Combining process optimization and atomistic simulations to screen metal-organic frameworks (MOFs) for Direct Air Capture (DAC) of CO₂

Bhubesh Murugappan Balasubramaniam\textsuperscript{a}, Jake Burner\textsuperscript{b}, Ohmin Kwon\textsuperscript{b}, Javad Naroozi\textsuperscript{b}, Phuc–Tien Thierry\textsuperscript{c}, Samuel Lethier\textsuperscript{c}, Philip Llewellyn\textsuperscript{c}, Cecile Pereira\textsuperscript{c}, Veronique Pugnet\textsuperscript{c}, Tom K. Woo\textsuperscript{b*}, Arvind Rajendran\textsuperscript{a*}

\textsuperscript{a}Department of Chemical and Materials Engineering University of Alberta, Edmonton, Alberta Canada T6G 1H9
\textsuperscript{b}Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Ontario Canada, K1N 6N5
\textsuperscript{c}TotalEnergies E&P Research and Technology, Houston, TX 77008, USA

Abstract

Huge databases of experimental and hypothetical porous materials (zeolites and Metal-organic frameworks or MOFs) are available and have been screened for various gas separation processes [1,2]. Compared to adsorbents for flue gas CO₂ capture, there are very materials that offer high uptakes at 400 ppm of CO₂; a property that is essential for direct air capture (DAC) of CO₂. The current work is aimed at computationally mining large databases of MOFs; both real and hypothetical for this challenging application. Grand Canonical Monte Carlo (GCMC) simulations are performed to obtain pure CO₂, N₂ and CO₂/N₂ binary isotherms at various temperatures and partial pressures of interest. Isotherm parameters are obtained by fitting single site Langmuir (SSL) equation for pure CO₂ and N₂. Binary loadings are predicted using extended Langmuir isotherm and validated with the values from GCMC. To realize the optimal “marriage” between processes and materials, we combine GCMC simulations with a benchmark temperature-vacuum swing adsorption (TVSA) processes for DAC.

A detailed model TVSA process has been developed for solid sorbent-based DAC and has been validated against the literature [3]. In the TVSA process, two regeneration options are considered: one employing steam, and the other using low-grade indirect heat. For the sorbent APDES – NFC considered detailed energy - productivity optimizations (with a constraint on the dry purity of CO₂ > 95%) have also been performed to understand the trade-offs involved and this serves as a benchmark for DAC screening in this study. To screen adsorbents for the application of DAC, two approaches have been considered: The first involves using isotherms obtained from GCMC simulations as simulation inputs to our detailed process model. In this approach, energy – productivity optimizations are performed and the results of this study will shed light on how these physisorbents stand in comparison with the traditional amine – functionalized sorbents (APDES – NFC) developed for DAC. The second, deals with identifying the potentially ideal material using the concept of process inversion. In this approach the adsorption isotherm parameters, material properties such as particle density and the cycle operating conditions are treated as optimization variables and a numerical optimization is performed to identify the best material for the given TVSA cycle. Both approaches provide key insights about the sorbent selection for DAC application. Considering the computational complexity, machine

* Corresponding author. Tel.: +0-000-000-0000 , E-mail address: arvind.rajendran@ualberta.ca, Tom.Woo@uottawa.ca, phuc-tien.thierry@totalenergies.com
learning techniques are used both at the GCMC and process simulation levels. Training datasets are generated with the second approach leading to unique combinations of isotherm parameters and operating conditions. ANN based surrogate models are developed to predict process performance metrics such as purity, recovery, productivity and energy. Surrogate models are validated against the traditional optimization results and show superior performance in screening of MOFs. The approach of screening presented here will help chemists synthesize new “best performing” sorbents and also help us find a suitable sorbent metric for future screening of MOFs for DAC. With our approach, we demonstrate the ability to screen large databases both reliably and rapidly.

3. V. Stampi – Bombelli et al., *Adsorption*, 2020, 26, 1183-1197

*Keywords:* Direct Air Capture; GCMC Simulations; process screening