Binder-free Zeolite 4A for Biogas Upgrading and CO_2 Capture

L.F.A.S. Zafanelli[1,2,3], E. Aly [1,4], A. Henrique[1,2,3], A. E. Rodrigues[2,3], J.A.C. Silva[1*]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253, Bragança, Portugal

[2]Laboratory of Separation and Reaction Engineering-Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, R. Dr. Roberto Frias S/N, 4200-465, Porto, Portugal

[3]Associate Laboratory in Chemical Engineering (ALiCE), Faculdade de Engenharia, Universidade do Porto, R. Dr. Roberto Frias, S/N, 4200-465, Porto, Portugal.

[4]Aveiro Institute of Materials, CICECO, Department of Chemical Engineering, University of Aveiro, Campus Universitario de Santiago, 3810-168, Aveiro, Portugal.

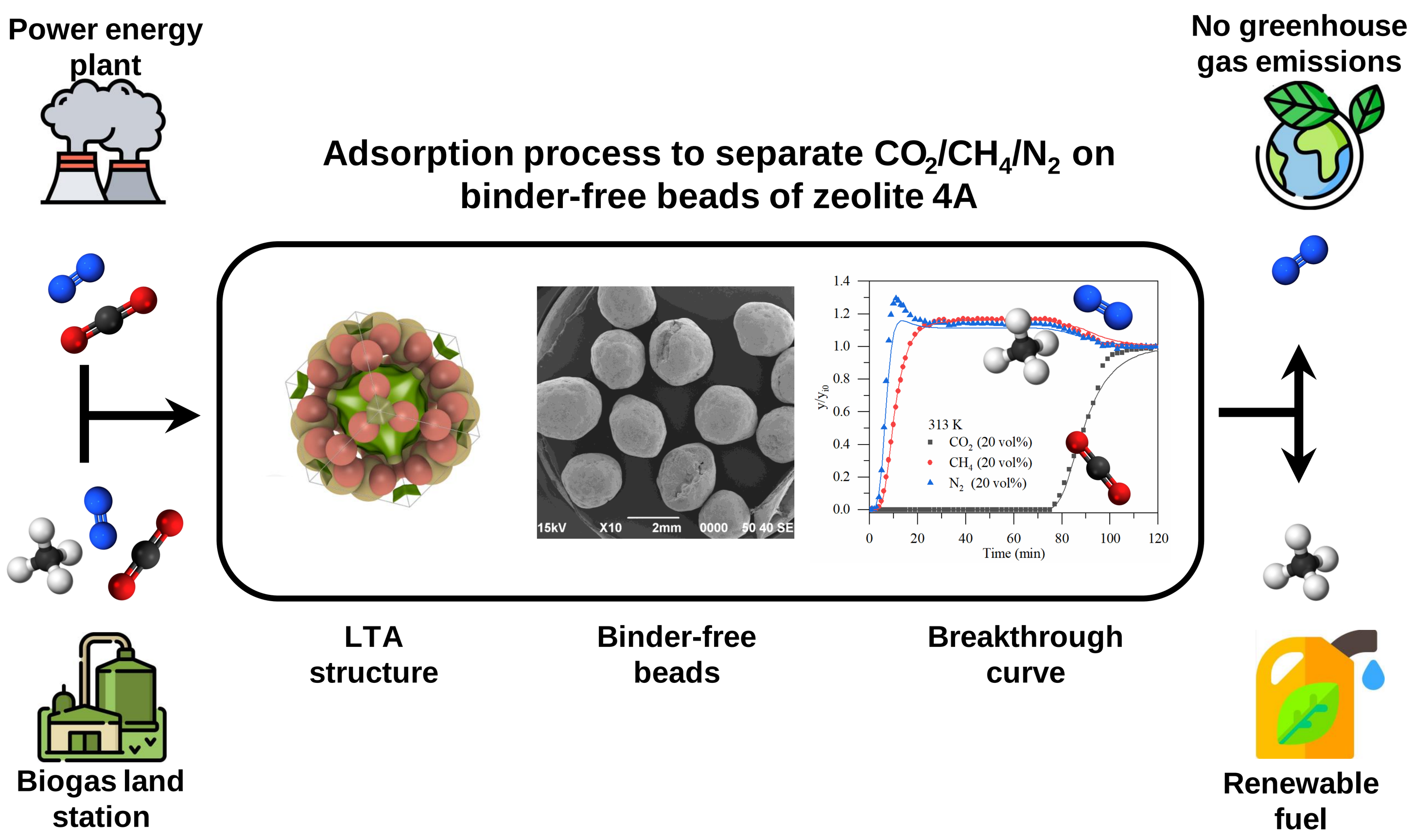
*jsilva@ipb.pt

Motivation and Objectives

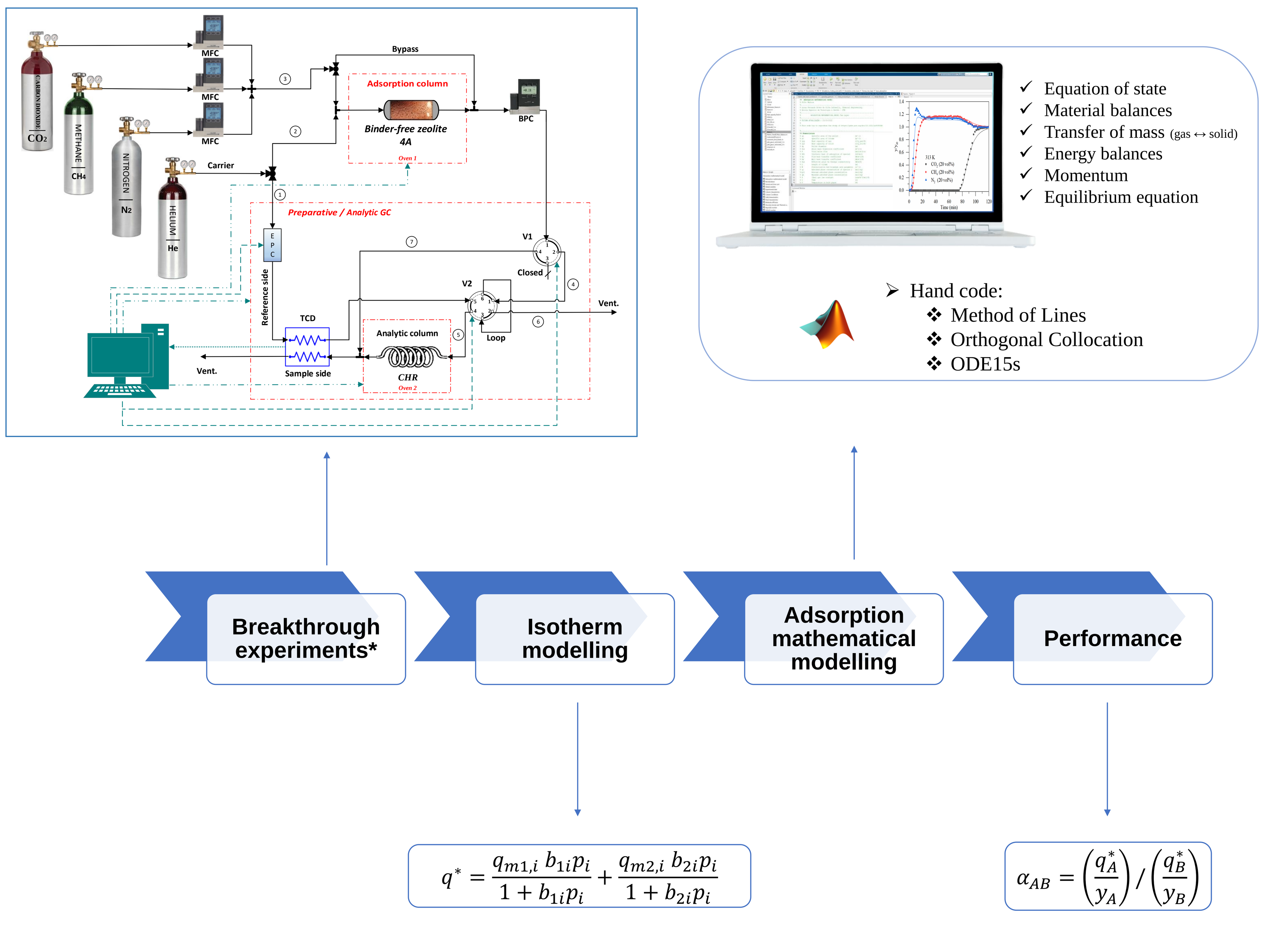
The presence of CO_2 (40 vol.%) in the biogas composition can reduce its calorific value, impairs its transport via pipelines, and, consequently, limits its use [1]. CO_2 released from coal-fired power plants has been contributing to a massive 73% of annual emissions for the energy sector [2]. In this way, this work seeks to evaluate the separation of CO_2, CH_4, and N_2 on binder-free zeolite 4A in conditions of interest to biogas upgrading and CO_2 capture from the post-combustion stream.

