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Simulation of H_2S and CO_2 removal from model natural gas by pressure swing adsorption (PSA) processes

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Abstract

Natural gas contains acidic and toxic contaminants, such as CO_2 and H_2S, which need to be separated from CH_4 as its primary component. Among the purification technologies, adsorption is notable for some advantages, particularly its ability to regenerate the adsorbent through temperature and/or pressure variations. This study aims to computationally evaluate pressure swing adsorption (PSA) processes using simulations in Aspen Adsorption® to separate CO_2 and H_2S from CH_4 at high pressures. PSA performance indicators were determined based on two different inlet compositions and flow rates. Simulations were carried out with adsorption step at 50 bar, desorption step at 1 bar, and 298.15 K feed temperature. In case studies 1 and 2, feed streams with molar fractions of 64.98 mol% (CH_4), 35.00 mol% (CO_2), and 0.02 mol% (H_2S), at flow rates of 1 and 10 m³/day were used. In case studies 3 and 4, feeds with 89.98 mol% (CH_4), 10.00 mol% (CO_2), and 0.02 mol% (H_2S), also at 1 and 10 m³/day. It was verified that case 4, with a flow rate of 10 Nm³/day, yielded the best results: 99.86% purity; 84.90% recovery; and productivity of 13.6 ($kg_{CH4}\ kg_{Ads}^{-1}\ day^{-1}$). These results highlight the regenerative capacity of the adsorbent material (NaY zeolite) and its potential for effective natural gas purification.

Keywords: Pressure Swing Adsorption; Natural gas; Aspen Adsorption; Perfomance Indicators.

1. Introduction

Natural gas has the potential to replace oil as the dominant fuel in the industrial sector [1]. Different natural gas purification processes have been studied with the proposal of alternative technologies [2]. Among these, adsorption processes showed potential for contaminants removal such as H_2S [3], CO_2 [4], H_2O [5] and N_2 [6].

One of the advantages of adsorption processes is the regeneration of the adsorbent material [5]. This regeneration can be carried out by pressure swing [7], vaccum application [8], temperature variation [9] and the use of purge streams [10], referred to as processes PSA, VSA, TSA e CSA, respectively. Thus, the objective of this work was to computationally evaluate the performance indicators of a pressure swing adsorption bench scale unit using Aspen Adsorption® to separate CO_2 and H_2S from CH_4 at high pressures.

2. Mathematical model

The adsorption process for natural gas upgrading was modeled using Aspen Adsorption V14 (AspenTech). This software employs a set of partial differential equations, encompassing momentum, mass, and energy balances, along with a numerical integrator to create a detailed model. The following assumptions were made:

- The gas phase behavior follows the Peng-Robinson equation of state;
- The energy balance is considered as isothermal [11];
- Momentum balance in the column is described using the Ergun Equation [12];
- Mass balance is described by convection only [11];
- Momentum and mass variations in the radial direction are neglected;
- The mass transfer rate is described by a linear driving force model (LDF) [3];
- The adsorption isotherm is described by a multicomponent extended Langmuir equation with partial pressure dependence [3, 13].

3. Pressure Swing Adsorption (PSA)

The adsorption columns were simulated with the aim of representing a bench/pilot plant, and all the tests conducted in this work considered the same system presented in Figure 1. Its dimensions and the characteristics of the adsorbent material (NaY) [3] are shown in Table 1.

Table 1. Fixed bed characteristics.

Parameter	Value	Unit
Column height	50.0	cm
Column diameter	3.81	cm
Porosity	0.373	
Particle porosity	0.38	
Particle density	440.0	kg/m³
Particle radius	0.72	mm

The operational conditions used in the PSA plant simulations are presented in Table 2.

Table 2. Inputs and parameters to Aspen.

Variable	Case 1	Case 2	Case 3	Case 4
P_{Ads} (bar)	50	50	50	50
P_{Bd} (bar)	5011	555	16822	1676
T (K)	298.15	298.15	298.15	298.15
y_{CH_4}	0.6498	0.6498	0.8998	0.8998
y_{CO_2}	0.35	0.35	0.10	0.10
y_{H_2S}	0.0002	0.0002	0.0002	0.0002
$\dot{V}_{FEED}$ (Nm³/day)	1.0	10.0	1.0	10.0
$\dot{V}_{PG}$ (Nm³/day)	0.1	1.0	0.1	1.0
k_{n,CH_4} (s^{-1})	2.4619	3.9658	2.4758	4.0210
k_{n,CO_2} (s^{-1})	2.4616	3.9653	2.4755	4.0204
k_{n,H_2S} (s^{-1})	2.2024	3.5909	2.4486	3.9816

where P_{Ads} and P_{Bd} are adsorption and desorption pressures, T is temperature, y_i is the molar fraction, $\dot{V}_{FEED}$ and $\dot{V}_{PG}$ are feed and purge flow rates, and $k_{n,i}$ are mass transfer coefficients.

