

Research Article

Simulation of Binary CO₂/CH₄ Mixture Breakthrough Profiles in MIL-53 (Al)

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MIL-53 (Al) aluminum terephthalate, a commercial metal-organic framework, has been studied as a potential candidate for pressure swing adsorption separation of CO₂/CH₄ binary mixtures. Pure gas isotherms of CH₄ and CO₂ measured over 0–6 MPa and at room temperature are fitted with the Dubinin-Astakhov (D-A) model. The D-A model parameters are used in the Doong-Yang Multicomponent adsorption model to predict the binary mixture isotherms. A one-dimensional multicomponent adsorption breakthrough model is then used to perform a parametric study of the effect of adsorbent particle diameter, inlet pressures, feed flow rates, and feed compositions on the breakthrough performance. Commercial MIL-53 with a particle diameter of 20   m renders high tortuous flow; therefore it is less effective for separation. More effective separation can be achieved if MIL-53 monoliths of diameters above 200   m are used. Faster separation is possible by increasing the feed pressure or if the starting compositions are richer in CO₂. More CH₄ is produced per cycle at higher feed pressures, but the shortened time at higher pressures can result in the reduction of the CH₄ purity.

1. Introduction

Pressure swing adsorption (PSA) is a well-established gas purification process which has already been employed in multiple applications, including hydrogen separation and purification [1–3], air purification [4], raw natural gas purification, and CO₂ capture [5, 6]. Due to its potential to purify CH₄ from CO₂/CH₄ mixtures especially in small and medium industrial scales, PSA techniques are currently being extended to new areas like methane purification from biogas and landfill gas [7–10]. For zeolites [11] or activated carbon [12], which are the most commonly used adsorbent materials for PSA purification of biogas/landfill gas, the adsorbent regeneration is still difficult and energy consuming, leading to lower productivity and higher expenses [9, 13].

Discovery of novel nanoporous materials like metal-organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs), and covalent frameworks (COFs) has started a new chapter in adsorbent search for applications including

gas storage, drug delivery [14], carriers for nanomaterials [15, 16], and gas separation and purification [17]. Due to their high porosity and large CO₂ adsorption capacities, MOFs are specifically suitable for adsorptive separation and purification of CH₄ from CO₂/CH₄ mixtures, such as those from biogas or natural gas sources. Different types of extended framework materials have been reported with high adsorption capacities for CH₄, CO₂, and H₂ [18–26].

Breakthrough performance of adsorbent columns is an important characteristic required to evaluate the potential of adsorbents for PSA applications. There have been a few experimental measurements of breakthrough performance of MOF adsorbents for separating CO₂/CH₄ mixtures [17, 19]. Heymans et al. used experiments and simulations to predict breakthrough performance of MIL-53 (Al) for acidic gas separation from CH₄/CO₂ mixture [27]. Even though they used both the experiments and simulations, their studies were restricted to a single gas mixture composition (50 : 50) at a single pressure of 1.06 bar and no parametric effects

of process variables such as feed pressure, composition, and feed flow were considered. Investigating parametric effects of the process variables and their influence on the separation process is necessary to perform preliminary screening of novel adsorbents like MOFs. This work is a novel attempt in that direction. Furthermore, the isotherms of MIL-53 (Al) sample used in our studies do not have breathing behavior as for the MIL-53 (Al) reported in previous studies [17, 19]. Therefore, our work offers a comparison of the breakthrough characteristics of MIL-53 (Al) with different structural flexibility. In order to calculate the multicomponent adsorption isotherms in this work, we have used an analytical model, namely, Doong-Yang Model. This model has already been used previously by our group and has been shown to fit the experimental isotherms rather well. Use of analytical models, such as DYM, allows one to easily implement the model in the computational fluid dynamics calculations of the breakthrough performance.

In this work, we present a systematic study of the parametric effects of an aluminum terephthalate MOF-MIL-53 (Al) particle size, feed pressure, flow rates, and composition of CO₂/CH₄ binary gas mixtures on the dynamic breakthrough separation process. This parametric study is performed using the computational fluid dynamics simulation platform COMSOL Multiphysics. This paper is organized as follows. First, we present the characterization of MIL-53 framework used in this work. Then we present the experimentally measured pure gas CO₂ and CH₄ isotherms on MIL-53 which are used to predict the binary mixture adsorption isotherms. A parametric study of the effects of adsorbent particle size, feed pressures, gas flow rates, and gas composition on the breakthrough profiles of CO₂/CH₄ mixtures and on the adsorbent bed temperatures is finally presented.

2. Experimental

Particle size distribution, pure gas isotherms, and adsorption isosteric heat of commercial MIL-53 (Al) aluminum terephthalate C₈H₅AlO₅ were measured using standard methods. A JEOL Scanning Electron Microscope (JSM-5510) was used to measure the particle diameter and estimate the diameter distribution of the MOF particles. The pure gas adsorption isotherms of CO₂ and CH₄ were performed at room temperature in the range of pressures between 0 and 6 MPa using Sievert's volumetric gas adsorption system. The BET specific surface area, pore size distribution, and other pore characteristics were measured by adsorbing N₂ at 77 K in a Micromeritics ASAP 2020 analyzer. Gases used for the measurements are high purity gases (99.999%) supplied by Praxair Canada. Isothermic heat of adsorption and heat capacity of MIL-53 were measured using a coupled volumetric-calorimetric system. Powder X-ray diffractometer (Bruker D8 FOCUS, Cu K α) was used to examine the crystalline structure of the MIL-53. The coefficients of diffusions for equimolar binary mixtures of CH₄ and CO₂ were measured using an isotope exchange system.

3. Theory

A one-dimensional multicomponent adsorption breakthrough model based on the approach proposed by Casas

et al. is presented here [29]. This model accounts for the mass and heat transfer inside a nonisothermal adsorbent column filled with MIL-53, the heat transfer in the fluid and in the gas-phase, and the conductive and convective heat transfer between the column wall and the surroundings. The following restrictions are assumed in the model: ambient temperature is considered to be constant, radial gradients in the column are negligible, mass transfer coefficients and isosteric heat of adsorption and heat capacities of the solid phase and of the wall are constants, and axial conductivity on the wall of the column is assumed to be zero. The adsorptive mass transfer rate is expressed in the form of a linear driving force (LDF) model. This breakthrough model was extensively validated by different authors for the PSA applications with good results [5, 6, 29, 30].

3.1. Mass and Energy Balance. The total mass balance in the breakthrough column is given by

$$\epsilon_t \frac{\partial c}{\partial t} + \frac{\partial (uc)}{\partial z} = -\rho_b \sum_{i=1}^n \frac{\partial q_i}{\partial t}. \quad (1)$$

Mass balance for each species is given by

$$\epsilon_t \frac{\partial c_i}{\partial t} + \frac{\partial (uc_i)}{\partial z} + \rho_b \frac{\partial q_i}{\partial t} - \epsilon_b \frac{\partial}{\partial z} \left(D_L c \frac{\partial y_i}{\partial z} \right) = 0, \quad (2)$$

where c is the total concentration of the fluid phase, c_i the fluid phase concentration for each component, q_i the adsorbed phase concentration for each species, u the superficial gas velocity, ϵ_t the total porosity, ϵ_b the bed porosity, ρ_b the column bulk density, D_L the axial dispersion coefficient (for all components), t the time, z the longitudinal coordinate on the column, y_i the gas-phase mole fraction of the i th component, and n the number of components in the gas mixture.

The pressure drop is calculated from Darcy's law, where pressure gradient, velocity, and porosity are correlated as

$$u = -\frac{\kappa}{\mu} \nabla p; \quad (3)$$

$$\nabla p = -\frac{150\mu(1-\epsilon_b)^2}{\epsilon_b^3 d_p^2} u.$$

Here, κ is the permeability of the material, μ the dynamic viscosity, and d_p the particle diameter.

