Simulation of Fixed-Bed Adsorption for Biogas Upgrading

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1 Introduction

Great efforts have been devoted to developing clean energy sources of energy that can contribute to keeping global warming below 2 °C in the incoming 30 years. Global warming is mainly caused by the emission of anthropogenic greenhouse gas such as methane (CH_4) and carbon dioxide (CO_2), being CH_4 almost 28 times more damaging than CO_2 [4]. Biogas is a sustainable and renewable source of energy mainly composed of CH_4 and CO_2 and low levels of N_2 [2, 8]. In this way, producing biogas and upgrading it to biomethane is an alternative solution to prevent greenhouse gas emissions at the same time it can be supplied as a renewable source of biofuel. Furthermore, biogas can be a decentralized alternative to produce clean energy everywhere, as it is easily produced from the methanation of biomass and organic wastes from sewage sludge anaerobic digestion, commercial composting, landfills, biomass gasification (thermos-chemical production process), animal farm manure anaerobic

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co-digestion with energy crops, agro-food industry digestion facilities [2], among others.

The presence of CO_2 (up to 40 vol. %) and N_2 (up to 15 vol.%) in the biogas composition (landfill gas), reduces its calorific value and causes corrosion of engines and pipelines, limiting its use and transportation via natural gas pipelines [2]. Accordingly, biogas needs to be upgraded (by removing CO_2 and N_2) to obtain biomethane that can be either injected into natural gas grids or directly used as a vehicle/domestic fuel. However, to use biomethane as a vehicle fuel or to inject it into natural gas pipelines, standard requirements must be followed depending on country rules. For example, the methane content in Switzerland must be $\geq$96 vol%, and only $\geq$86 vol% in France. In these two countries, the CO_2 content is also different, being $\leq$4 (Switzerland) and $\leq$2.5 vol% (France) [2].

To meet the standard requirements for biogas upgrading the main separation techniques reported in the literature can be water or organic solvent scrubbing, chemical absorption, adsorption, cryogenic separation, membrane technology, biological upgrading, and in-situ upgrading methods [2, 5, 6]. Among them, adsorption processes such as Pressure/Vacuum or Temperature Swing Adsorption (PSA/VSA or TSA) have been employed, being very competitive with low energy consumption. At the same time, a variety of solid adsorbents are already available or will be developed in the future to increase the performance of the adsorption processes [6, 8, 16]. Moreover, several operating parameters namely pressure, flow rates, temperatures, different cycle steps (e.g. pressurization, feed-high pressure, blowdown/depressurization, equalization, backfill, low-pressure purge, etc.), and their tuning should be optimized to provide efficient performance in the biogas upgrading. Thus, mathematical modeling is a fundamental tool for the design of adsorption processes allowing us to evaluate the effect of several operating parameters to find the best-operating conditions, besides significantly reducing the number of experiments required.

In this work, an adsorption simulation package to study the separation of the main components of biogas (CO_2/CH_4/N_2) in a fixed bed was developed and validated by predicting experimental single and ternary breakthrough curves on binder-free zeolite 4A and KY. Overall, the simulator proved to be very efficient to predict the fixed-bed experimental data adsorption dynamics, and it has now been used in the simulation and design of more complex systems like PSA/VSA to TSA processes for biogas upgrading at the industrial level with proper boundary conditions.

2 Materials and Methods

2.1 Materials

In this work, two types of benchmark zeolites were studied, namely, potassium exchanged (95%) type Y (BFKY) and sodium type A (BF4A). These zeolites were synthesized and transformed into beads through the binder-free method [10, 11] by Chemiewerk Bas Köstritz GmbH (Germany). The adsorbent bead's particle diameter ranges from 1.6 to 2.5 mm. He (99.9998%), CO_2 (99.998%), CH_4 (99.95%), and N_2 (99.999%) were supplied by Air Liquide.