Purity

The refined product (the less adsorbed component) should be as pure as possible, while the waste (the more adsorbed component) is typically discharged in an impure form [14]. The purity of the product is obtained by [15]:

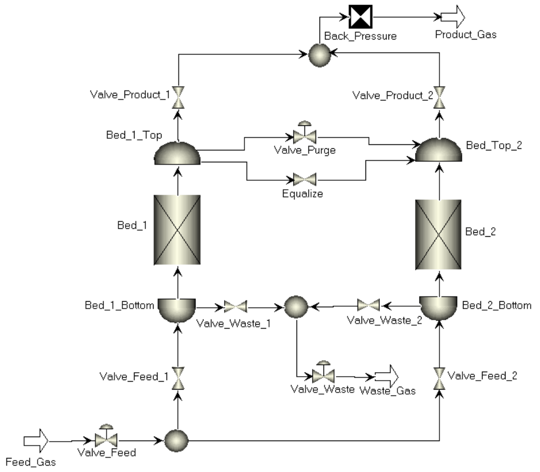

Figure 1. Pressure swing adsorption model built in Aspen Adsorption®.

$$Purity = \frac{\int_0^t y_{i,prod}\dot{V}_{prod}dt}{\sum_{i=1}^{n}\int_0^t y_{i,prod}\dot{V}_{prod}dt} \qquad (1)$$

where $\dot{V}_{prod}$ is the product flow rate and $y_{i,prod}$ is the molar fraction in the product.

Recovery

In a PSA process, the amount of gas recovered as refined product relative to the amount of feed gas entering in the bed is usually relatively lower compared to other unit operations such as distillation. Therefore, this is an important parameter in evaluating CAPEX, or the capital cost of the process [14]. This indicator is obtained by [16]:

$$Recovery = \frac{\int_0^t y_{i,prod}\dot{V}_{prod}dt}{\int_0^t y_i\dot{V}_{FEED}dt} \qquad (2)$$

Productivity

The productivity of an adsorbent material is a measurable parameter defined by the amount of refined product per unit of time per unit of adsorbent mass [17], and in a PSA process it is determined by [18]:

$$Productivity = \frac{\int_0^{t_{ads}} F_{i,prod} dt}{t_{Ads} m_{ads}} \quad (3)$$

where t_{ads} is the adsorption cycle, $F_{i,prod}$ is the molar flow rate of the product and m_{ads} is the mass of the adsorbent.

4. Results

The simulation results can show how pilot plants for pressure swing adsorption can be applied to the separation of CO_2 and H_2S from natural gas. In Table 3, the PSA cycle time outputs for each stage, the number of simulated cycles, and the performance indicators are shown.

Table 3. Outputs and results obtained with PSA process simulation.

	Case 1	Case 2	Case 3	Case 4
Press/Dep (s)	2160	213	2153	213
Ads/Bd (s)	5011	555	16822	1676
Eq (s)	29	13	29	12
N° cycles	2206	20247	833	7970
Purity (%)	97.10	93.36	99.89	99.86
CO_2 (ppm)	29044	66431	10.65	1365
H_2S (ppm)	0.06	0.38	0.0001	0.015
Recovery (%)	82,67	61,66	85,28	84,90
Productivity*	0.96	9.78	1.37	13.60

*kg_{CH4} kg_{ads}^{-1} day^{-1}

The time outputs for the PSA pressurization/depressurization (Press/Dep) and equalization (Eq) stages in the simulated cases undergoing slight changes, indicating minimal dependence on the raw gas composition and primary dependence on the feed flow rate. The adsorption/desorption (Ads/Bd) times were adjusted to between 10 to 20% before the CO_2 breakthrough times according to the respective breakthrough curves.

H_2S content in the product varies between 0.000001 and 0.0038 mol%. These values are in accordance with Brazilian rule ANP N° 886 for natural gas, indicating the potential for desulfurization of natural gas using the proposed adsorption processes.

CO_2 rates ranged from 0.1065 to 0.66431 mol%. Notably, in cases with higher flow rates, an increase in flow rate results in lower efficiency in contaminant separation. This could be due to the fluid flow conditions (higher velocity) resulting in lower resistance to mass transfer, a common phenomenon shown in similar studies. However, with the exception of Case 2, all other simulations were able to predict the reduction of CO_2 content to levels accepted by current Brazilian standards.

PSA performance indicators are also shown in Table 3. Thus, over 93% methane purity was obtained, with higher concentrations of CH_4 in cases 3 and 4 (>99.8%), which are extremely positive results for this type of operation. The methane recovery significantly decreases for case 2 (61.66%), while the other simulations achieved margins above 82%. Therefore, it is possible that for Case 2, there is an issue with the dimensioning of the PSA valve coefficients, resulting in a considerable loss of CH_4. It is also observed that the NaY productivity is highly dependent on the feed flow rate, with the best results (Cases 2 and 4) being those with the highest flow rates.

5. Conclusions

Time outputs for each step of the PSA cycle were adjusted in an attempt to maximize the product quantity, achieving high purity and maximum recovery. In relation to analysis done on purity indicators, Case 4 showed the best relative performance, achieving 99.86% CH_4 purity in the final product, 84.90% CH_4 recovery, and 13.60 kg_{CH4} kg_{Ads}^{-1} day^{-1} of productivity. Although the purity and methane recovery indicators were not the highest among those obtained, these values are relatively close to the maximum purity and recovery (99.89% and 85.28%, respectively) achieved in Case 3. However, the productivity indicator is much higher in Case 4 compared to Case 3 (1.37 kg_{CH4} kg_{Ads}^{-1} day^{-1}).

Simulation of Case 2 showed the worst performance among the simulations conducted, as there is a significant loss of the target product (only

61.66% methane recovery), and the product stream purity (93.36%) does not meet the requirements established by Brazilian standards. Future studies are going to be focused on optimizing the valve coefficients used, as well as the steps of the PSA cycle may provide further insights for the development of the proposed technology.

Finally, the evaluation of the performance indicators of the studied processes demonstrates that the PSA technology for separation and purification is suitable to be applied in the treatment of natural gas streams at high pressures.

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