The time-dependent variation of the absolute adsorption is described using the LDF adsorption kinetics model:

$$\frac{\partial q_i}{\partial t} = k_i (q_i^* - q_i), \quad (4)$$

where k_i is the mass transfer coefficient, q_i^* the solid phase concentration at equilibrium pressure, and q the solid phase concentration at time t . To describe the adsorption isotherms, we use the D-A isotherm model. The absolute adsorption in the D-A model is given by

$$q_i = q_{\max} \exp \left[-\left(\frac{RT}{\epsilon} \ln \frac{P_s}{p} \right)^n \right]. \quad (5)$$

Here, q_i is the absolute adsorption of i th component of the mixture, $q_{\max}$ the maximum absolute adsorption corresponding to saturation pressure P_s , ε the characteristic energy of adsorption, n the measure of the pore heterogeneity of the microporous material [31–33], R the ideal gas constant, T the temperature, and p the gas pressure. The measured excess adsorptions of pure gases are converted into absolute adsorption using [34]

$$n_{\text{abs}} = \frac{n_{\text{exc}}}{1 - \rho_{\text{gas}}/\rho_{\text{sat}}}, \quad (6)$$

where n_{abs} , n_{exc} , ρ_{gas} , and ρ_{sat} are the absolute adsorption, the excess of adsorption, and the density of the gas phase and of the adsorbed phase, respectively.

3.2. State Equation (EOS). In the range of temperature and pressures considered in this study, we note that the compressibility factors of CO_2/CH_4 gas mixtures (reported in the NIST REFPROP Standard Reference Database [35]) are between 0.9 and 1. Hence to describe the state of the gases, we use the equation of state of an ideal gas:

$$c_i = \frac{pY_i}{RT}. \quad (7)$$

3.3. Porosity. The porosities are determined using

$$\begin{aligned} \epsilon_t &= 1 - \frac{\rho_b}{\rho_{\text{sk}}}, \\ \epsilon_b &= \epsilon_t - \epsilon_{\text{mi}}, \\ \epsilon_{\text{mi}} &= V_a \times \rho_b, \end{aligned} \quad (8)$$

where ρ_b is the bulk density, ρ_{sk} the skeletal density, ϵ_b the bed porosity, ϵ_{mi} the microporosity, ϵ_t the total porosity, and V_a the micropore volume. The skeleton density ρ_{sk} is determined using the helium expansion method in standard Sievert's apparatus, ρ_b is the bulk density measured using ASTM standard procedure (ASTM D 2854-96), and the micropore volume V_a is obtained from the measurements of the pore size distribution with nitrogen at 77 K in an ASAP instrument.

For describing the multicomponent adsorption isotherms, we use the Doong-Yang Model. The DYM is based on the pure gas isotherms D-A model parameters reported in Table 3. The DYM adsorption model for a multicomponent mixture is given by

$$V = V_0 \exp \left[- \left(\frac{RT}{\varepsilon} \ln \frac{P_s}{p} \right)^n \right]. \quad (9)$$

For binary gas adsorption, the respective amount of each adsorbed component is given by

$$\begin{aligned} V_1 &= (V_{01} - V_2) \exp \left[- \left(\frac{RT}{\varepsilon_1} \ln \frac{P_{s1}}{p_1} \right)^{n1} \right], \\ V_2 &= (V_{02} - V_1) \exp \left[- \left(\frac{RT}{\varepsilon_2} \ln \frac{P_{s2}}{p_2} \right)^{n2} \right]. \end{aligned} \quad (10)$$

Equations (10) can be written as

$$\begin{aligned} V_1 &= \frac{A_1 (V_{01} - V_{02} A_2)}{1 - A_1 A_2}, \\ V_2 &= \frac{A_2 (V_{02} - V_{01} A_1)}{1 - A_1 A_2} \end{aligned} \quad (11)$$

by substituting

$$\begin{aligned} A_1 &= \exp \left[- \left(\frac{RT}{\varepsilon_1} \ln \frac{P_{s1}}{p_1} \right)^{n1} \right], \\ A_2 &= \exp \left[- \left(\frac{RT}{\varepsilon_2} \ln \frac{P_{s2}}{p_2} \right)^{n2} \right]. \end{aligned} \quad (12)$$

In (10)–(11) V_{0i} is the limiting micropore volume of component i and V_i the volumetric amount of adsorbate for each component. For converting the experimental isotherms between molar and volume units, the following expressions are used:

$$q_i^* = \frac{V_a}{V}, \quad (13)$$

$$V_a = V_{ls, nbp}, \quad T < T_{nbp}, \quad (14a)$$

$$V_a = V_c - (V_c - V_{ls, nbp}) \left(\frac{T_c - T}{T_c - T_{nbp}} \right), \quad (14b)$$

$$T_{nbp} \leq T < T_c,$$

$$V_a = V_c T_r^{0.6}, \quad T > T_c. \quad (14c)$$

Further details of DYM are available in Doong and Yang, Rege et al. [4, 36], and the authors' previous work [34].

The energy balance equation for the column (fluid and the solid phase) is given by the following equation:

$$\begin{aligned} &(\epsilon_t C_g + \rho_b C_s + \rho_b C_{\text{ads}}) \frac{\partial T}{\partial t} - \epsilon_t \frac{\partial p}{\partial t} + u C_g \frac{\partial T}{\partial z} \\ &- \rho_b \sum (-\Delta H_i) \frac{\partial q_i}{\partial t} + \frac{4h_L}{d_i} (T - T_w) \\ &- \epsilon_b \frac{\partial}{\partial z} \left(K_L \frac{\partial T}{\partial z} \right) = 0, \end{aligned} \quad (15)$$

where C_g is the heat capacity of the gas, C_s the heat capacity of the solid, C_{ads} the heat capacity of the adsorbed phase, ΔH_i the isosteric heat of adsorption for each component, h_L the heat transfer coefficient (inside the column + wall), K_L the axial thermal conductivity in the fluid phase, T the temperature inside the column, T_w the temperature of the column's external wall, and d_i the inner diameter of the tube. The energy balance is also defined for the heat exchange between the wall and the surroundings, where the effects of

conduction between the column and the ambient are considered. This is given by

$$\begin{aligned} \frac{\partial T_w}{\partial t} &= \frac{2\pi}{C_w A_w} \left(h_L R_i (T - T_w) - \frac{H_w d_o}{2} (T_w - T_{\text{amb}}) \right) \\ &+ \frac{1}{C_w} \frac{\partial}{\partial z} \left(K_w \frac{\partial T_w}{\partial z} \right), \end{aligned} \quad (16)$$

where H_w is the heat transfer coefficient between the wall and the surroundings, C_w the heat capacity of the column wall, A_w the area of the cross section of the column, and d_o the column's external diameter.

3.4. Boundary and Initial Conditions. The boundary conditions used in the model are described below.

Inlet boundary conditions of the system (i.e., at $z = 0$) are

$$\begin{aligned} (uc)_{\text{inlet}} &= uc, \\ (uc_i)_{\text{inlet}} &= uc_i - \varepsilon_b D_L c \frac{\partial y_i}{\partial z}, \\ (uC_g T)_{\text{inlet}} &= u_{\text{inlet}} c_{g,\text{inlet}} T - \varepsilon_b K_L \frac{\partial T}{\partial z}. \end{aligned} \quad (17)$$

Outlet boundary conditions (i.e., at $z = L$) are

$$\begin{aligned} \frac{\partial c_i}{\partial z} &= 0, \\ \frac{\partial T}{\partial z} &= 0, \\ P &= P_{\text{outlet}}. \end{aligned} \quad (18)$$

Initial conditions at $t = 0$ for $0 \leq z \leq L$ are

$$\begin{aligned} c_{\text{CO}_2} &= c_{\text{CH}_4} = 0, \\ T_w &= T_{\text{amb}}, \\ T &= T_{\text{init}}. \end{aligned} \quad (19)$$

The heat capacities of the fluid and the adsorbed phase in (15) are defined using

$$\begin{aligned} C_g &= \sum_i^N c_i C_{g,i}^{\text{mol}}, \quad i = 1, \dots, N, \\ C_{\text{ads}} &= \sum_i^N q_i C_{g,i}^{\text{mol}}, \quad i = 1, \dots, N, \end{aligned} \quad (20)$$

where the specific heat capacities $iC_{g,i}^{\text{mol}}$ are calculated as an average over a range of temperatures from ambient temperature to the highest temperature reached in the adsorption column for each pressure under study. This assumption will add also more simplicity to the model, without affecting the accuracy of the results [29]. Note that the concentration and heat capacity of the fluid and of the adsorbed phase are temperature-dependent quantities.