2.2 Experimental Procedure

A homemade fixed-bed adsorption apparatus has been used to collect the breakthrough curves of CO_2, CH_4, and N_2 and their binary/ternary mixtures which were used to validate the adsorption mathematical model simulation package. This apparatus has been used in our previous work [15], where detailed information on its layout can be found. In the adsorption studies, a stainless steel adsorption column (0.0286 m i.d. and 0.0646 m length) has been used. For the experiments, the column was filled with 23.8 g of BF4A and 26.2 g of BFKY, which leads to a bulk density of 590 and 649 kg m^{-3}, respectively.

2.3 Mathematical Model

The adsorption mathematical model and respective boundary conditions for fixed-bed adsorption are shown in Table 1 and were derived according to the following assumptions: (i) the gas is considered to follow the ideal gas law; (ii) an axially dispersed plug flow model is used to represent the bulk fluid flow through the bed; (iii) constant bulk density in the bed; (iv) the pressure drop is negligible; (v) the radial gradients of concentration, temperature, and pressure are negligible; and (vi) the adsorption equilibrium is described by the extended dual-site Langmuir isotherm model (DSL). Moreover, it was considered a column of length L, void fraction ε_b (=0.4), packed with a solid adsorbent through which an ideal biogas stream (mainly $CH_4/CO_2/N_2$) flows at a molar flow rate F, where C is the total gas concentration of the species in the mixture, y_i represent the molar fraction of adsorbable species i in the fluid, and $\overline{q}i$ the average adsorbed concentration of adsorbable species i in the adsorbent solid phase.

Table 1 Fixed-bed adsorption mathematical model equations

Model	Equations	
Ideal gas	$C = \frac{P}{RT}$	(1)
Overall mass balance	$\frac{\partial F}{\partial z} + \varepsilon_b \frac{\partial C}{\partial t} + \rho_p(1-\varepsilon_b)\sum_{i=1}^{n} \frac{\partial \overline{q}_i}{\partial t} = 0$	(2)
Component mass balance	$-\varepsilon_b D_{ax} \frac{\partial}{\partial z}\left(C \frac{\partial y_i}{\partial z}\right) + \frac{\partial (F y_i)}{\partial z} + \varepsilon_b \frac{\partial (C y_i)}{\partial t} + \rho_p(1-\varepsilon_b)\frac{\partial \overline{q}_i}{\partial t} = 0$	(3)
Mass transfer rate	$\frac{\partial \overline{q}_i}{\partial t} = K_{LDF}\left(q^* - \overline{q}_i\right)$	(4)
Linear Driving Force (LDF)	$\frac{1}{K_{LDF}} = \frac{R_p}{3k_f} + \frac{R_p^2}{15\varepsilon_p D_p} + \frac{r_c^2}{15KD_c}$	(5)
Gas-phase energy balance	$-K_{ax}\frac{\partial^2 T}{\partial z^2} + Fc_{pg}\frac{\partial T}{\partial z} + C\varepsilon_b C_{pg}\frac{\partial T}{\partial t} + (1-\varepsilon_b)a_p h_p(T - T_s) + a_c h_w(T - T_w) = 0$	(6)
Solid-phase energy balance	$C_{ps}\frac{\partial T_s}{\partial t} = a_p h_p(T - T_s) + \rho_p \sum_{i=1}^{n}\left(-\Delta H_{st,i}\right)\frac{\partial \overline{q}_i}{\partial t}$	(7)
Isotherm model (DSL)	$q_i = \frac{q_{m1} b_{1i} p_i}{1+\sum_{j=1}^{n} b_{1j} p_j} + \frac{q_{m2} b_{2i} p_i}{1+\sum_{j=1}^{n} b_{2j} p_j}$	(8)
Boundary conditions	$z = 0 \begin{cases} Fy_{if} = Fy_i - \varepsilon_b D_{ax} C \frac{\partial y_i}{\partial z} \\ Fc_{pg} T_f = Fc_{pg} T - K_{ax}\frac{\partial T}{\partial z} \\ F = F_f \end{cases}$ $z = L \begin{cases} \frac{\partial y_i}{\partial z} = 0 \\ \frac{\partial T}{\partial z} = 0 \end{cases}$	(9)

