

CFD study on the effects of different temperatures and feed velocities for CO₂, CH₄, and C₂H₄ adsorption using 5A molecular sieve

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Abstract. The removal of carbon dioxide (CO₂) from natural gas is a practical measure in dealing with problems such as CO₂ emissions into the atmosphere and reducing the cost of gas processing operations. Adsorption is a promising technology currently used, specifically pressure swing adsorption (PSA) method. In this paper, the adsorption column packed with 5A molecular sieve was simulated using COMSOL Multiphysics software for the separation of CO₂ from natural gas components, which are methane (CH₄) and ethylene (C₂H₄). The effects of different temperatures on adsorption time were investigated and the optimum adsorption time was determined by the purity of CH₄ and C₂H₄ at the column outlet. This study will be beneficial for optimising the design and process configuration of PSA.

1 Introduction

In the atmosphere, the concentration of greenhouse gases keeps on increasing to an alarming level due to the rise of worldwide demand for energy that is bound to a strong dependence on fossil fuels. Fossil fuels such as coal, oil, and natural gas (NG) are the major contributors to the emission of anthropogenic carbon dioxide (CO₂) to the atmosphere, leading to global warming, a challenging issue to both researchers and industries [1]. Nevertheless, NG is considered as the cleanest fossil fuel compared to oil and coal [2, 3]. It has been used for residential, commercial, and industrial heating [2, 4, 5]. NG reservoirs are usually found with other impurities, mainly CO₂, which eventually enhances the formation of carbonic acids and dry ice, and causes corrosion and clogging of delivery pipelines. CO₂ concentration above 2% or 3% significantly reduces the heat capacity of the gas and makes it economically less viable [6, 7]. Therefore, to utilise crude NG, CO₂ must be removed so

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that it will comply with the necessary technical standards before supplying NG to the market. For such reason, several separation technologies are widely used to remove CO₂ from NG such as absorption, adsorption, cryogenics, and membrane separation. Adsorption has been reported as the most feasible emerging alternative to remove CO₂, specifically pressure swing adsorption (PSA) method [8, 9].

PSA is a transient cyclical process in which CO₂ is adsorbed from the NG stream and CO₂ accumulates on the surface of a solid material called adsorbate. The solid adsorbent is purified using the difference in pressure to desorb/remove CO₂ and the gas is compressed for storage. Adsorption technology depends on the strong integration of both material science and process engineering. Ideal adsorbent materials with inherent characteristics have high working capacity, high selectivity, fast adsorption and desorption kinetics, chemical stability, and recyclability. The characteristics can be optimised by suitable design and process configuration. Although there are numerous studies regarding the equilibrium of adsorption on different adsorbents, it is important to study the column dynamic behaviour of a packed bed based on different operating parameters prior to designing an optimum adsorption process configuration with a selected adsorbent. The study was conducted to investigate the effects of three different temperatures (29.85, 99.85, and 299.85 °C) on the adsorption time and also the effects of different feed velocities on the adsorption of CO₂, methane (CH₄), and ethylene (C₂H₄) on 5A molecular sieve using COMSOL Multiphysics version 5.3. The optimum adsorption time or breakthrough time is determined when the concentration found at the outlet reaches the limiting permissible value of 0.01–0.05 of the initial concentration. As an addition to the study, the effects of feed velocity and optimum bed height were also investigated.

2 Methodology

2.1 Mathematical model

The mass transfer of CO₂ adsorption in a packed-bed column at different operating temperature was modelled in this study. Figure 1 shows a two-dimensional geometric model used in the present study for the simulation of CO₂ adsorption in a packed-bed column. During the adsorption process, the gas mixture flows into the porous media column and CO₂ is adsorbed onto the adsorbent materials. The model was developed using the following assumptions:

- The gas phase obeys the ideal gas law.
- The adsorbent is considered as a homogeneous phase.
- The mass transfer rate during the adsorption process is described by the linear driving force (LDF) model.
- The physical properties of the adsorbent are constant.