Evaluate the binder-free zeolite 4A (BF4A) to separate CO_2, CH_4, and N_2.

Increase knowledge on equilibrium and dymanic interaction between BF4A and CO_2, CH_4, and N_2.



Methodology



$$q^* = \frac{q_{m1,i}\, b_{1i} p_i}{1 + b_{1i} p_i} + \frac{q_{m2,i}\, b_{2i} p_i}{1 + b_{2i} p_i}$$

$$\alpha_{AB} = \left(\frac{q_A^*}{y_A}\right) / \left(\frac{q_B^*}{y_B}\right)$$

* Experiments performed at 313, 373, and 423 K and up to 3.5 bar.

Conclusions and Future Work

- **Binder-free zeolite 4A** act as an **efficient separator** of CO_2 from CH_4 and N_2
- **Selectivities** to CO_2 around **72** over N_2 and **38** over CH_4
- **Dual-site Langmuir** and **Standard Langmuir described well** the equilibrium data
- **Mathematical model predicted well** the breakthrough experiments

Ongoing/Future work: development of a conceptual pressure swing adsorption to evaluate the performance of binder-free zeolite 4A to address the biogas upgrading and CO_2 capture from post-combustion streams.

Equilibrium

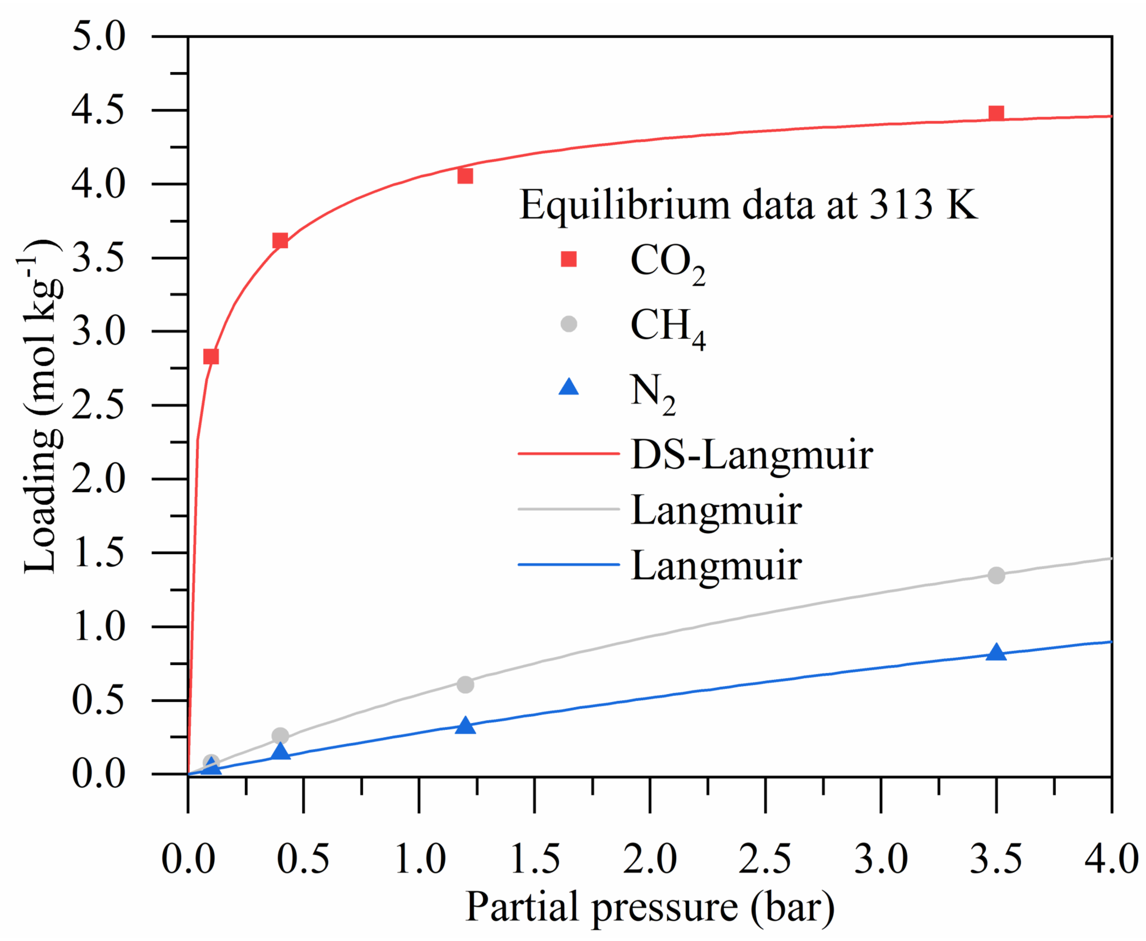
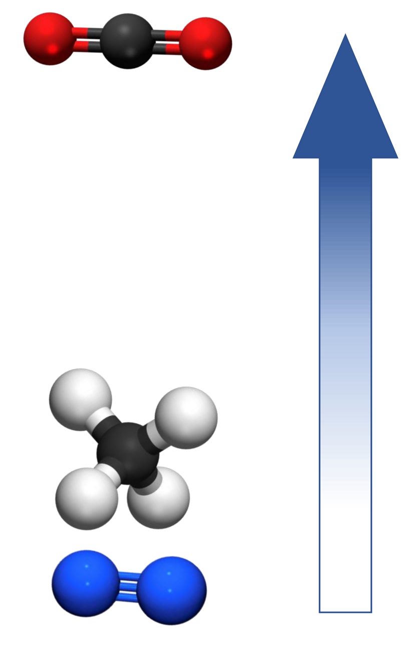