2.4 Numerical Model

For the solution of the model, the method of the lines was applied to reduce the set of coupled partial and algebraic differential equations into a system of ordinary and algebraic differential equations [9]. The spatial coordinate was discretized by the orthogonal collocation method [14]. In the orthogonal collocation method, the collocation points which represent each spatial coordinate or node in the numerical grid are determined by using Jacobi polynomials, $P_{N^{(\alpha,\beta)}}(x)$, with $\alpha = 0$, $\beta = 0$, where N is the number of collocation points. The approximation of the first and second derivatives was made by collocation matrices routines $A_{i,j}$ and $B_{i,j}$, respectively. Therefore, the reduced system of ordinary differential equations was solved using the integrator ode15s available in the MATLAB library [12], and the algebraic differential equations were solved by Gauss elimination described elsewhere [14]. The simulator shows satisfactory accuracy and stability by using 25 spatial collocation points.

3 Results and Discussion

3.1 Equilibrium of Adsorption

The adsorption equilibrium data of CO_2, CH_4, and N_2 in BF4A and BFKY were collected at 313 K and partial pressures up to 3.5 bar by fixed-bed breakthrough experiments described in a previous work [1, 15]. Figure 1 shows the isotherms collected for CO_2, CH_4, and N_2 together with the standard Langmuir (for CH_4 and N_2) and dual-site Langmuir (DSL for CO_2) isotherm models fittings (lines), for BF4A (open symbols) and BFKY (closed symbols) at 313 K.

From Fig. 1, it is possible to see that, as the pressure increases, the amount adsorbed of all components increases, which means that the equilibrium data is thermodynamic consistent. At 3.5 bar, the adsorbed equilibrium amount for CO_2, CH_4, and N_2 in BFKY is around 6.42, 1.45, and 0.67 mol kg^{-1}, respectively, against 4.48, 1.34, and 0.81 mol kg^{-1} in BF4A. Regarding the affinity of adsorption for each component, CO_2 has a much higher affinity than CH_4 and N_2 in both adsorbents. This can be explained due to its large linear quadrupole moment, which leads to a strong interaction with the intracrystalline charge density framework. An important note is that the CO_2 adsorption equilibrium amount is 45% higher on BFKY than BF4A, which can be explained by the higher electric field in the zeolite faujasite type Y framework induced by an increasing number of charged sites present at the surface as compared to the type A framework [3]. However, the CH_4 and N_2 equilibrium of adsorption on both BF4A and BFKY do not present significant differences at the temperature and pressure studied.

Table 2 summarizes the DSL and standard (one-site) Langmuir isotherm parameters obtained from the fitting of the adsorption equilibrium data of CO_2, CH_4, and N_2 in the BF4A and BFKY. Figure 1 clearly shows that the DSL and Langmuir models

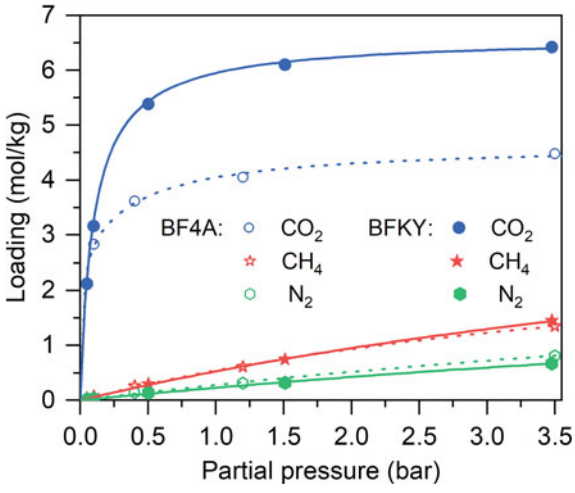

Fig. 1 Adsorption equilibrium isotherms of CO_2, CH_4, and N_2 at 313 K in binder-free zeolite 4A (open) and KY (closed symbols); Experimental = symbols; numerical = lines