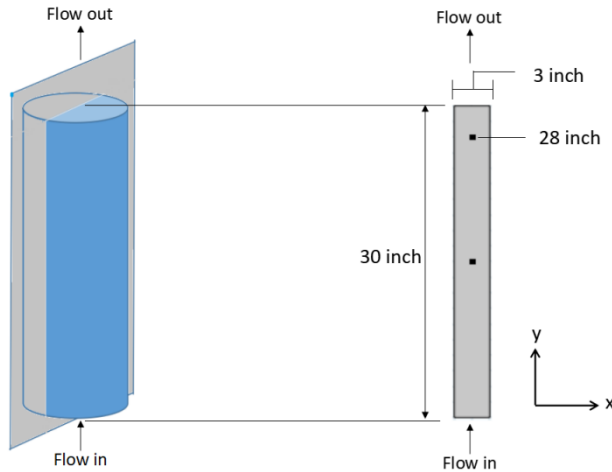


Fig. 1. Two-dimensional geometric model.

Based on the assumptions, the transient gas-phase mass balance for a differential control volume of the adsorption column can be described by the following equation:

$$\frac{\partial u_i C_i}{\partial z_i} + \frac{\partial C_i}{\partial t} + \left[\frac{1-\varepsilon}{\varepsilon} \right] \frac{\partial q_i}{\partial t} - D_{zi} \frac{\partial^2 C_i}{\partial z_i^2} = 0 \quad (1)$$

Where C_i is the bulk concentration (kg m^{-3}), ε is the bed porosity, and q is the component concentration on the solid phase at time t .

The rate of adsorption based on the LDF model is as follows:

$$\frac{\partial q_i}{\partial t} = k_i (q_i^* - q_i) \quad (2)$$

Where k_i is the mass transfer coefficient and q^* is the component concentration on the solid phase at equilibrium.

The adsorption isotherm is described by the Langmuir isotherm:

$$q_i^* = \frac{q_m K C_i}{1 + K C_i} \quad (3)$$

Where Q_m is the maximum capacity of adsorption and K is the equilibrium adsorption constant for the Langmuir isotherm.

K is the equilibrium adsorption constant described by the van't Hoff equation as follows:

$$K = K_0 \exp\left(\frac{-\Delta H}{RT}\right) \quad (4)$$

Where ΔH is the enthalpy change, R is the gas constant, and T is the temperature.

2.2 Case study

Previous experimental work on CO₂, CH₄, and C₂H₄ at three different temperatures by Pakseresht (2010) was used as the case study. The results from the work in the form of isotherm data were used to simulate the adsorption process in this study [10].

Table 1. Langmuir isotherm parameters for CO₂, CH₄, and C₂H₄ at 303, 373, and 573 K [10].

Gases	T (°C)	q _s (mmol g ⁻¹)	b (kPa ⁻¹)
CO ₂	29.85	3.919	0.0195
	99.85	3.440	0.0142
	299.85	1.701	0.0013
CH ₄	29.85	2.029	0.00509
	99.85	1.464	0.00441
	299.85	1.290	0.000743
C ₂ H ₄	29.85	3.338	0.0150
	99.85	2.507	0.0100
	299.85	2.419	0.000658

2.2 Computational methodology

The optimum adsorption time to separate CO₂ from CH₄ and C₂H₄ was determined through computational fluid dynamics (CFD) using COMSOL version 5.3. The transport diluted species through porous media interfaces was selected as the main physics package that describes mass balance in the bulk flow through the porous material. Table 2 shows the parameters used. A point plotted on the column at the height of 28 inch, approximately at the end of the packed-bed column, was used as a reference point for identifying the presence of gases and the limiting allowed composition.

Table 2. Parameters used in the separation of binary gas mixtures.

Adsorbent	5A molecular sieve
Bed Length	30 inch
Bed Diameter	3 inch
Operating Temperature	303, 373, & 573K
Inlet Velocity	100 & 160 cm s ⁻¹
Inlet Concentration	60% CH ₄ , 25% CO ₂ , & 15% C ₂ H ₄
Adsorbent Porosity	0.4
Adsorbent Density	600 kg m ⁻³

3 Results and discussion

3.1 Effects of operating temperature

Figure 2 shows the plots of breakthrough curves of CO₂, CH₄, and C₂H₄ concentration in the column versus time at 29.85, 99.85, and 299.85 °C at the column height of 28 inch. The result shows that the breakthrough curve of CH₄ (green) increases at a quick pace, around 400 s for 29.85 °C, 250 s for 99.85 °C, and <100 s for 299.85 °C. This is followed by C.H. (red) around 2,000 s for 29.85 °C, 1,000 s for 99.85 °C, and 100 s for 299.85 °C. CO₂ is the last gas that reached the end of the packed-bed column. This is due to the high adsorption capacity of CO₂ compared to the other two gases. The optimum adsorption time for the removal of CO₂ can be determined from the breakthrough points for 29.85 °C at 3,000 s, 99.85°C at 1,800 s, and 299.85 °C at 100 s.

