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**BOOK OF ABSTRACTS**





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## P09.002. BINDER-FREE ZEOLITE 4A FOR BIOGAS UPGRADING AND CO<sub>2</sub> CAPTURE

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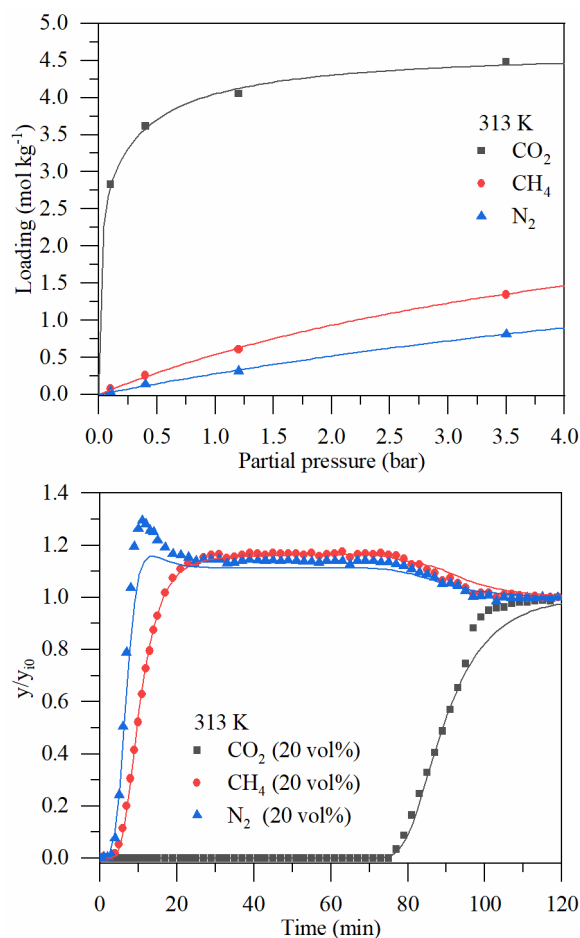
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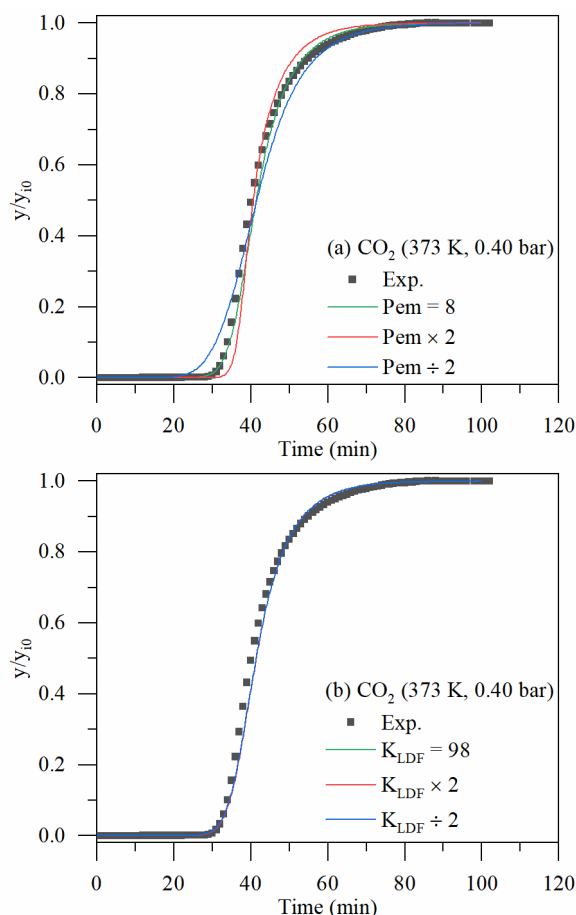
To keep global warming below 2 °C in the coming 30 years, the development and valorization of renewable sources of energy and also the CO<sub>2</sub> capture from coal-fired power plants are important steps for the transition to a clean energy economy. Biogas is a sustainable and renewable source of energy from the anaerobic decomposition of organic matter and, together with natural gas, they are a more environmentally friendly alternative. The presence of CO<sub>2</sub> in the biogas composition can reach up to 40 vol.%, which reduces biogas calorific value, impairs its transport via pipelines, and, consequently, limits its use [1]. CO<sub>2</sub> released from coal-fired power plants has been contributing to a massive 73% of annual emissions for the energy sector [2]. This value could be reduced by attaching a recovery unit downstream of these power plants to recover CO<sub>2</sub>, avoiding its emissions. Among the processes available to recover CO<sub>2</sub> and purify biogas, the adsorption is easy to operate, efficient to provide high recovery and purity, and more economical when compared to absorption and cryogenic separations, which have intensive energy consumption. Therefore, this work seeks to evaluate the adsorption equilibrium and dynamic separation of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> on binder-free zeolite 4A in conditions of interest to biogas upgrading and CO<sub>2</sub> capture