Table 2 Dual-site and standard Langmuir model parameters for sorption of CO_2, CH4, and N_2 on BF4A and BFKY

Material	Species	q_m (mol·kg^{-1})		b (bar^{-1})[a]		(ΔH_i) (kJ·mol^{-1})	
		q_{m1}	q_{m2}	b_1	b_2	$(\Delta H_i)_1$	$(\Delta H_i)_2$
BF4A	CO_2	1.97	2.68	2.44	88.3	−35.6	−38.7
	CH_4	3.39	–	0.19	–	−18.0	–
	N_2	3.47	–	0.09	–	−16.2	–
BFKY	CO_2	3.35	3.25	6.27	16.2	−45.0	−37.4
	CH_4	4.81	–	0.12	–	−16.9	–
	N_2	2.98	–	0.08	–	−18.7	–

[a]The reference temperature used is 313.15 K

describe the equilibrium data with good accuracy. The extended DSL (Eqs. 2–8) model was used to predict the multicomponent data in the simulations.

The selectivity of CO_2 over CH_4 and N_2 on BF4A in a typical biogas composition from landfill gas ($CO_2/CH_4/N_2$:33/52/15 vol.% at 1 bar and 313 K) is equal to 38 and 37, respectively. In the case of BFKY, the selectivity increases to 68 and 66 for CO_2 over CH_4 and N_2, respectively. These results point out that the BF4A and BFKY can be used to efficiently separate CO_2 from $CO_2/CH_4/N_2$. These values were calculated by using the extended DSL model and validated experimentally.

It is worth mentioning that raw biogas contains other contaminants such as H_2O, H_2S, O_2, ammonia, and siloxanes whose concentration depends on the source of biogas production [2, 13]. These contaminants can affect significantly the adsorption and separation of $CH_4/CO_2/N_2$. For example, water can strongly adsorb on both zeolites studied in this work which could reduce their adsorption capacity towards CO_2 leading to a decrease in the overall performance. To use zeolites for biogas upgrading, pretreatment beds (guard beds), for example, for drying the gas stream before feeding the main adsorption column, are necessary to protect it from these contaminants. However, we focus here only on the study of the adsorption dynamics of an ideal mixture of $CH_4/CO_2/N_2$ free of contaminants. For more information about the effect of these contaminants and how they can be removed, detailed information can be found in the work of [2].

3.2 Modeling the Breakthrough Data of $CH_4/CO_2/N_2$

Mathematical modeling of fixed-bed adsorption breakthrough data is a valuable tool to collect adsorption equilibrium data, as well as find the kinetics sorption. The fitting of the experimental breakthrough curves makes it also possible to calculate all model parameters, and thereafter predict the adsorption process performance in a more complex cyclic system, such as: pressure/vacuum swing adsorption; necessary to assure continuous operation in biogas upgrading or any other gas separation process

by adsorption. In this section, the mathematical model developed will be validated and used to predict the dynamics of fixed-bed adsorption by matching the history profiles of the breakthrough curves. As an example, two simulations of a ternary mixture of $CH_4/CO_2/N_2$ at a certain feed biogas concentration (Table 3) were selected and depicted in Figs. 2 and 3. The experimental conditions and mathematical model parameters are summarized in Table 3.