The heat transfer coefficient h_L is obtained from the Nusselt number, N_u :

$$N_u \equiv \frac{h_L 2R_i}{K_L} = \eta_1 \text{Re}^{\eta_2} \exp\left(-\frac{4.6d_p}{2R_i}\right), \quad (21)$$

where

$$\text{Re} = \frac{\rho u d_p}{\mu}. \quad (22)$$

In (21) and (22), R_i is the internal radius of the column, K_L the axial thermal conductivity in the fluid phase, and Re the Reynolds number. The values for η_1 and η_2 are calculated from the correlation of heat transfer coefficients for gases through packed tubes [37].

The thermal conductivity is estimated using

$$K_L = D_L C_g, \quad (23)$$

where D_L is the axial dispersion coefficient which is calculated with the Edwards-Richardson correlation [38]:

$$D_L = 0.73 D_m + \frac{0.5 d_p u}{1 + 9.49 \times D_m / d_p u}, \quad (24)$$

where u is the velocity, D_m is the molecular diffusion coefficient calculated according to the Fuller method [39], and d_p is the particle diameter. The heat transfer coefficient between the wall and surrounding is calculated using

$$h_w = a d_o^{3m-1} (T_{\text{max}} - T_{\text{min}})^{1/4}, \quad (25)$$

where the heat transfer parameters a and m are reported in the literature for free convection cases [40]. T_{max} is the maximum temperature during the adsorption process and T_{min} is assumed to be room temperature.

The system of mass and energy balance partial differential equations is solved using the commercial software platform COMSOL Multiphysics using modules for heat transfer of porous media, heat transfer of fluids, transport of diluted species, and Darcy's law. The default equations of COMSOL modules are redefined according to the aforementioned system of equations. Table 1 lists the model parameters used in our study. Column properties used are typical values of stainless steel.

4. Results and Discussions

4.1. Material Characterization. The XRD pattern of MIL-53 shown in Figure 1(a) is similar to that of MIL-53 samples reported previously [41]. Results for the particle size and particle size distribution are shown in Figures 1(b) and 1(c). The particle size distribution histogram obtained using a bin width of $1 \mu\text{m}$ shows that most particles have diameters between 17 and $25 \mu\text{m}$ with a peak distribution at $\sim 20 \mu\text{m}$. Pore and surface characterization, densities, and porosities of MIL-53 are given in Table 2.

Since no reported diffusion coefficients of CO_2 and CH_4 in MIL-53 are available yet, we used those available for MOF-5. These coefficients of diffusion k_i were measured for

TABLE 1: Model parameters.

Parameter	Value	Description
ρ_b	385 [kg/m ³]	Bulk density of the adsorbent bed
R	8.314 [J/(mol K)]	Ideal gas constant
η_1	3.5	Nusselt number parameter
η_2	0.7	Nusselt number parameter
k_{CO_2}	0.8 [1/s]	CO ₂ lumped mass transfer coefficient
k_{CH_4}	0.5 [1/s]	CH ₄ lumped mass transfer coefficient
h_w	4.5 [J/(m ² s K)]	Heat transfer coefficient (lumping wall + heating)
D_m	1.12×10^{-6} [m ² /s]	Molecular diffusion coefficient
d_p	5×10^{-6} – 500×10^{-6} [m]	Particle diameter
ϵ_{to}	0.719	Overall void fraction
C_s	845 [J/(kg K)]	Heat capacity of the solid
ϵ_b	0.573	Bed void fraction
ΔH_{CO_2}	–23600 [J/mol]	Heat of adsorption of CO ₂
ΔH_{CH_4}	–15800 [J/mol]	Heat of adsorption of CH ₄
R_i	3.5 [mm]	Inner column radius
R_o	4.5 [mm]	Outer column radius (lumped)
$m_w \text{CH}_4$	16 [g/mol]	Molar mass of CH ₄
$m_w \text{CO}_2$	44 [g/mol]	Molar mass of CO ₂
$C_{g \text{CO}_2}$	[J/(mol K)] [‡]	Specific heat capacity of CO ₂
$C_{g \text{CH}_4}$	[J/(mol K)] [‡]	Specific heat capacity of CH ₄
ρ_{CO_2}	[kg/m ³] [‡]	CO ₂ fluid phase density
ρ_{CH_4}	[kg/m ³] [‡]	CH ₄ fluid phase density
C_w	4×10^6 [J/(Km ³)]	Lumped heat capacity of the wall
A_w	$3.1416 \times (R_o^2 - R_i^2)$	Cross section of the column wall
T_{amb}	294.15 [K]	Ambient temperature
T_{in}	294.15 [K]	Temperature at the inlet
P_{in}	0.2–2.5 [MPa]	Inlet fluid pressure
V_{ini}	0.013 [m/s]	Inlet velocity

[‡] Properties are determined from NIST REFPROP as functions of the pressure and temperature at the inlet.

an equimolar mixture of CO₂ and CH₄ on MOF-5 using the isotope exchange technique [34]. Diffusion coefficients of CO₂/CH₄ on different MOFs (MIL-53, MIL-101, and Cu-BTC) are found to have similar order of magnitudes, so this approximation is not expected to cause significant errors [42, 43]. The mass transfer coefficients are listed in Table 1. The isosteric heat of CO₂ and CH₄ adsorption on MIL-53 is measured using a coupled volumetric-calorimetric system. The absolute adsorption required for the isosteric heat is obtained using Tóth's adsorption model fit for the measured excess adsorption isotherms [44]. The specific heat capacity of MIL-53 was measured using a SETARAM calorimeter and is given in Table 1.

4.2. Pure and Mixed Gas Isotherms. Pure gas adsorption isotherms of methane and carbon dioxide on MIL-53 are given as symbols in Figure 2. These measurements are made at 294.15 K for a pressure range between 0 and 6 MPa using a conventional Sieverts volumetric apparatus. The detailed description of the method is available from earlier works [34, 45].

TABLE 2: Pore and surface characterization, densities, and porosities of MIL-53.

BET surface area (m ² /g)	984.2
Bulk density (g/cm ³)	0.385
Skeletal density (g/mL)	1.37
Micropore volume (cm ³ /g)	0.3787
Total porosity	0.719
Bed porosity	0.573

Doong and Yang Multicomponent (DYM) model is an empirical multicomponent adsorption model which has shown excellent predictive properties for multicomponent mixtures of CO₂, CH₄, and N₂ on microporous adsorbents. We have used this model in the past to predict the isotherms of binary mixtures of CH₄ and CO₂ on MOF: Cu-BTC. DYM model is an extension of Dubinin-Astakhov analytical model, which accurately predicts the pure gas adsorption isotherms on microporous adsorbents over wide temperature

