How to accurately fast-track sorbent selection for post-combustion CO_2 capture? A comparative assessment of data-driven and simplified physical models for screening sorbents

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Abstract

The recent discovery of a multitude of hypothetical materials for CO_2 capture applications necessitated the development of reliable computational models to aid the quest for better-performing sorbents. Given the computational challenges associated with existing detailed adsorption process design and optimization frameworks, two types of screening methodologies based on computationally inexpensive models, namely, data-driven and simplified physical models, have been proposed in the literature. This study compares these two screening methodologies for their effectiveness in identifying best-performing sorbents from a set of 369 metal-organic frameworks (MOFs). The results showed that almost 60% of the MOFs in the top 20 best-performing materials ranked by each of these approaches were found to be common. The validation of these results against detailed process simulation and optimization-based screening approach is currently underway.

Keywords: adsorption; metal-organic frameworks; post-combustion CO_2 capture; machine learning; modelling and optimization.

1. Introduction

Among several CO_2 capture technologies considered for post-combustion CO_2 capture, solid adsorbents are seen as a promising alternative to traditional liquid solvents for the separation of CO_2 from flue gases. These adsorbents are typically deployed in pressure/vacuum swing adsorption (PVSA) or temperature swing adsorption (TSA) processes. The choice of the adsorbent plays a critical role in determining the separation performance of PVSA or TSA processes [1][2]. Conventionally, better-performing adsorbents are identified through experimentation and testing of a few handfuls of adsorbents as means to understand their performance in the real process [3]. However, this approach is challenged by the recent advent of highly tunable adsorbents, such as metal-organic frameworks (MOFs) for CO_2 capture applications, resulting in thousands of potential hypothetical adsorbents [3]. As the experimental evaluation of a multitude of adsorbents is practically impossible, computational screening of the adsorbents has been considered, where process simulations and optimizations based on adsorbent properties are carried out to evaluate the process-scale performance [2][4]. This approach is computationally expensive and time-consuming [2][4][5], which makes it computationally inadequate to handle large databases of adsorbents.

Different approaches have been proposed to reduce the computational costs of existing simulation and optimization tools. One approach is the development of simplified physical models obtained through a simpler description of the process which can be solved in seconds [6][7]. These models proved able to provide reasonable estimations of the process performance. The other approach is the development of surrogate or data-driven models built based on statistical methods that act as faster approximations of process metrics [5]. With groundbreaking advances in machine learning, novel approaches that incorporate physics into surrogate models are also developed to reliably represent physical processes [8].

The goal of this study is to compare the performance of data-driven and simplified physical modeling approaches in rapidly screening databases of adsorbents based on a techno-economic assessment for post-combustion CO_2 capture applications. For this analysis, a set of 369 MOFs from the CoREMOF 2014 database provided by Leperi et al. [4] is used and the material performance is assessed using a four-step PVSA cycle with light product pressurization [1].

2. Screening methodologies

2.1. Data-driven model-based optimization framework

This methodology utilizes data-driven models built based on machine learning principles as a faster approximation for calculating process performance metrics. The data-driven models are coupled with the cost model and the non-dominated sorting genetic algorithm (NSGA – II) to optimize each material for the minimum cost of CO_2 avoided. The data-driven models used in this study are artificial neural networks (ANNs) based on the machine-assisted adsorption process learning and emulation (MAPLE) framework [5].

The inputs to the MAPLE model are process features consisting of process operating conditions: adsorption step duration, vacuum pump flow rates, column size, high pressure, intermediate pressure, low pressure, and feed composition; and adsorbent features comprising dual-site Langmuir isotherm parameters of CO_2 and N_2, and particle morphology. Individual ANN models were trained for each output, namely, step durations, purity, recovery, and energy consumption. These predicted quantities form inputs to the cost model to calculate the cost of the CO_2 avoided based on the approach presented in Subraveti et al. [1]. The neural network architecture comprises a feed-forward fully connected network with one input layer including 19 process and adsorbent features, three hidden layers with 10-15 neurons, and an output layer with one output. A tanh activation function was used in the hidden layers and a linear activation was used for the output layer. Around 9000 unique combinations of the input variables generated using the Latin hypercube sampling along with the corresponding outputs were used as samples in the training of the neural networks. Note that the outputs were previously obtained by simulating the detailed adsorption process model until the cyclic-steady state condition [1][9]. The neural networks were trained using Bayesian regularization with the back-propagation algorithm '*trainbr*' in MATLAB 2022a [5][9].

2.2. Simplified physical model-based optimization framework

The other approach for the screening of adsorbent materials involves utilizing models that describe the physical phenomena occurring in an adsorption process but introducing simplifications to decrease the computational effort. The larger the simplification level applied, the lower the computational effort. Conversely, the expected accuracy of the

models is expected to decrease. For this work, two simplified models are proposed. The first one termed the modified equilibrium model (MEM), relies on the key assumption of local equilibrium, i.e., CO_2 gets instantaneously adsorbed onto the adsorbent materials. The model is an extension of an approach presented in the literature [6]. The main modifications with respect to its original formulation include a different routine to solve the adsorption step and the possibility to simulate a 4-step cycle [10]. The second model, termed the reduced-order kinetic model (ROKM), attempts to go beyond the equilibrium assumption by introducing a methodology to implicitly solve the linear driving force (LDF) approximation and, hence, account for mass transfer resistances. The methodology builds on a set of simplifying assumptions, therefore a degree of inaccuracy in capturing the kinetics effects is expected.