The relative importance of the individual transport mechanisms such as the axial dispersion coefficient (D_{ax}) and mass transfer resistance (K_{LDF}) was evaluated by performing simulations, where these two parameters were varied to see their effects on the history profile of the breakthrough curves. The K_{LDF} is the linear driving force coefficient that represents the mass transfer resistance regarding the transport of the solute between the bulk fluid gas phase and the solid phase, and the axial dispersion coefficient (D_{ax}) is a resistance arising from fluid mixing and molecular diffusivity in the bulk fluid gas phase.

Figure 2 shows the parametric study performed to evaluate the effect of D_{ax} and K_{LDF} in the profile of the breakthrough curves. Figure 2a, c shows that by increasing or decreasing two times the K_{LDF} and kept D_{ax} constant, the history profiles of the breakthrough curves are unchanged. On contrary, Fig. 2b, d show that by changing the same values the D_{ax} and kept K_{LDF} constant the breakthrough curves are affected. Thus, from this parametric study, we can conclude that experimental breakthrough curves are dependent on the D_{ax} value. These results agree with the method of moments [7] explored in our previous work [15], where it was shown that axial dispersion mechanisms (D_{ax}) are prevailing over the mass transfer resistances (K_{LDF}), in the experimental system studied being the numerical model a valuable tool to evaluate such effects.

Figure 3 shows the experimental (symbols) and simulation (lines) ternary breakthrough curve of a mixture $CO_2/CH_4/N_2$ (20/20/20 vol% balanced with He) in the zeolites (a) BF4A and (b) BFKY. As shown in Fig. 3a-b, CO_2 is the most retained component due to its high interaction with both zeolite frameworks. In the case of CH_4 and N_2, they break through the column practically at the beginning of the experiments. Thus, we can conclude that both zeolites are excellent adsorbents to separate CO_2 from a mixture of $CO_2/CH_4/N_2$. In general, the numerical simulations represented by the lines in Figs. 2 and 3 describe very well the dynamics of the fixed-bed adsorption system for pure and mixture adsorption. Moreover, the methodology shown here with the validation of the mathematical through laboratory experimentation is the first step and the basis for the rapid scale-up of column testing for the design of cyclic adsorption processes such as PSA/VSA or TSA at an industrial scale regarding biogas upgrading applications.

Table 3 Experimental conditions and mathematical model parameters

Run	T (K)	P (bar)	Specie	F (mLn/min)	K_{LDF} (1/s)	D_{ax} (m^2/s)	K_{ax} (W/m/K)	C_{pg} (J/mol/K)	h_p (W/m/K)	h_w (W/m/K)
1	313	1	CO_2	28.6	98	1.94×10^{-4}	0.25	29.0	190	27
			He	42.4	-	1.94×10^{-4}				
2	313	1	CO_2	12.8	15.5	4.17×10^{-5}	0.13	30.4	37	30
			N_2	72.2	16.7	4.17×10^{-5}				
3	313	5	CO_2	117	13	1.50×10^{-5}	0.20	18.4	50	137
			CH_4	110	5.3	1.72×10^{-5}				
			N_2	121	12.7	1.70×10^{-5}				
			He	351	-	3.62×10^{-5}				
4	313	1	CO_2	17.3	29.4	3.09×10^{-5}	0.17	29.0	63.4	10.0
			CH_4	17.4	42.8	3.54×10^{-5}				
			N_2	17.5	42.8	3.45×10^{-5}				
			He	33.7	-	7.10×10^{-5}				

