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CO_2 CAPTURE IN 3D-PRINTED CARBON MONOLITH BY ADSORPTION

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ABSTRACT
Hierarchically structured 3D-printed porous carbon monoliths were evaluated for their applicability in CO_2 capture from post-combustion streams. Two materials of the same macroscopic shape were studied, which varied in the micro- and mesoporosity by changing the final CO_2 activation time: activated at 1133 K for 6 h (M1) and 12 h (M2), respectively. Fixed bed breakthrough experiments with single (CO_2 and N_2) and multicomponent (CO_2/N_2: 15/85 v.%) feed mixtures were conducted, covering the temperature range of 313 - 373 K. Results demonstrated that both materials enable a thermodynamic-based separation of these components due to their strong interaction with CO_2. While a higher burn-off during monolith activation enhances its adsorption capacity by increasing the surface area, the highest selectivities were obtained in M1, 18, against 10 in M2. The dual-site and standard Langmuir isotherm models conveniently fitted the adsorption equilibrium data, and a dynamic adsorption model suitably predicted the breakthrough curves.

Keywords: 3D printed monoliths, post-combustion CO_2 capture, fixed bed adsorption, modelling.

INTRODUCTION
CO_2 capture from post-combustion streams in coal-fired power plants has become a worldwide research topic over the past decade since it plays a vital role in mitigating global warming [1]. This carbon source accounts for at least 73 % of annual energy sector emissions [2]. Therefore, to achieve the International Panel on Climate Change (IPCC) target by keeping the global warming average under 2 K, great efforts have been made towards decreasing penalty energy and increasing CO_2 recovery on existing capture technologies [1]. The chemical absorption technology with monoethanolamine still is the most widely used for CO_2 capture [1]. However, its regeneration step requires high energy consumption, making the process expensive [3].
Among other technologies, material-assisted separation, such as adsorptive separation by porous solids, which uses the difference in molecular dimensions/shape/affinity of the molecules, has been recognized as an attractive and costly alternative. In this context, structuring adsorbent materials for optimal process efficiency and easy implementation in large-scale processes is a fundamental step in their way to commercialization. Accordingly, the present work seeks to evaluate the applicability of a recently presented new route towards 3D-printed porous carbon monoliths, combining micropores from CO_2 activation and meso- and macropores from porogen templating [4], for the CO_2 capture from post-combustion streams.

MATERIAL AND METHODS
The 3D-printed porous carbon monoliths were synthesized following 4 main steps: (1) resin preparation: two monomers, 35 % pentaerythritol tetraacrylate and 35 % divinylbenzene, an inert porogen 30 % bis(2-ethylhexyl) phthalate, an initiator, 10 $mg.mL^{-1}$ phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide, and a dye, 0.4 $mg.mL^{-1}$ sudan1; (2) photopolymerization: a porous polymer open cell structure comprising 8 tetragonal cubic centered unit cells (with a unit cell diameter of 5.7 mm and a thread diameter of 2 mm) is generated by stereolithographic 3D print; (3) porogen extraction: the porogen and color agent were extracted from the structure using Soxhlet extraction with acetone (>20 $mL.g_{Polymer}^{-1}$) for 24 h at 373 K and then dried at 333 K over night; and (4) thermal treatment:

the resultant 3D-printed polymer was stabilized in air (at 573 K for 6 h), pyrolyzed in nitrogen (at 1173 K for 0.3 h) and activated in CO_2 (at 1133 K). For this study, two monoliths with different degrees of CO_2 activation were prepared: (1) activated for 6 h (M1) and (2) activated for 12 h (M2).
The breakthrough experiments of CO_2 and N_2 and their mixtures were performed in chromatographic-based adsorption apparatus, which consists of three main sections: (1) a gas preparation, (2) an adsorption, and (3) an analytical section. In the gas preparation section, the flow rates of adsorbates and the carrier gas helium are set up through thermal mass flow controllers. The adsorption section comprises a stainless-steel column (internal diameter 10 mm and length 100 mm) filled with the adsorbent material and placed inside the chromatographic oven. In the analytical section, the output stream of the packed bed is directed to a thermal conductivity detector (TCD). Before going to TCD, each minute (with a 6-way sampling valve), a sample of the column outlet is first directed to a capillary column (HayeSep N packed column, 24 g, and mesh 80/100).
The equilibrium data obtained from the single component breakthrough curves were fitted with the dual-site Langmuir (CO_2) and Langmuir (N_2) isotherm models, and the data from the multicomponent experiments were modelled with the extended dual-site Langmuir model. In addition, a general dynamic adsorption model developed in Matlab was used to simulate and analyze the transient adsorption behavior of the binary breakthrough system (N_2/CO_2). To account for the transport rate from the bulk gas phase to the adsorbent, a linear driving force rate approximation was used [5].

RESULTS AND DISCUSSION

The 3D-printed monoliths were characterized by nitrogen physisorption at 77 K. By increasing the activation time at a temperature of 1133 K from 6 to 12 h, the burn-off of the material almost linearly scales from 14 wt.% to 26 wt.%, indicating the creation of additional microporosity. The prolonged activation equally increases the specific surface area and pore volume for monolith M2 (S_{QSDFT}: 1307 $m^2.g^{-1}$; 0.52 $cm^3.g^{-1}$) compared to M1 (S_{QSDFT}: 1048 $m^2.g^{-1}$; 0.39 $cm^3.g^{-1}$) by ca. 30 %.
Fig. 1 gathers the corresponding single-component adsorption equilibrium isotherms for CO_2 and N_2 in monoliths M1 (closed symbols) and M2 (open symbols). The equilibrium data reveals that both materials have a promising capacity for CO_2 capture, showing loadings significantly higher than N_2, especially at the lowest temperatures. For instance, at 313 K and 120 kPa, the loading obtained for CO_2 is 3.00 mol/kg (M1) and 3.17 mol/kg (M2) in contrast with 0.47 $mol.kg^{-1}$ (M1) and 0.54 $mol.kg^{-1}$ (M2) for H_2. This also means a selectivity ratio $((q_{CO_2}/y_{CO_2})/(q_{N_2}/y_{N_2}))$ of around 6.

