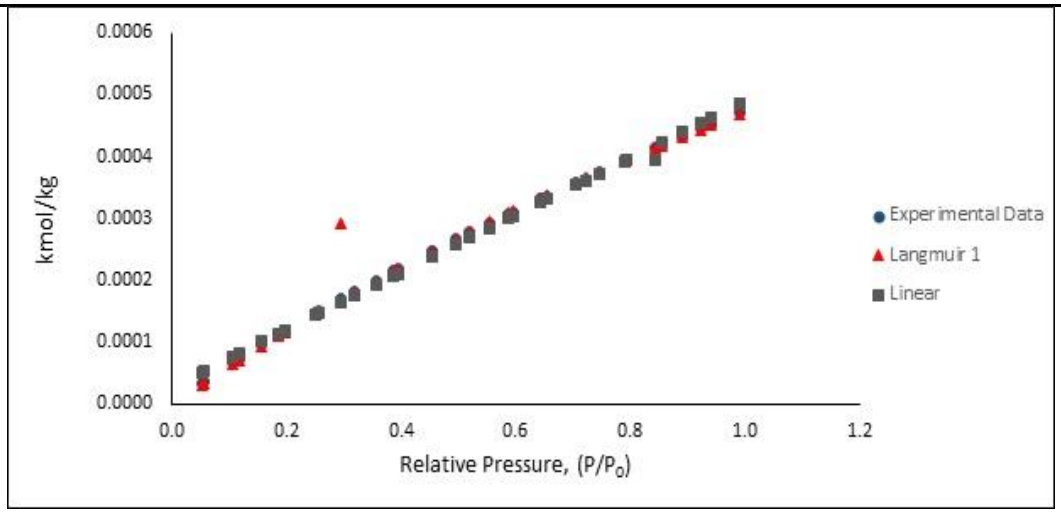

Figure 5. Comparison between actual loading of H_2 on 5A MS and calculated values by the isotherm model

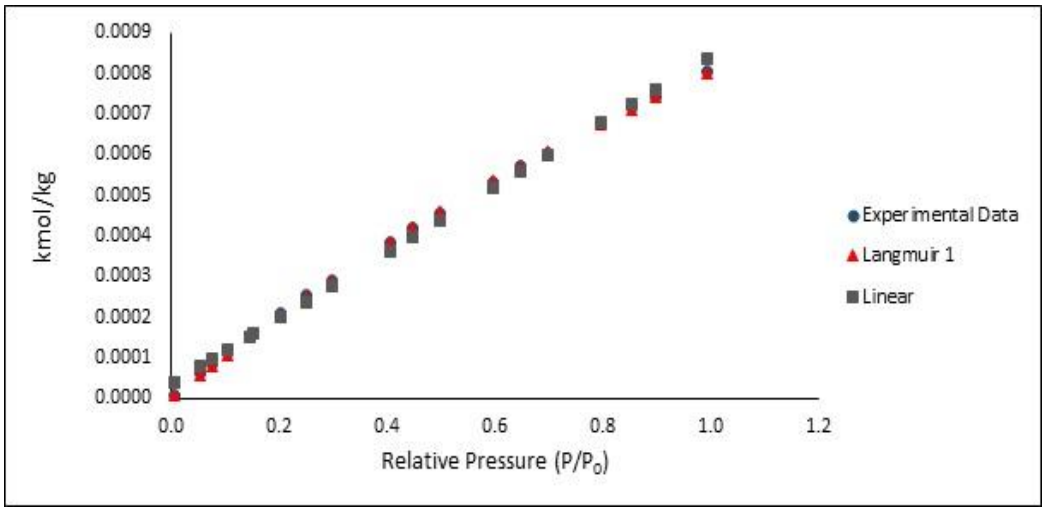

Figure 6. Comparison between actual loading of CH_4 on 5A MS and calculated values by isotherm model