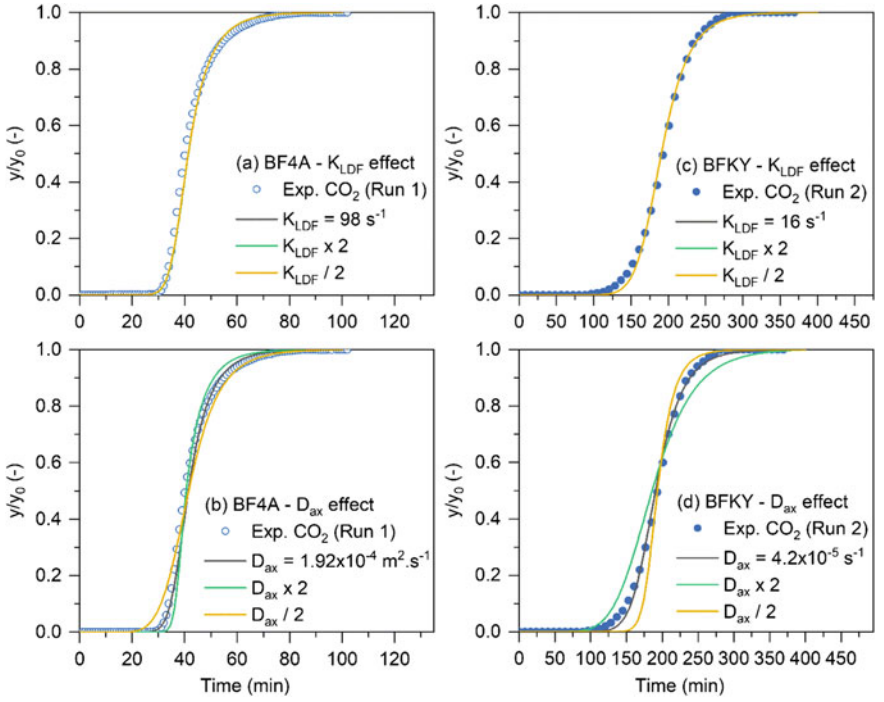

Fig. 2 Effect of changing overall mass transfer coefficient K_{LDF} (**a** and **c**) and axial dispersion Dax (**b** and **d**) on the simulated breakthrough curves of CO_2 at 313 K

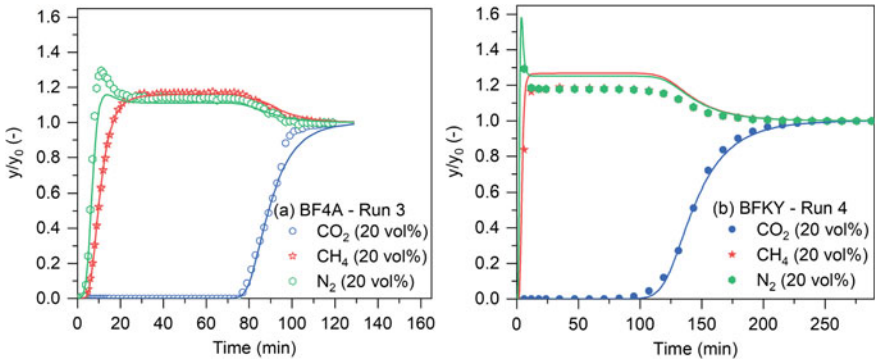

Fig. 3 Ternary breakthrough curves of $CO_2/CH_4/N_2$ on **a** BF4A and **b** BFKY. Experimental = symbols; Simulation = lines

4 Conclusions

In this work, an adsorption package simulator to study the separation of the main components of biogas ($CO_2/CH_4/N_2$) in a fixed bed was developed and validated by fitting experimental single and ternary breakthrough curves on binder-free zeolite 4A and KY. Both zeolites show a significant CO_2 adsorption capacity with also excellent selectivity over CH_4 and N_2. BFKY adsorbs almost 45% more CO_2 than BF4A, which is related to the higher electric field presented in the faujasite framework. The mathematical model was validated by predicting the experimental data, at the same time, it gives insights into the prevailing mass transport mechanisms in the fixed bed, being clear that the axial dispersion is the dominant one affecting the history profile of the single and multicomponent breakthrough curves. Overall, the adsorption simulator predicts very well the experimental data shown in this work and, therefore, can be a valuable tool for designing pilot-scale columns and also the development of cyclic adsorption processes, such as PSA, VPSA, and TSA for biogas upgrading.

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