The increase in temperature leads to the decrease of the breakthrough time for each component in reaching the packed-bed column. The trend can be observed from the graph with the shift to the left as the temperature increases. This phenomenon is unfavourable for gas adsorption resulting from less residence time of gas in the column, which leads to low amount of CO₂ adsorbed on the adsorbent and subsequently low adsorption capacity. This supports the relation in the van't Hoff equation where equilibrium constant (K) is inversely proportional to the temperature. When the equilibrium constant is small, the adsorption capacity will also be low. The same pattern was also observed in the previous research at low temperature, where the dissipation energy of the adsorption process was more efficient and the bed was provided with a higher adsorption capacity [11, 12].

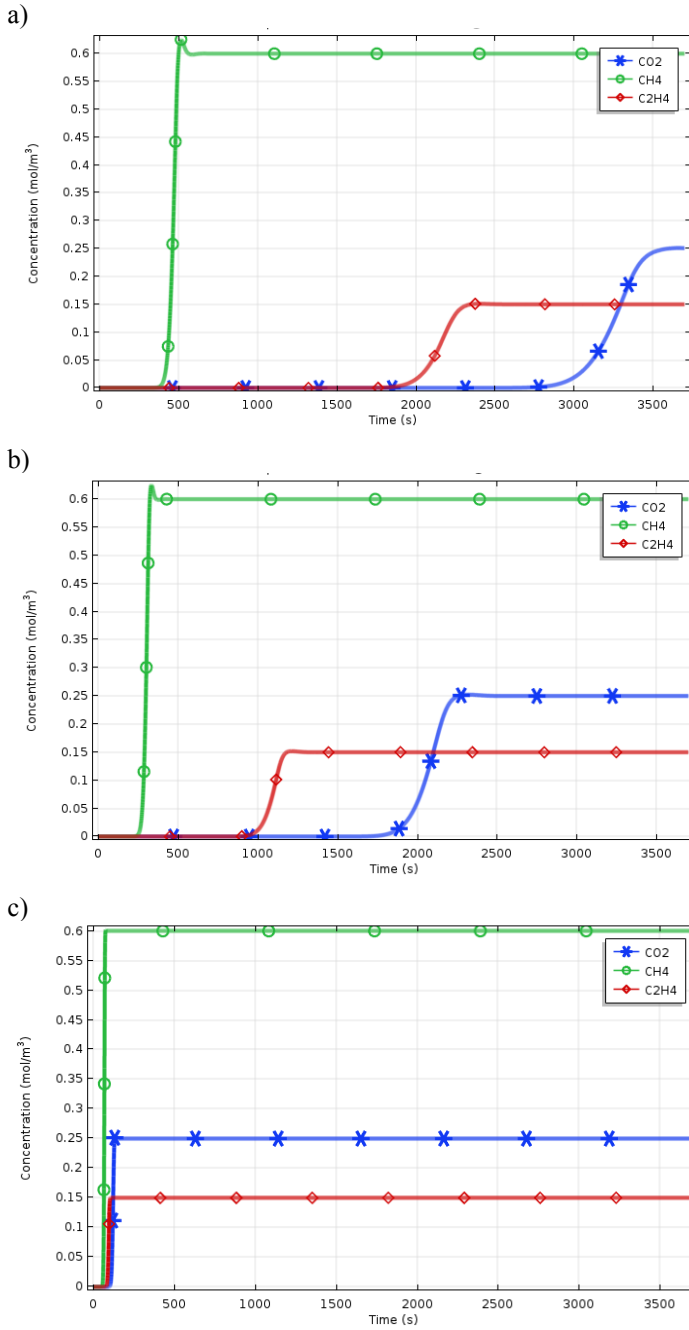


Fig. 2. Concentration of CO₂ (blue), CH₄ (green), and C₂H₄ (red) versus time at (a) 29.85 °C, (b) 99.85 °C, and (c) 299.85 °C.