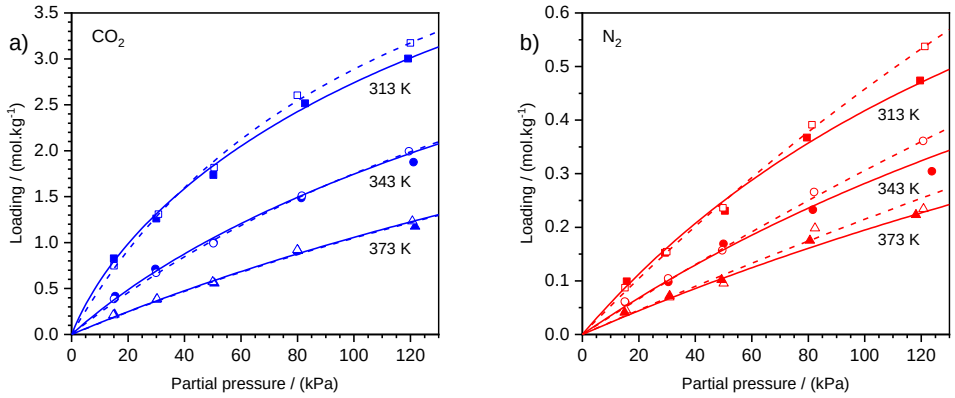

Figure 1. Single component adsorption equilibrium isotherms: a) CO_2 (solid symbols - M1 and open symbols - M2) and b) N_2 (solid symbols - M1 and open symbols - M2). The lines (continuous - M1 and dashed - M2) represent the model predictions.

The binary breakthrough curves of CO_2/N_2 at 343 K and 100 kPa are shown in Fig. 2, measured from a saturated bed with pure N_2. These experiments confirmed the separation performance of the 3D-printed monoliths. For a feed mixture of 15/85 v.% (panel a – M1), the CO_2 breaks the column at around 10 min and reaches saturation near 25 min. For the mixture ratio 50/50 v.% (panel b – M1), the breakthroughs become steeper due to the higher concentration of CO_2 in the feed. The calculated selectivities resulted in 18 and 24 for (M1) compared to 10 and 9.9 for M2, respectively. The lines in Fig. 2 represent the simulation results from the dynamic adsorption model, which suitably described

the experimental data. From the fitting of the breakthrough curves, mass transfer coefficients around 0.070 and 0.075 s^{-1} were found for CO_2 in M1 and M2, respectively.
Comparing the materials, both showed similar adsorption capacities, but the loadings are slightly higher in M2, especially for N_2. This means that the effect of creating additional microporosity, most favored the N_2 adsorption, thus decreasing the separation performance in M2.

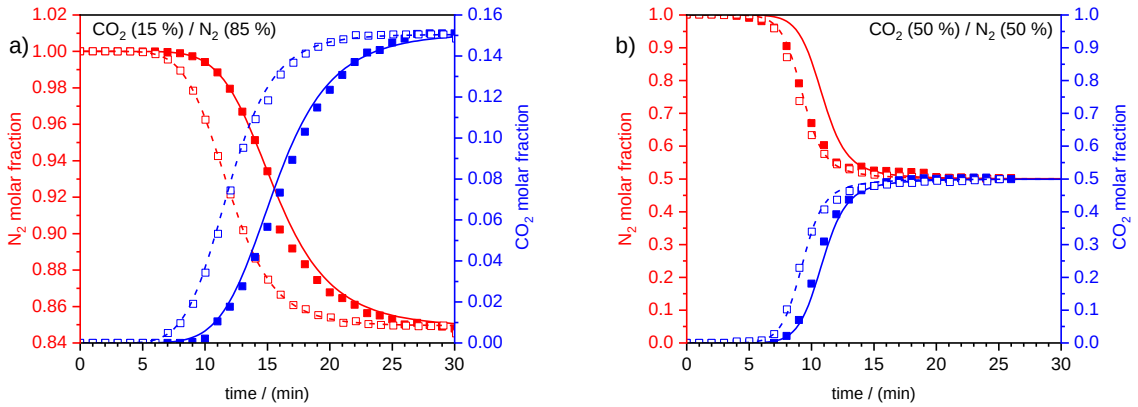

Figure 2. Breakthrough curves for a binary mixture of CO_2/N_2 in M1 (solid symbols) and M2 (open symbols) at 313 K: a) mixture ratio of 15/85 v.%, and b) mixture ratio of 50/50 v.%. The lines (continuous - M1 and dashed - M2) represent the numerical simulations.

CONCLUSIONS

The potential of hierarchically structured 3D-printed porous carbons monoliths has been investigated for their use in CO_2 capture in post-combustion streams. The breakthrough experiments demonstrated that the material performs significantly for the equilibrium separation of CO_2/N_2, by retaining the CO_2 inside the column. Regarding the activation time on the monoliths production, it was observed that a higher burn-off led to a higher specific surface area and pore volume. However, the additional microporosity created was most accessible to N_2 molecules. Considering the relevance of the above findings, this work provides an important reference for using structured materials not only in the field of CO_2 capture but also for separating any useful compound mixtures.

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