from the post-combustion stream. Thus, single- and multi-component studies of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> on binder-free zeolite 4A have been investigated through a series of fixed bed breakthroughs adsorption experiments at 313, 373, and 423 K and partial pressure up to 3.5 bar. Figure 1a shows the isotherm of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> on zeolite 4A at 313 K and partial pressure up to 3.5 bar. As can be seen, CO<sub>2</sub> is strongly adsorbed with a highly nonlinear isotherm (type I) compared to CH<sub>4</sub> and N<sub>2</sub> which have an almost linear isotherm and adsorbs much less. The amount adsorbed at 313 K and partial pressure 3.5 bar is significantly different between the compounds, which is around 4.48, 1.35, and 0.81 mol kg<sup>-1</sup> for CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> respectively. To model the equilibrium data, the dual-site Langmuir model was used for CO<sub>2</sub> equilibrium data and the standard Langmuir model was used for CH<sub>4</sub> and N<sub>2</sub> equilibrium data. The isotherm models describe very well the equilibrium data as can be seen in the lines shown in Figure 1a. The competitive selectivity of CO<sub>2</sub> over N<sub>2</sub> considering post-combustion stream condition (CO<sub>2</sub>/N<sub>2</sub>:15/85 vol.% at 1 bar and 313 K) is equal to 72. In the case of biogas condition (CO<sub>2</sub>/CH<sub>4</sub>:33/67 vol.% at 1 bar and 313 K), the competitive selectivity of CO<sub>2</sub> over CH<sub>4</sub> is equal to 38. These results point out that the binder-free zeolite 4A can be employed to efficiently separate CO<sub>2</sub> from CO<sub>2</sub>/CH<sub>4</sub>/N<sub>2</sub> due to the higher selectivity towards CO<sub>2</sub>. These selectivity values were calculated by using the extended dual-site Langmuir model. To verify a dynamic separation between the components, ternary breakthrough curves of a mixture of CO<sub>2</sub>/CH<sub>4</sub>/N<sub>2</sub> (20/20/20 vol.% balanced with He) at 5 bar and 313 K were performed and summarized in Figure 1b. As can be seen, CO<sub>2</sub> is the most retained component, and CH<sub>4</sub> and N<sub>2</sub> leave the column practically together at the beginning of the experiments. This observation is expected since the CO<sub>2</sub> adsorbs much more than CH<sub>4</sub> and N<sub>2</sub> on zeolite 4A. An adsorption mathematical model derived from mass and energy conservation laws was implemented in a personal computer to predict the dynamic behavior of the adsorption process. Moreover, this mathematical model includes both effects of axial dispersion and mass-transfer resistances taking into account an overall effective rate mass-transfer ( $K_{LDF}$ ) from the linear driving force model. Before the simulations, the relative importance of the individual axial dispersion ( $D_{ax}$ ) and mass-transfer ( $K_{LDF}$ ) resistances were evaluated from the method of moments for a linear system by an overall effective rate coefficient presented by Ruthven [3]. The  $K_{LDF}$  term is a lumped parameter that represents a sum of micropore, macropore, and film resistances, and the axial dispersion is a resistance caused by the spreading of the flow according to the fluid dynamic and column conditions [3–5]. Both parameters were estimated from the literature. The method of moments pointed out that axial dispersion is the dominant mechanism in all experiments performed in this work. To illustrate this result, CO<sub>2</sub> breakthrough curve on zeolite 4A at 373 K and 0.40 bar partial pressure was simulated and the result is shown in Figure 2, wherein the panel (a) the  $K_{LDF}$  was kept constant and Peclet ( $Pe_m = uL/D_{ax}$ ) was changed, and (b) the opposite. From Figure 2, it is clear that the fixed bed adsorption system is governed by the axial Peclet number for the column, instead of the overall mass transfer coefficient, since the changes in the  $Pe_m$  influences the concentration profile of the breakthrough curves and the global mass transfer resistance  $K_{LDF}$  has no effect in the spreading of the curve. Therefore, the zone spreading in the bed is completely dominated by axial dispersion. The mathematical model implemented in this work as well as the parameters  $D_{ax}$  and  $K_{LDF}$  estimated from the literature provide a good

prediction tool of the experimental breakthrough curves represented by the lines in Figures 1b and 2ab, which also can be useful to perform process simulation. To solve the mathematical model the method of lines [6] was used, being the spatial coordinates discretized by orthogonal collocation [7], and the resulting ordinary and algebraic differential equations were solved with a stiff integrator, ode15s, available in the MATLAB library [8]. In summary, this work has shown that the commercial binder-free zeolite 4A act as an efficient separator of CO<sub>2</sub> from CH<sub>4</sub> and N<sub>2</sub> with selectivities around 72 over N<sub>2</sub> and 38 over CH<sub>4</sub>, being a good alternative to be used in CO<sub>2</sub> capture and biogas upgrading.



**Figure 1** – (a) Isotherm of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> on binder-free zeolite 4A at 313 K; (b) Ternary breakthrough of a mixture CO<sub>2</sub>/CH<sub>4</sub>/N<sub>2</sub> (20/20/20 vol.% balanced with He) on binder-free zeolite 4A at 313 K. Symbols = experimental data; Lines = model.



**Figure 2** – (a) Effect of changing the axial Peclet number, and (b) effect of changing the overall mass transfer coefficient ( $K_{LDF}$ ) on  $\text{CO}_2$  breakthrough curve (373 K and 0.40 bar) on binder-free zeolite 4A.  $Pem$  and  $K_{LDF}$  were estimated from the literature. Symbols = experimental data; Lines = model.

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