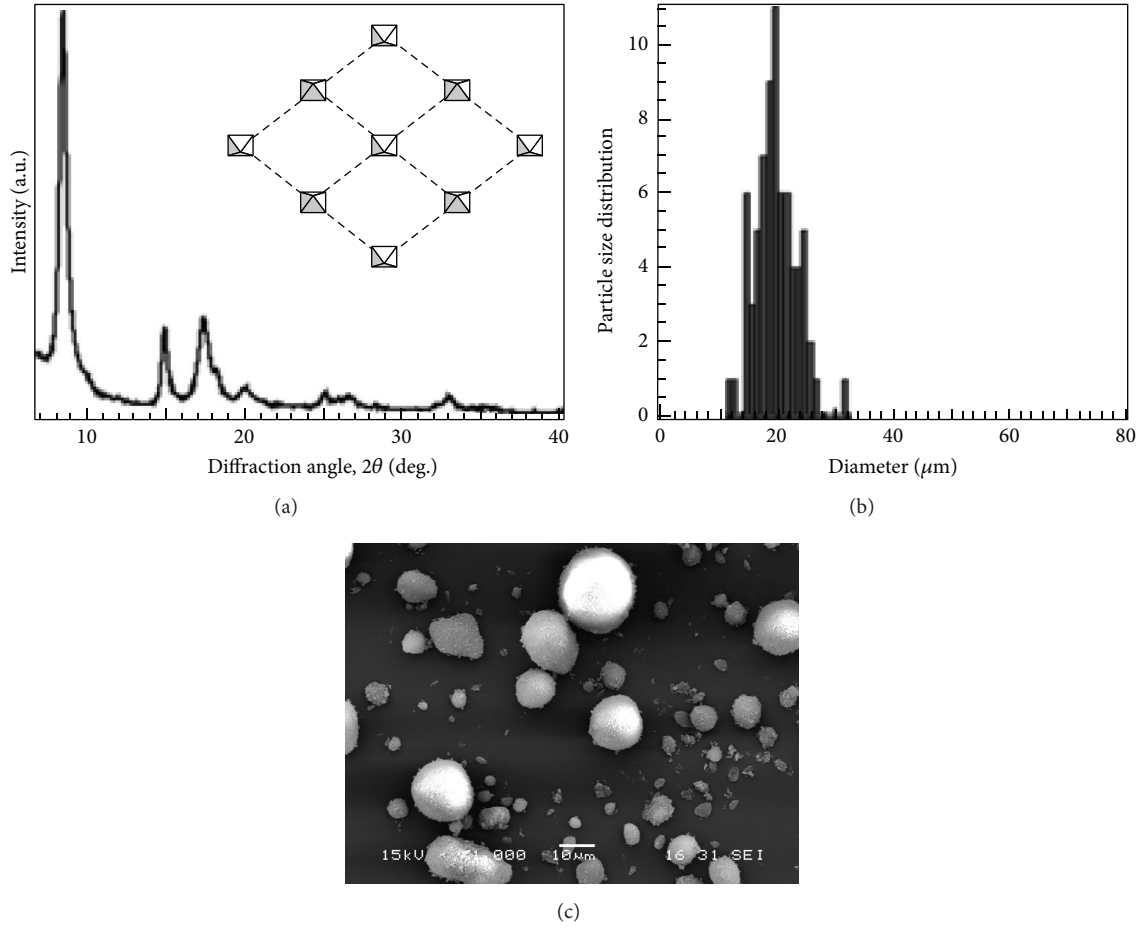


FIGURE 1: Characterization of MIL-53. (a) Powder X-ray diffraction pattern. The inset shows the structure of nonbreathable MIL-53 [28]. (b) Particle size distribution histogram. (c) Representative SEM image of the material.

and pressure ranges [4, 36]. One of the very important factors we need to consider when using the models is the ease of applicability of the models in computational fluid dynamics simulations. The parameters from the DYM/D-A models can be directly used to express the adsorptive mass source terms in the mass balance equation (q , (1)). Additionally, they provide an analytical expression for loading dependent-adsorption isosteric heat which can be easily implemented in the energy balance equation (ΔH , q , (15)). This is unlike certain other models, such as multipotential theory of adsorption, which requires either the parameterization of the predicted isotherms or the use of iterative techniques within the CFD models [46, 47]. Both D-A model and DYM are based on the theory of micropore volume filling which postulates that adsorption in microporous adsorbent occurs by filling of the micropore volume.

The pure gas isotherms are fitted with the D-A model and are given as lines in Figure 2(a). The data are compared with CO_2 and CH_4 pure gas isotherms on isotopic MIL-53 (Cr) reported by Hamon et al. The structures of both Al and Cr variants of MIL-53 MOFs series are built up from similar infinite chains of corner-sharing $\text{MO}_4(\text{OH})_2$ ($\text{M} = \text{Al}^{3+}$, Cr^{3+})

TABLE 3: D-A model parameters for the adsorption of pure methane and carbon dioxide on MIL-53 (Al).

Parameter	CH_4	CO_2
$n_{\max}$ [mol/kg]	6.84	11.16
ε [J/mol]	9373	8812
P_s [MPa]	32.7	6.8
n_i	2.84	1.87

octahedra interconnected by the dicarboxylate groups. This results in a similar 3D metal-organic framework containing 1D diamond shaped channels. Isotherms of CO_2 and CH_4 on MIL-53 (Al) compare well with those on MIL-53 (Cr). This agrees well with earlier results on isotopic MIL-53 reported by Bourrelly et al. and Alhamami et al. [13, 48].

Both pure gas isotherms are fitted with the D-A model with a standard error of estimate (SEE) of 1.05 for CO_2 and of 0.626 for CH_4 . The corresponding fit parameters are presented in Table 3. The mixed gas isotherms on MIL-53 (Al) are constructed using the Doong-Yang Multicomponent

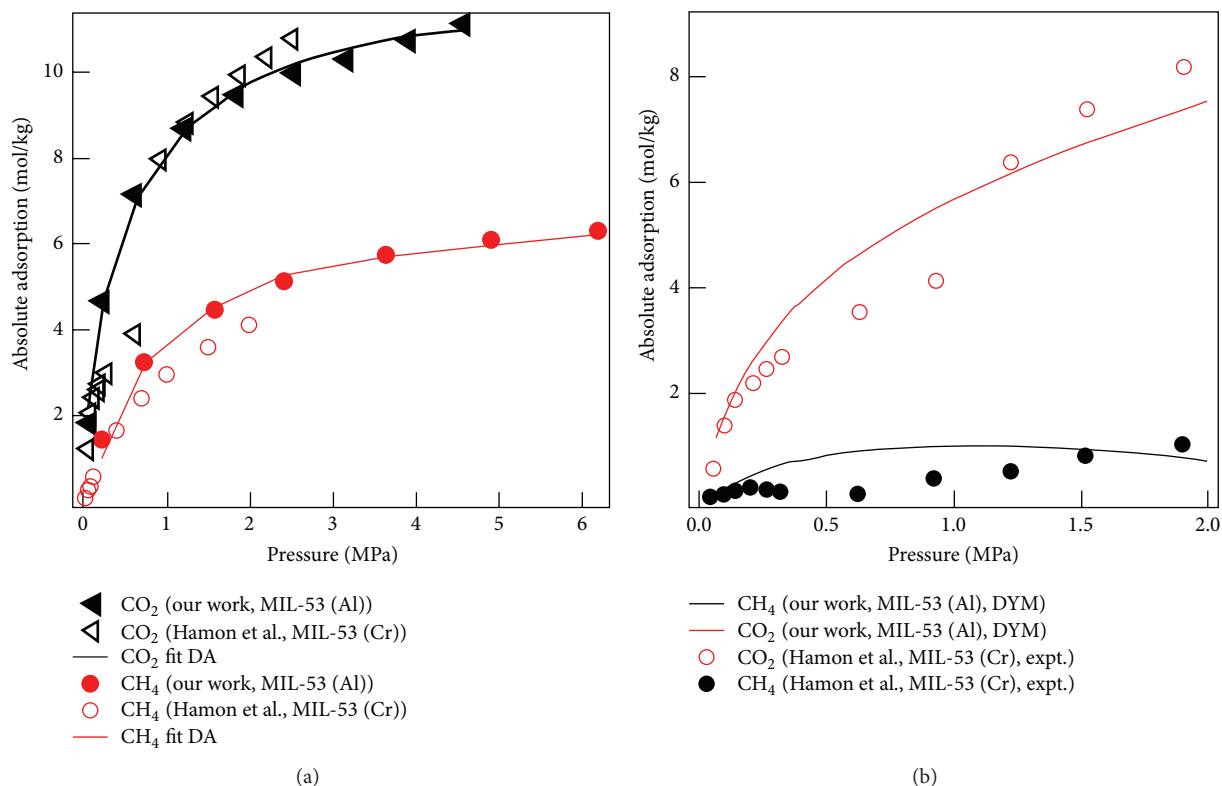


FIGURE 2: (a) Experimental pure gas isotherms of methane and carbon dioxide on MIL-53 measured at 294.15 K. (b) Equimolar binary gas isotherm comparison, Hamon et al., and DYM predictions.

isotherm model [36] using the pure gas isotherm regressions parameters. In Figure 2(b), the predicted binary adsorption isotherms are compared with the experimental equimolar binary adsorption isotherms on MIL-53 (Cr) measured by Hamon et al. Even though the isotherms cannot be quantitatively compared, they exhibit similar behavior for CH₄ and CO₂. We can conclude that our predictions are in agreement with the experimental data. The DYM isotherm equations are summarized in (9) to (14a), (14b), and (14c).