3.2 Effects of feed velocity

The evaluation of CO₂ concentration in the column at different feed velocities is presented in Figure 3. It shows the variation in the contours along the height of the bed by varying the feed velocity from 100 to 170 cm s⁻¹ with constant CO₂ inlet concentration, adsorption time (2,000 s), and temperature (29.85 °C). From the surface plot at 2,000 s, the mass transfer zone for the feed velocity of 100 cm s⁻¹ is at the middle (17 inch) of the bed, whereas the mass transfer zone for the feed velocity of 170 cm s⁻¹ is almost at the end of the packed bed (27 inch). At higher velocity, CO₂ would leave the column faster. This is supported by literature that showed a significantly higher CO₂ concentration was found at the outlet of the column under higher feed velocity. This indicates lower adsorption capacities because the gas mixture had shorter residence time and left the column before the equilibrium adsorption of CO₂ occurred [13, 14].

The optimum bed height can be determined from the concentration contours as shown in Figure 3(a). The dark blue contour indicates zero concentration of CO₂ inside the column. The optimum height for the packed-bed column with feed velocity of 100 cm s⁻¹ and adsorption time of 2,000 s is approximately 22 inch.

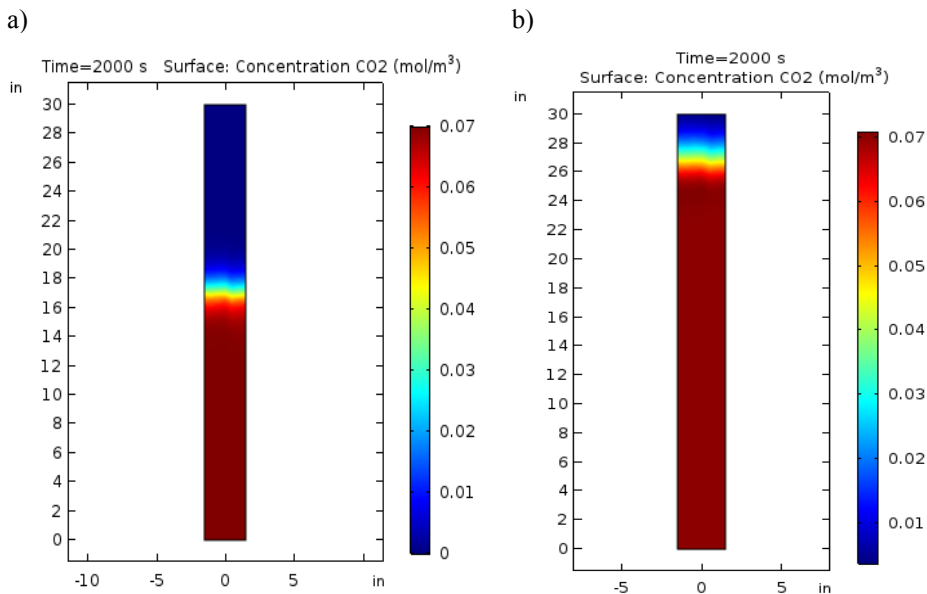


Fig. 3. Concentration contours of CO₂ with feed velocities at a) 100 and b) 170 cm s⁻¹.

4 Conclusion

The study used computational fluid dynamics to simulate the adsorption of CO₂, CH₄, and C₂H₄ in a packed-bed column with 5A molecular sieve. The breakthrough curves and concentration contours were used to study the effects of operating parameters on the adsorption dynamics inside the packed-bed column. The operating temperature and feed velocity are the two operating parameters that influence the adsorption process performance, and the parameters were accordingly investigated. The simulation showed

that the two variables investigated significantly affect adsorption dynamics. Based on the temperature, the time for the gas mixture to reach the packed-bed column outlet decreases as temperature increases. The residence time of the gases is low; hence, they might leave the column before equilibrium could be achieved, which subsequently reduces CO₂ removal efficiency and gives low adsorption capacity. The optimum adsorption time for CO₂ is 3,000 s at 29.85 °C, 1,800 s at 99.85 °C, and 100 s at 299.85 °C. Similarly, the results of the change in feed velocity of CO₂ with constant operating time, temperature, and feed concentration showed that the mass transfer zone moved faster towards the end of the packed-bed column with higher feed velocity. The optimum bed height for lower velocity is 22 inch.

The authors wish to acknowledge the financial and material support provided by Universiti Teknologi Malaysia and Malaysia-Thailand Joint Authority (MTJA) research grant (Vot. No. R.K130000.7643.4C116).

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