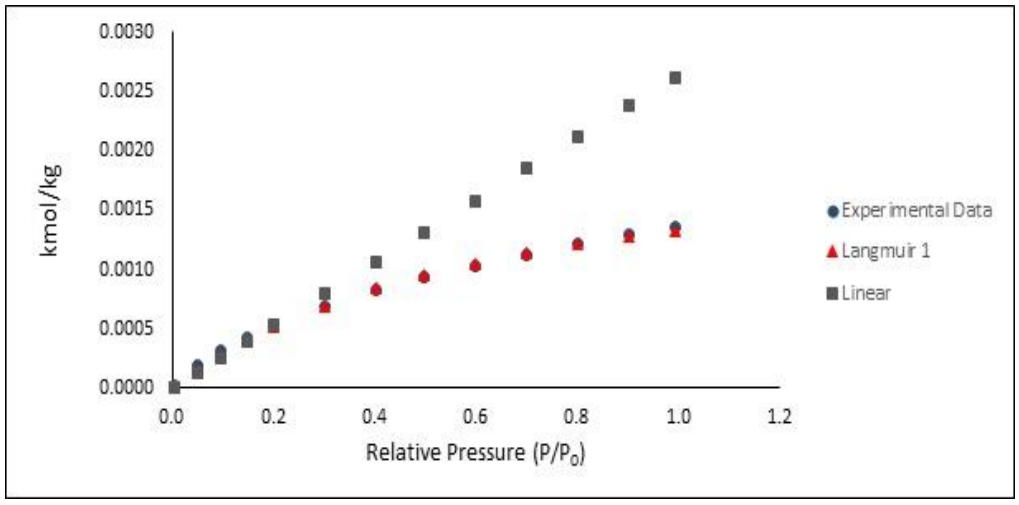

Figure 7. Comparison between actual loading of CO on 5A MS and calculated values by isotherm model

The bed in the industrial plant consists of three layers: 1. Silica gel (bottom layer) removes C_4H_{10}, iso-Butylene and 2-Butene trance; 2. Activated carbon (middle layer) removes C_2H_4, C_2H_6, C_3H_6, and C_3H_8, and 3. 5A Molecular sieve (top layer) removes CH_4 and CO. For this plant, the main impurities were CH_4 and CO which should be adsorbed by the 5A molecular sieve from the hydrogen feed. Therefore, it was assumed that the other impurities could be totally adsorbed by the bottom and middle layers; so, H_2 along with CO and CH_4 passed over the 5A molecular sieve layer. To perform the simulation, mass transfer coefficients (D_{CH4}=0.291 s^{-1}, D_{CO}=0.155 s^{-1} and D_{H2}=0.824 s^{-1}) and axial dispersion factors (Da_{CH4}=1.6212 cm^2s^{-1}, Da_{CO}=1.6411 cm^2s^{-1} and Da_{H2}=1.6234 cm^2s^{-1}) were calculated using equations presented in sections 3.1 and 3.2. Then, Aspen adsorption was employed to simulate the PSA process based on the estimated isotherm constants using all assumptions mentioned in section 3. Moreover, at the start of run, it was assumed that the bed was filled by the pure hydrogen. Therefore, about 25 sec was needed to push the existing pure H_2 out of the bed; therefore, the actual time of adsorption step was 25 sec less than the calculated breakthrough time.

Figure 8 shows the H_2 breakthrough curve obtained from the proposed simulation. As can be seen, after 440 sec, the breakthrough time for the hydrogen purification was happened. According to the literature, the dynamic adsorption capacity is normally 40 to 60 % less than the static adsorption one [22]. So, after considering the pushing time (25 sec), the actual breakthrough time would possibly occur between 166 and 249 sec after starting the adsorption step. According to the industrial data collected from the target commercial plant, it was necessary to stop the adsorption step after 165 sec after starting up the adsorption step to prevent from reaching the breakthrough point. Therefore, the lower margin of the simulated breakthrough time (166 sec) could be enough reliable to be used as a criteria during the design of the PSA plant.