The efficiency of MOF MIL-53 (Al) for the separation of a binary CH₄/CO₂ mixture can be analyzed and compared in terms of the sorption selectivity. The selectivity of i th component in a mixture of components i and j is defined on a molar basis as $S_{i,j} = (n_{\text{sat},i}/y_i)/(n_{\text{sat},j}/y_j)$. Here, we compare the selectivity of our sample to selectively remove CO₂ from an equimolar CO₂/CH₄ mixture with the selectivities of other MOFs reported in the literature. In the pressure range below 0.5 MPa, the selectivity of our sample shown in Figure 3 decreases initially rapidly with pressure of about 0.1 MPa, after which it remains almost constant. The selectivity of MIL-53 reported by Hamon et al. on the other hand shows a step-like decrease, by a factor of ~ 3 at 0.6 MPa, after which it shows only a slight decrease [19]. The sample used by Hamon et al. showed two characteristic adsorption steps which were attributed to the breathing phenomenon. As the CO₂ pressure increases, a step is observed at around 0.6 MPa [13] leading to large uptake. This uptake is attributed

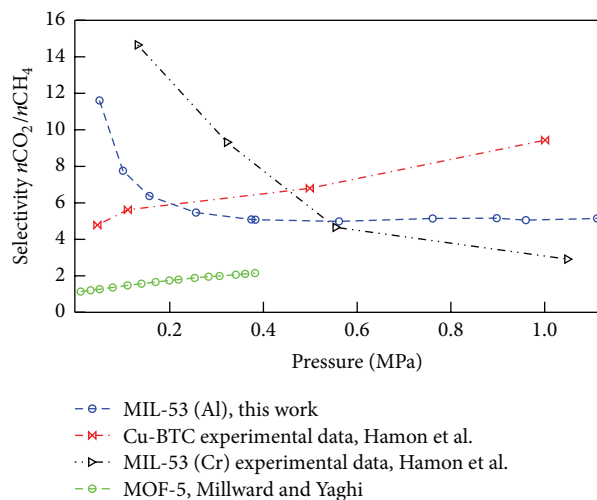


FIGURE 3: Selectivity of MIL-53 (Al) towards CO₂ at 303 K. For comparison purposes we included experimental data of Cu-BTC, MIL-53 (Cr), and MOF-5.

to the change of MIL-53 from “narrow pore” to “large-pore” structure. On the other hand, the sample used in our work is a commercial material that shows no breathing phenomena. No drastic change in the selectivity is observed at around 0.6 MPa. Among all MOFs compared here, Cu-BTC [18] has

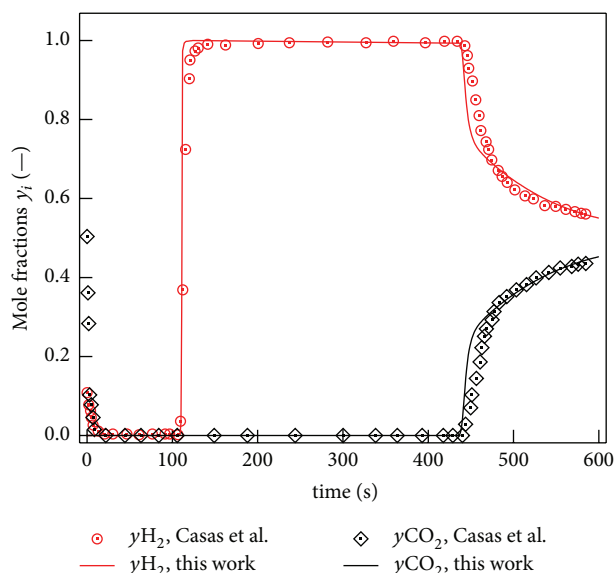


FIGURE 4: Validation of breakthrough model by simulating the adsorption and separation of equimolar mixture of CH_4 and CO_2 in an activated carbon column. Symbols represent our results while the lines represent the experimental results reported by Casas et al. [29].

the best selectivity at pressures above 0.2 MPa, while MOF-5 reported by Millward and Yaghi [21] has lowest selectivity. We conclude that MIL-53 (Al) offers a good separation for all ranges of pressure of up to 10 bar.

4.3. Validation of Breakthrough Curve Model. We start by validating the breakthrough model by applying it to simulate the breakthrough of a CO_2/H_2 mixture in an activated carbon column and comparing the model results with those reported by Casas et al. The model parameters and boundary and initial conditions required for validating the model are also obtained from Casas et al. [6, 29]. Figure 4 shows very good agreement between our validation results and those reported by Casas et al. The model has also been extensively validated experimentally and numerically by Casas et al., for different breakthrough curves cases of CO_2/CH_4 gas mixtures flowing through beds of activated carbon [29] and a hybrid MOF UiO-67/MCM-41 [6].

4.4. Parametric Study of Adsorbent Particle Size, Inlet Pressure, Gas Flow Rate, and Feed Composition on the Breakthrough. We used the validated model to study the effects of particle size, inlet pressure, feed composition, and gas flow rate on the breakthrough of CO_2/CH_4 gas mixtures through the MIL-53 adsorbent column. The inlet and wall temperatures are set to 294.15 K. A 25 cm column length is considered for all simulations. For monitoring the evolution of temperature in the bed, four axial positions at 5, 10, 15, and 20 cm from the inlet of the column are chosen.

4.4.1. Effect of Particle Diameter. In order to study the effect of MIL-53 (Al) particle size on breakthrough performance, we considered particle diameters 20, 200, 300, 500, and 1000 μm . Inlet pressure is fixed at 0.2 MPa and an equimolar CO_2/CH_4 mixture is fed at a rate of 30 mL/min. In general, for the simulations with particle diameters lower than 20 μm , we found that the numerical model presents some limitations. An examination of the mass balance shows that the numerical results start to deviate from the mass predicted by the local pressure. This perhaps arises due to the large pressure drop caused by smaller particles, which is consistent with the general recommendation to use particle sizes of the order of 1 mm to avoid large pressure drops in gas-phase separations [6, 7, 17]. Therefore, we present the results only for 200, 500, and 1000 μm . Based on the literature, we set the particle size to 500 μm to investigate the effects of inlet pressure, flow rates, and feed concentration in further sections.

In left panels of Figure 5, breakthrough times for $Y_i/Y_0 = 10\%$, where Y_i is the molar fraction of the component and Y_0 is the feed concentration, are found to be around 7.9 minutes when particle sizes are 200 and 500 μm , while they are 7.7 minutes when the particle size is 1000 μm . In the right panels of Figure 5, the evolution of temperature at the positions 5, 10, 15, and 20 cm from the inlet of the column is shown. As adsorption is an exothermic process, the resulting adsorption heat is released into the bed. This increases the column temperature as the gas fronts move from the inlet to the outlet. We simulate the temperature evolution at four axial positions in the column. The temperature rises to around 333 K when 200 and 500 μm particles are used, while for the 1000 μm particles the temperature rises up to 336 K. At each position two different temperature peaks are observed; the low temperature peak corresponds to the CH_4 front and the higher temperature peak to the CO_2 front. From the simulation results, we find that the CH_4 front moves faster than CO_2 front. The peaks shape is influenced by the mass and heat transfer parameters: the initial fast abrupt front indicates fast mass transfer, whereas the shape of the tail is controlled mainly by the heat transfer from the column to the environment. The latter one is responsible for the time required to reach the feed composition at the outlet of the column, once the CO_2 breakthrough is noticed. Since the temperature of the column continues to decrease until it reaches the initial temperature, more CO_2 is adsorbed which finally results in a CO_2 flat front.

Larger particles can be prepared either by mechanically compacting pristine MOFs to monoliths or by applying a binder, such as polyvinyl alcohol (PVA) or expanded natural graphite (ENG). Depending on the activation temperature, the preparation of monoliths by the addition of binder will cause partial pore blocking. The blocked pores reduce the adsorption capacity by as much as 19% of pristine powder MOF material. But this has minimum impact on the overall pore size distribution [17]. Binderless mechanical compaction of MOFs on the other hand causes partial collapse of frameworks, which reduces the sorption capacity by $\sim 15\%$ [49]. Our results are in agreement with Grande who recommends using the pellets instead of powder materials for efficient PSA separation [50].