Fig. 1 – Equilibrium data of CO_2, CH_4, and N_2 on BF4A.



- At 313 K and 3.5 bar: CO_2 (4.48 mol/kg) > CH_4 (1.35 mol/kg) > N_2 (0.81 mol/kg)
- Isotherm shape: CO_2 (highly nonlinear), CH_4 (linear), N_2 (linear)
- Isotherm model: Dual-site Langmuir (CO_2), Langmuir (CH_4 and N_2)
- Equilibrium data well described by isotherm model

Kinetic Study

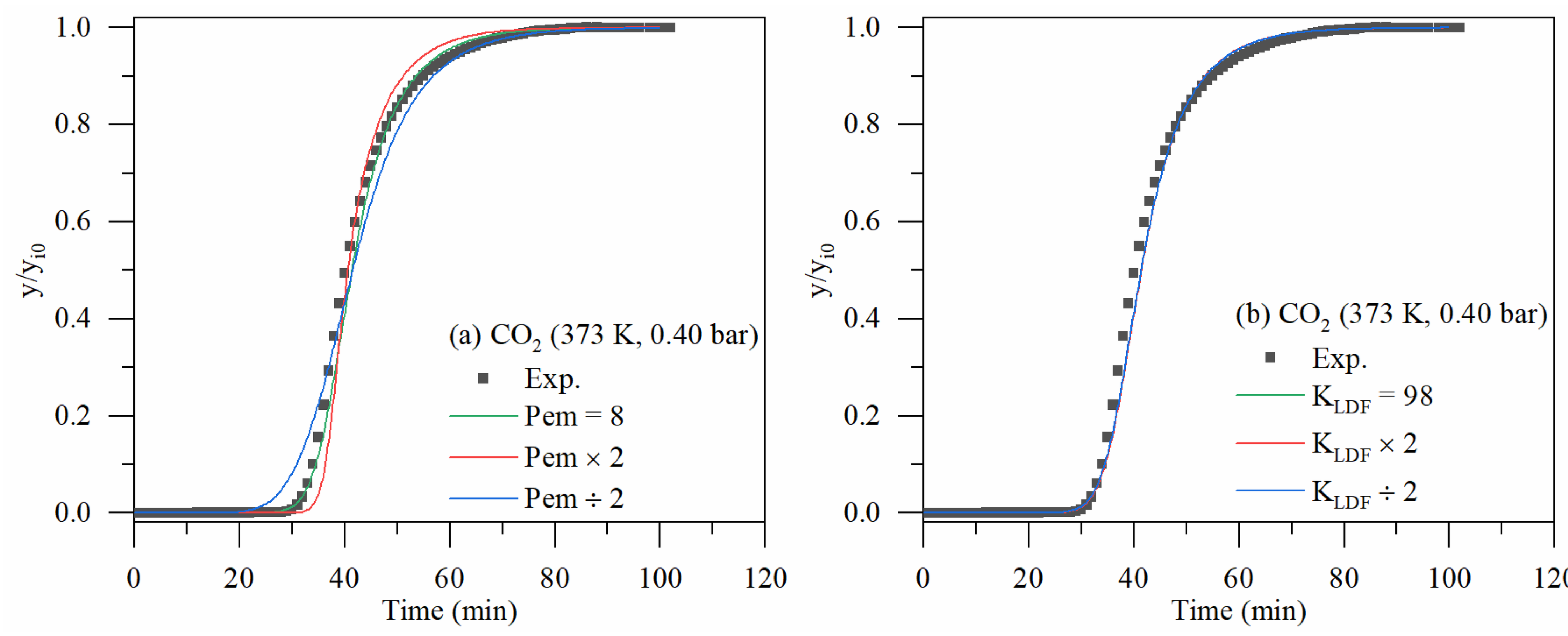


Fig. 2 – Effect of (a) axial Peclet number, and (b) overall mass transfer coeficient (K_{LDF}), on BF4A.