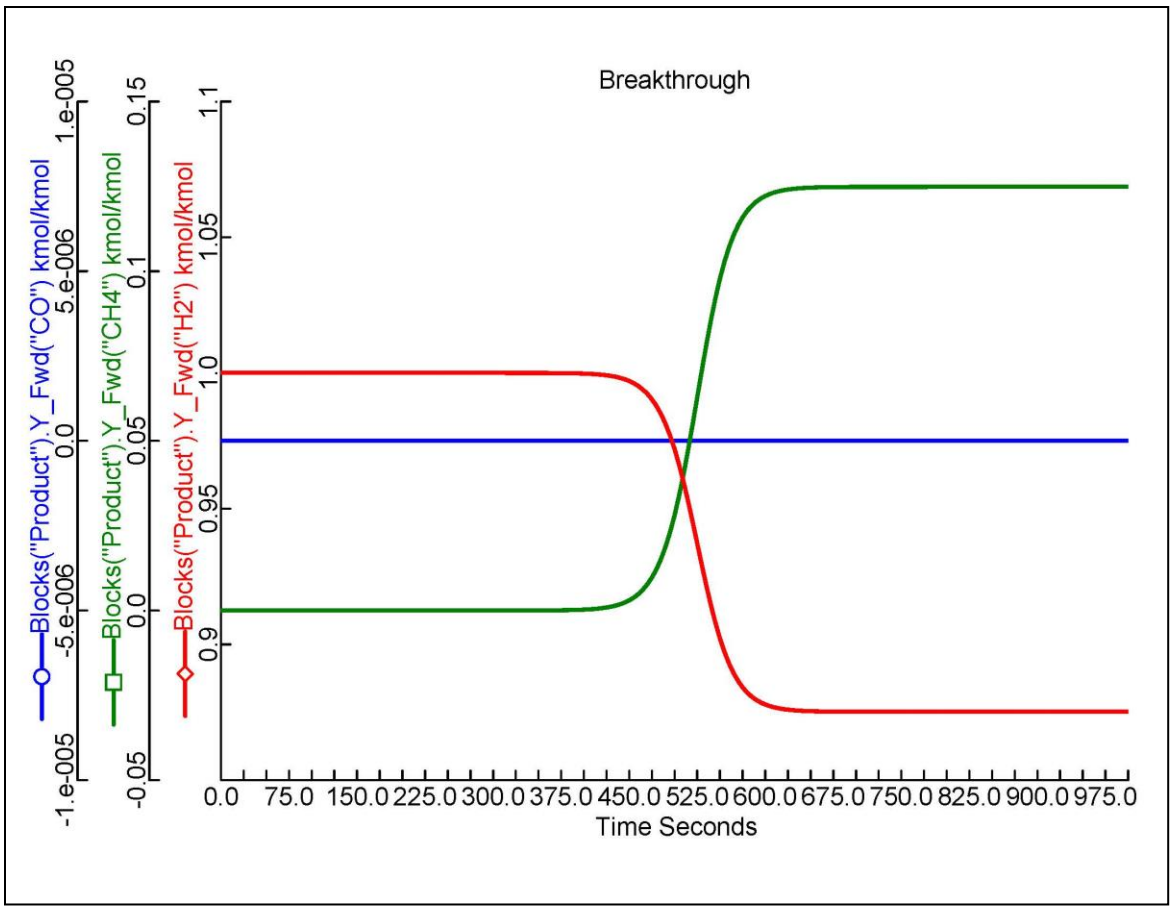

Figure 8. H_2 breakthrough curve obtained from the Aspen adsorption simulator

5. Conclusion

With increasing demands for efficient cycles, and growing needs for precise modeling, it is essential to develop approaches to design and simulate the operation of pressure swing adsorption (PSA) systems. In this study, a method to estimate the breakthrough time of a commercial PSA process, designed to produce pure hydrogen product (>99.99 mol%) was presented. At first, experiments were carried out on a commercial sample of 5A molecular sieve at standard conditions. Then, the volume of adsorbed materials was sketched versus the operational pressure. As it was expected, by increasing the pressure, the loading capacity of the 5A molecular sieve increased. Then, these data were used to estimate the isotherm constants for Langmuir and linear models. It was found that Langmuir isotherm can simulate the absorbed hydrogen with the higher precision (AAD%= 4.315 for linear isotherm and 0.92% for Langmuir one); so, the Langmuir isotherm was valid to be utilized for developing the adsorption simulator using Aspen adsorption software.

Results of the simulation showed that the breakthrough time of the hydrogen purification would occur in the range of 166-249 sec from starting the adsorption step. The lower margin i.e., 166 sec was so close to the actual breakthrough time (165 sec), strictly recommended by the licensor to prevent entering impurities to the hydrogen product. Therefore, the presented approach can be reliably used to design the PSA systems without bridging the breakthrough point.

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Nomenclature (Units)

T	*Temperature (K)*
P	*Pressure (atm)*
Σ_v	*Summation of atomic diffusion Volume*
ε	*Bed void fraction*
r_p	*Particle radius (m)*
ψ	*Shape factor*
μ	*Dynamic viscosity (Pa.s)*
υ_g	*Superficial velocity (m/s)*
M	*Molecular weight*
ρ_g	*Gas density (kg/m^3)*
D_{ax}	*Axial dispersion coefficient (cm^2/s)*
ρ_b	*Solid bulk density (kg/m^3)*
k_{MTC_i}	*Mass transfer coefficient (1/s)*
k_{fi}	*Film resistance coefficient (1/s)*
ε_p	*Particle porosity*
D_{pi}	*Macro pore diffusion coefficient (cm^2/s)*
sh	*Sherwood number*
D_{mi}	*Gas mixtures molecular diffusion (cm^2/s)*
Sc	*Schmidt number*
Re	*Reynolds number*
$Tort$	*Tortuosity factor*
D_{ki}	*Knudsen diffusion (cm^2/s)*
q_i	*Loading of component i (cc/gr)*
IP	*Isotherm parameter*
p_i	*Partial pressure of component i*

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