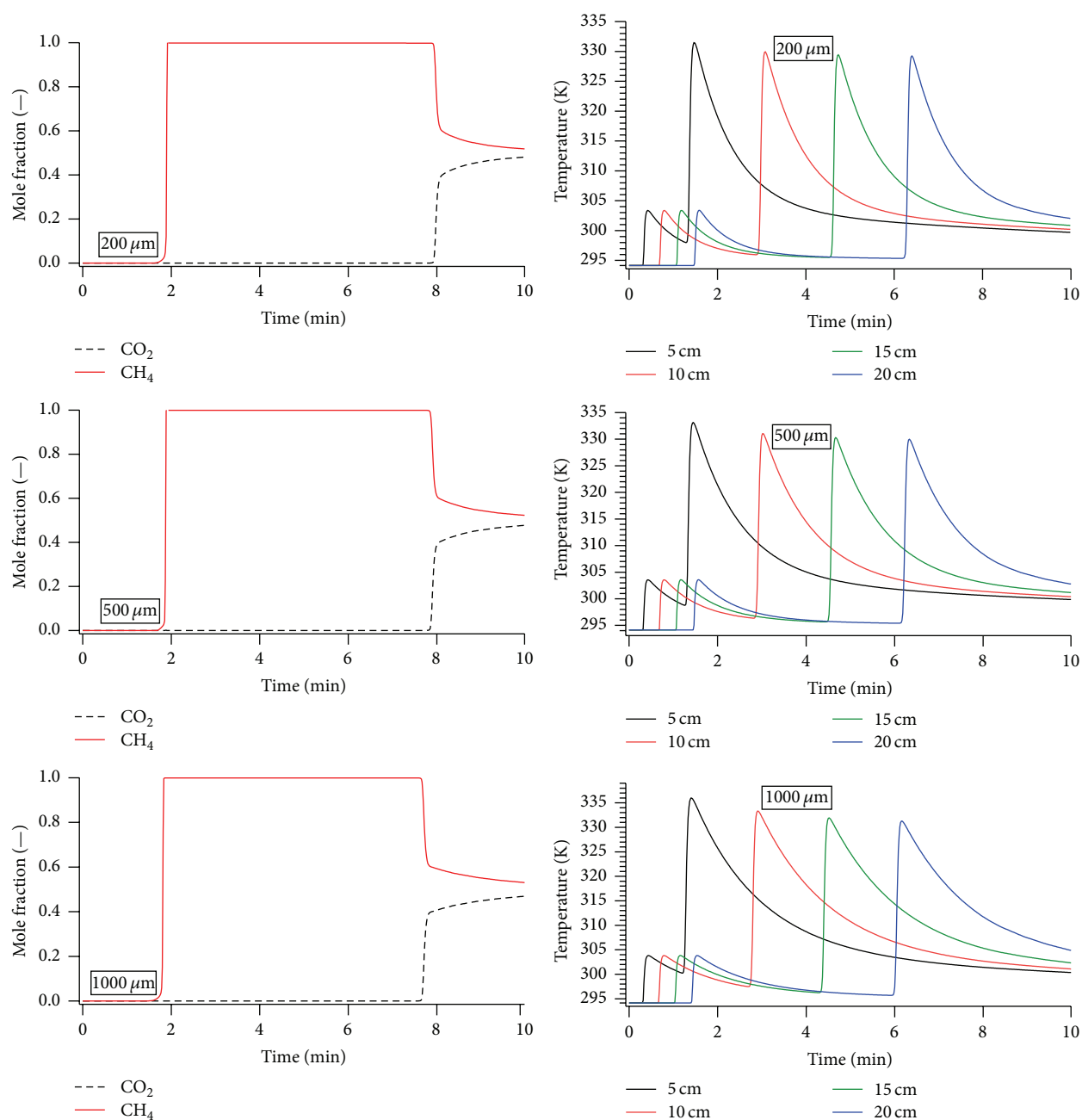


FIGURE 5: Breakthrough curves for an equimolar CO_2/CH_4 mixture, column length 25 cm, inlet pressure 0.2 MPa, for 3 different particle diameters. For simulation parameters refer to Table 1.

4.4.2. Effect of the Inlet Pressure. In order to study the effect of the inlet pressure on the breakthrough curves, we set the inlet pressure to 0.5, 1, and 2.5 MPa. Figure 6 displays the breakthrough and temperature profiles for different inlet pressures. The particle size is fixed at $500\ \mu\text{m}$ for all simulations. As seen in the left panels of Figure 6, the breakthrough time decreases with increasing feed pressure. The breakthrough times of 5, 3.3, and 1.9 minutes are obtained with the feed pressures 0.5, 1, and 2.5 MPa, respectively. Furthermore, the higher

the feed pressure, the higher the temperature along the column, ~ 358 , 388 , and $444\ \text{K}$, respectively, for 0.5, 1, and 2.5 MPa. As gas with higher inlet pressure flows through the bed, larger amounts of gases are adsorbed, leading to higher amounts of adsorption heat released into the bed.

4.4.3. Effect of the Mass Flow Rate. In order to study the impact of the mass flow rates on the breakthrough curves, we set the mass flow rate to 10, 25, and 50 mL/min. Figure 7

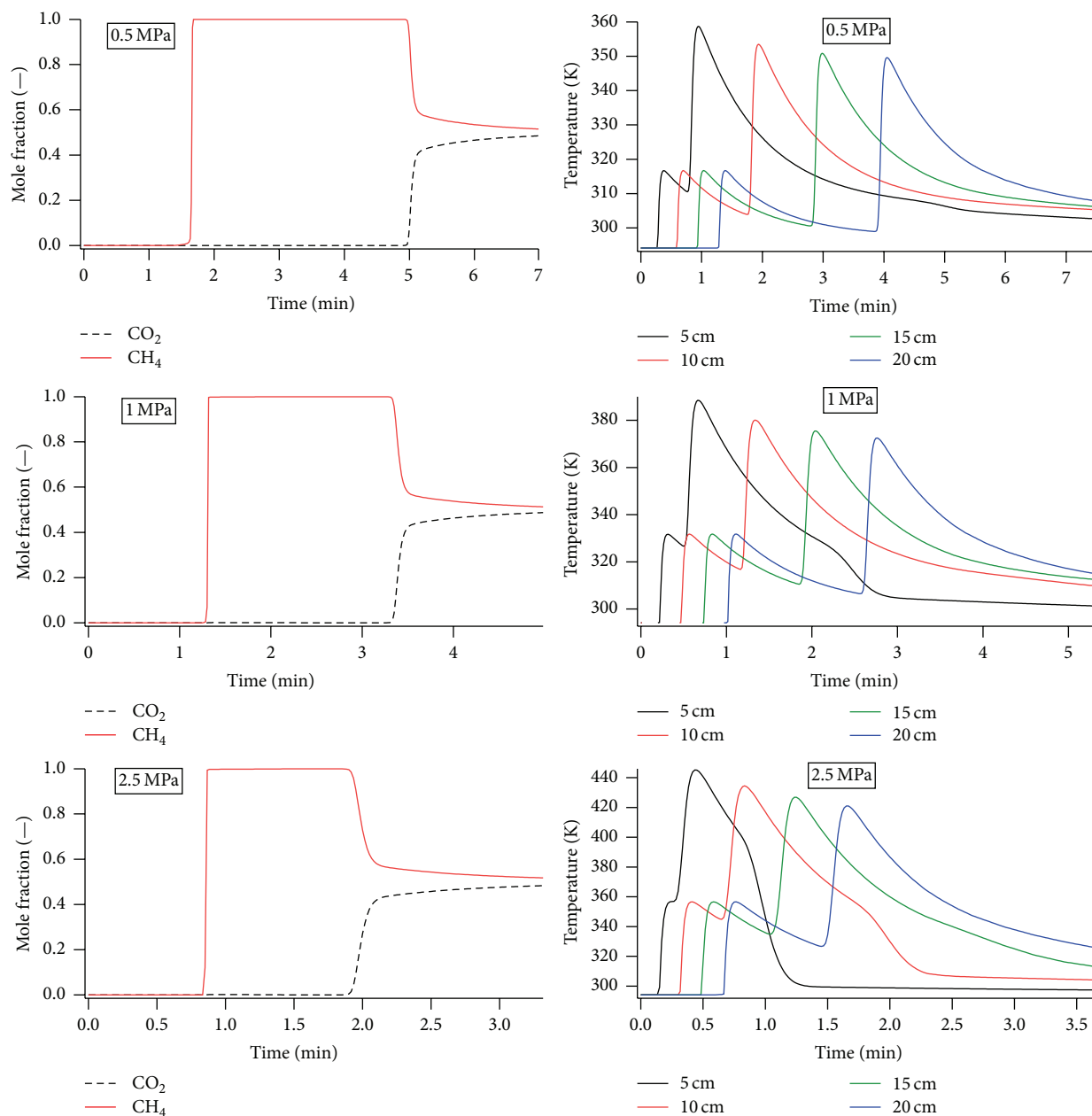


FIGURE 6: Effect of feed pressure on the breakthrough profile and temperature on MIL-53 for an equimolar CO_2/CH_4 mixture.

displays the breakthrough and the temperature profiles for different mass flow rates. As in the case of previous simulations, the particle size is fixed at $500\ \mu\text{m}$ for all simulations. As seen in the left panels of Figure 7, the breakthrough time decreases with increasing of the mass flow rate. For mass flow rates of 10, 25, and $50\ \text{mL/min}$, the breakthrough times are 10.65, 4, and 1.9 minutes. Also, the higher the mass flow rate, the higher the temperature along the column, ~ 375 , 385, and $392\ \text{K}$ for 10, 25, and $50\ \text{mL/min}$. Gas with the higher mass flow rate leads to larger amount of adsorption. This leads to higher amounts of adsorption heat released into the bed.