Peclet number

$$Pem = \frac{uL}{D_{ax}}$$

Lumped mass transfer

$$\frac{1}{K_{LDF}} = \frac{R_p}{3k_f} + \frac{R_p^2}{15\varepsilon_p D_p} + \frac{r_c^2}{15KD_c}$$

- The zone spreading in the fixed bed is completely dominated by axial dispersion

Dynamic separation and Selectivity

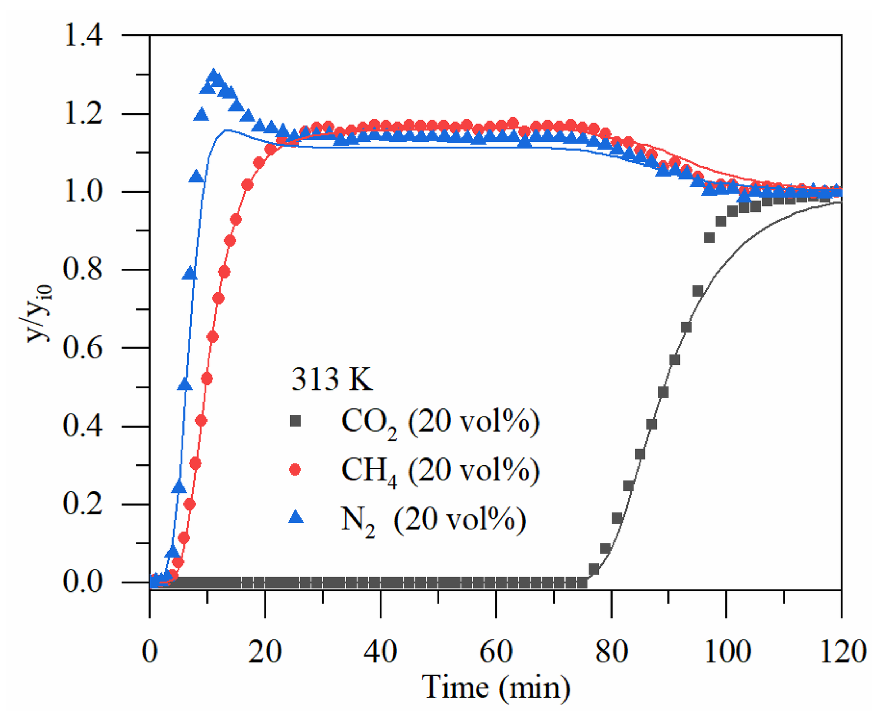


Fig. 3 – Ternary breakthrough of a mixture $CO_2/CH_4/N_2$ on BF4A at 5 bar.

Selectivity post-combustion condition*:

$$\alpha_{CO_2,N_2} = 72$$

Selectivity biogas condition**:

$$\alpha_{CO_2,CH_4} = 38$$

- BF4A completely separates CO_2 from a mixture of $CO_2/CH_4/N_2$
- High selectivity towards CO_2 for two targets of application

* CO_2/N_2:15/85 vol.% at 1 bar and 313 K – predicted using extended isotherm (DS-Langmuir)
** CO_2/CH_4:33/67 vol.% at 1 bar and 313 K – predicted using extended isotherm (DS-Langmuir)

References and Acknowledgments

Acknowledgments. CIMO (UIDB/00690/2020), LSRE-LCM (UIDB/50020/2020), and ALiCE (LA/P/0045/2020), funded by FCT/MCTES (PIDDAC). FCT, P.I.; FCT under Programme PTDC 2020 *3599-PPCDTI* project no. PTDC/EQU-EPQ/0467/2020; FCT individual research grant no. DFA/BD/7925/2020 for L.F.A.S. Zafanelli. The authors are thankful to Kristin Gleichman and Chemiewerk Bad Koestritz GmbH for kindly providing the binder-free beads of zeolite 4A studied in this work.

References.

[1] M.P.S. Santos, C.A. Grande, A.E. Rodrigues, Ind. Eng. Chem. Res. 50 (2011) 974–985.
[2] S. Lawson, M. Snarzyk, D. Hanify, A.A. Rownaghi, F. Rezaei, Ind. Eng. Chem. Res. 59 (2020) 7151–7160.