4.4.4. Effect of the Feed Concentration. The influence of the CO_2 concentration on the MIL-53 adsorption kinetics is studied for three CO_2 concentrations: 25%, 50%, and 75% in the CO_2/CH_4 mixture. For each composition, we also considered three feed pressures: 0.2, 0.5, and 2.5 MPa. Figure 8 displays the breakthrough and temperature profiles corresponding to each composition and pressure. The breakthrough point for 25% CO_2 composition at a 0.2 MPa inlet pressure appears at 9.8 minutes, while shorter breakthrough times of 7.8 and 6.7 minutes are observed when the CO_2 feed composition is increased to 50 and 75%. In other words, we see that the larger

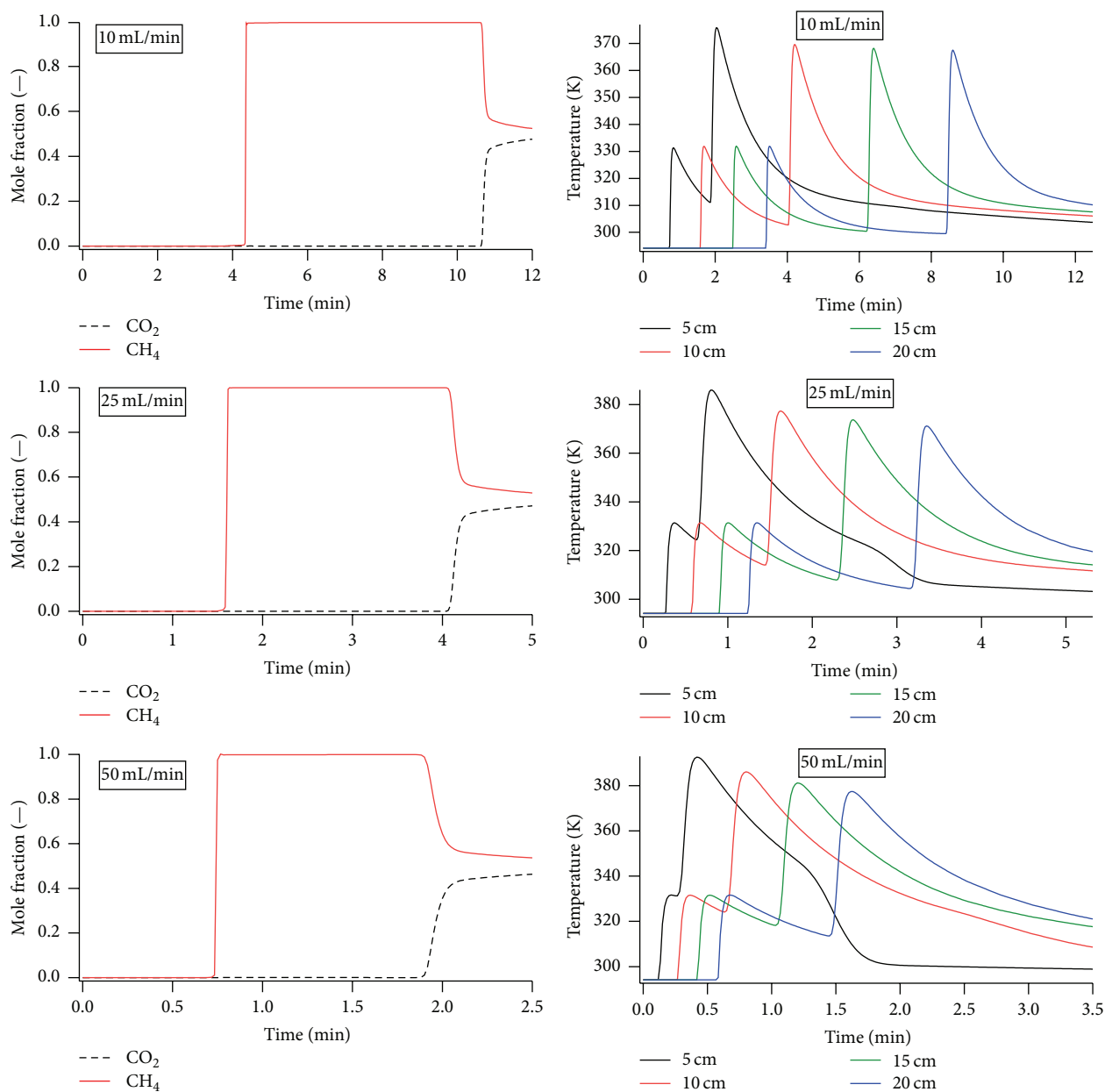


FIGURE 7: Effect of the mass flow rate on the breakthrough profile and temperature on MIL-53 for an equimolar CO_2/CH_4 mixture.

CO_2 concentration in the feed gas mixture accelerates the breakthrough time [29, 51]. Similar behavior is also observed for the 0.5 and 2.5 MPa feed pressures. Larger concentration difference between the compositions results in faster saturation of the adsorbent with one component which eventually leads to shorter breakthrough times. The lowest breakthrough time of as short as 1.55 minutes is observed for the highest feed pressure (2.5 MPa) and highest CO_2 molar concentrations (75%). The behavior of the temperature evolution on the other hand shows an increase at increasing the feed concentration and the feed pressure which is attributed to the larger amount of gases adsorbed.

The different breakthrough times for CH_4 and CO_2 obtained with different feed pressures and molar compositions directly affect the amount of pure CH_4 produced in each PSA cycle. The amount of pure CH_4 produced in a cycle can be calculated from the outlet flow rate and time between the onset of the flow and breakthrough. Note that the reduction of adsorption capacity due to pelletization should also be accounted for while calculating the amount of pure CH_4 produced in each cycle. Based on the reported adsorption capacities of monoliths, we used 15% reduction factor to calculate the amount of pure CH_4 produced. As seen in Figure 9, at higher feed pressure, more CH_4 is produced per

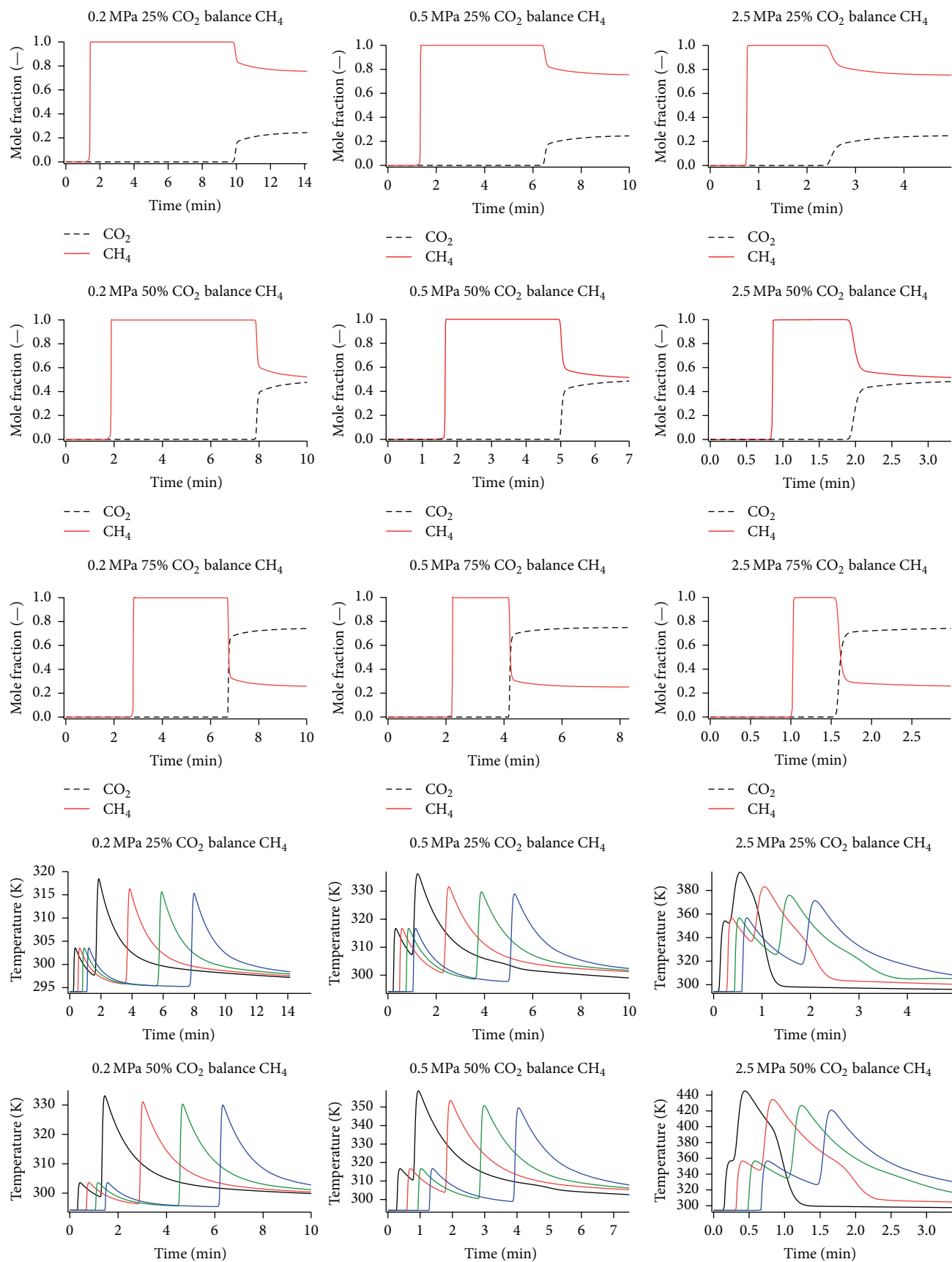


FIGURE 8: Continued.

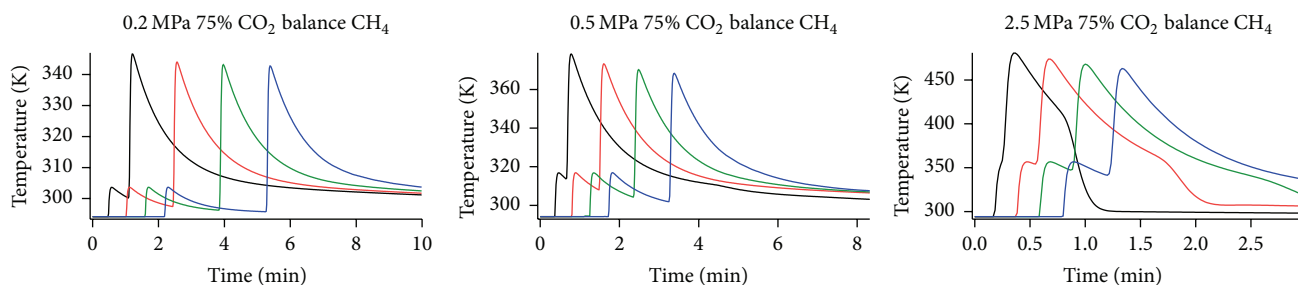


FIGURE 8: Breakthrough and temperature profiles when feed pressures and CO_2/CH_4 mixture compositions are varied. The range of feeding pressures is between 0.2 and 2.5 MPa and a range of concentration is between 25 and 75% mole fraction of CO_2 .

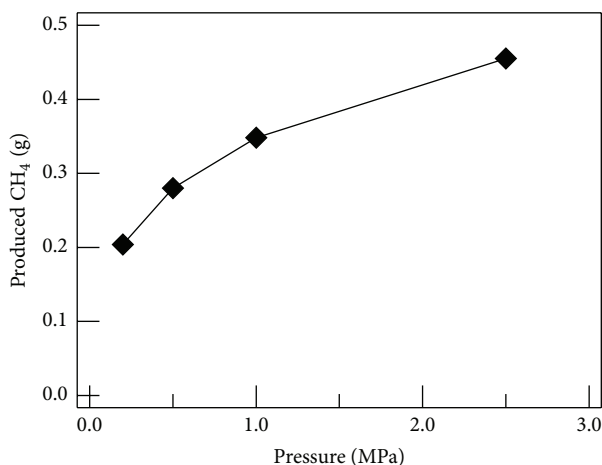


FIGURE 9: Amount of pure CH_4 obtained in a breakthrough prediction for a feed mixture containing equimolar CO_2/CH_4 mixture.

cycle, even though each cycle lasts less than that for lower feed pressures (from left to right of Figure 8). On the other hand, the amount of CH_4 produced at the specified purity with respect to the feed composition decreases with the increasing pressure. This means that more CH_4 remains in the column by the time CO_2 breaks through, as it is confirmed in a similar case for a CO_2/H_2 gas mixture [6, 29]. In a continuous process this is circumvented by adjusting the cycle time in such a way that the CH_4 loss is minimized [29].

The separation capacity of MIL-53 (Al) for CO_2 and CH_4 is between 7.8 at 0.1 MPa and 7.1 at 1.5 MPa at 294.15 K based on the selectivity correlation $S_{i,j} = (n_{\text{sat},i}/y_i)/(n_{\text{sat},j}/y_j)$ [34]. These values are consistent with the values reported by Finsy et al. on the separation of an equimolar CH_4/CO_2 mixture at 303 K in a packed column with MIL-53 (Al, PVA) pellets containing 13 wt% PVA binder [17]. Selectivities calculated from pure component isotherms on the 13X zeolite [11] and the activated carbon material Norit R1 Extra [12] are 2 and 2.7 at 1 MPa compared with 5.5 for MIL-53 (Al).

5. Conclusions

To conclude, we presented a parametric study of MIL-53 aluminum terephthalate particle size, inlet pressure, mass flow

rate, and feed composition on the breakthrough of CO_2/CH_4 binary gas mixtures. Pure gas CO_2 and CH_4 adsorption isotherms on commercial MIL-53 were measured using Sieverts method and were fitted with the D-A analytical model. Using the D-A model fit parameters, binary adsorption isotherms were predicted. These isotherms agree well with the reported experimental binary isotherms measured on isotypic MIL-53 chromium terephthalate. A one-dimensional multicomponent adsorption model was used to simulate the breakthrough behavior of CO_2/CH_4 mixtures in a column packed with MIL-53 (Al). The model was initially validated by applying it to simulate the breakthrough of H_2/CO_2 mixtures reported in the literature. Experimentally measured particle size, porosity, kinetic diffusion parameters, isosteric heat, and specific heat were used in the model to increase the reliability of its predictions. In the parametric study, we considered the effect of adsorbent particle diameters (5, 20, 200, 300, 500, and 1000 μm), feed pressures (0.2, 1, and 2.5 MPa), feed flow rates (10, 25, and 50 mL/min), and inlet compositions (25%, 50%, and 75% CO_2) on the breakthrough performance. As-purchased MIL-53, with a peak particle diameter of 20 μm , was found to be less effective for separation because of the higher pressure drops. Effective separation within two minutes of the onset of flow was achieved for MIL-53 monoliths of diameters above 200 μm . We found that faster separation can be made possible by increasing the feed pressure from 0.2 MPa to 2.5 MPa and also if the starting compositions are rich in CO_2 . As higher pressure CO_2 richer stream passed through the column, more heat was generated in the column when compared with the low-feed pressure CH_4 rich stream. More CH_4 was produced per cycle at higher feed pressures, even though each cycle lasted less than that for lower feed pressures. On the other hand, increasing pressure decreases the CH_4 recovery.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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