The simplified physical models are coupled with the same cost model as in the MAPLE approach and a Bayesian optimization (BO) algorithm to optimize each material for the minimum cost of CO_2 avoided. The BO algorithm was developed in-house and tested for the optimization of PSA processes, showing a good balance between computational time and reliability [11]. Simplified physical models might not directly provide all necessary inputs to the cost model owing to the inherent assumptions made while developing these models. For example, the MEM model cannot provide the step durations that are critical for estimating cost. In such cases, relevant and consistent assumptions were made for all the materials to enable the integration of the techno-economic analysis framework for these simplified models. The MEM model needs more assumptions compared to the ROKM model for cost evaluation.

3. Results and discussion

The two methodologies are compared in their ability to reliably screen adsorbents for post-combustion CO_2 capture. Table 1 briefly summarizes the merits and demerits of each screening model in evaluating the adsorbent performance. In this study, a dry flue gas with CO_2/N_2 binary mixture is separated using a four-step PVSA process, a widely studied process that has been demonstrated at the pilot scale [12]. The cycle consists of adsorption (ADS) step, a co-current blowdown (BLO) step, a counter-current evacuation (EVAC), and a light-product pressurization (LPP) step.

Table 1: Merits and demerits of both types of screening models for rapid evaluation of adsorbent performance.

Screening model type	Strengths	Limitations
Data-driven models	• Very fast computations • Embeds all physical phenomena from the detailed model • Predictions represent the real process performance	• Requires computational efforts to generate data for training • Black-box model – Applicability within the training range
Simplified physical models	• Interpretability through the simplified description of physics • Easy to develop • Entails wider model applicability	• Simulations may not represent the real process performance • May lead to convergence failures and false optima in optimizations

The performance of each MOF is assessed based on its techno-economic performance in the four-step PVSA cycle. The metric used for ranking the materials was the minimum CO_2 avoided cost obtained after optimizing the process operating conditions for each material. It is worth reiterating that both the surrogate and the simplified physical models

predict the process performance indicators which are later used as inputs to the cost model within the optimization framework. As mentioned earlier, the cost model employed herein is based on Subraveti et al. [1] for both approaches.

The screening of 369 MOFs was individually carried out for MAPLE, MEM, and ROKM, and the top 20 best-performing materials in terms of cost from each of these methodologies are reported in Fig. 1 for three different CO_2 compositions in the flue gas, namely, 7.5%, 13%, and 20%. The top 20 MOFs from the MAPLE-based screening were compared with MEM and ROKM approaches, and the common MOFs are highlighted in green. For the 7.5% CO_2 composition case, 8 out of 20 MOFs were featured in both MAPLE and MEM screening methodologies. On the other hand, 12 out of 20 were found

MOF ID		
MAPLE	MEM	ROKM
CUGLTM01	NIKDAM	UBUROY
MEHPAQ	CUGLTM01	QEYWUN
CUGLTM02	CUGLTM02	MEHPAQ
CUGLTM	UBUROY	QUFFED
HIDBON	MEHPAQ	QUGNOV
NELWIL	FUFREE	CUGLTM02
QUFFED	PURQEZ	NICJUG
RIYDEJ	CUGLTM	ARIBOS
UMELUU	QEYWUN	LUMZUO
QAVDEW	CATART03	NIKDAM
WAJHIA	VODPOU	IWEPUW
ARIBOS	ZNGLUD	UGEPEB
NICJUG	XACZEH	VODPOU
TIVFEK	ESUMOU	WAJHIA
BOWQAG	NICJUG	UMELUU
NIRDOI	CDLGLU02	PURQEZ
TIVFAG	NICZAA01	TIVFEK
VODPOU	ZNGLUD01	WUDNAK
QEYWUN	IFENOY02	TIVFAG
QUGNOV	RIYDEJ	IFENOY02
	*8/20 are common	*12/20 are common

(a)

MOF ID		
MAPLE	MEM	ROKM
CUGLTM01	NIKDAM	QEYWUN
ARIBOS	MEHPAQ	MEHPAQ
MEHPAQ	CUGLTM02	CUGLTM01
NELWIL	CUGLTM	ARIBOS
CUGLTM02	QEYWUN	UBUROY
UMELUU	CUGLTM01	CUGLTM02
HIDBON	IWEPUW	LUMZUO
NICJUG	LUMZUO	CUGLTM
BEPPOD	ARIBOS	QUGNOV
QUFFED	FUFREE	QUFFED
CUGLTM	XACZEH	VODPOU
RIYDEJ	ZNGLUD	TIVFAG
TIVFEK	QUGNOV	NICJUG
NINHOH	PURQEZ	IWEPUW
QUGNOV	RIYDEJ	UMELUU
WAJHIA	QUFFED	TIVFEK
BOWQAG	CDLGLU02	XACZEH
QEYWUN	VODPOU	WAJHIA
IFENOY02	ZNGLUD01	WUDNAK
CEHWOD	ESUMOU	UGEPEB
	*9/20 are common	*12/20 are common

(b)

MOF ID		
MAPLE	MEM	ROKM
MEHPAQ	QEYWUN	MEHPAQ
CUGLTM01	UBUROY	CUGLTM02
CUGLTM02	MEHPAQ	QEYWUN
BEPPOD	CUGLTM01	CUGLTM
NELWIL	CUGLTM02	UBUROY
TIVFEK	NIKDAM	ARIBOS
HIDBON	CUGLTM	IWEPUW
UMELUU	PURQEZ	UMELUU
NAKLIW	ZNGLUD01	NICJUG
LUMZUO	ARIBOS	LUMZUO
ARIBOS	RIYDEJ	TIVFAG
CUGLTM	ZNGLUD	WUDNAK
QUGNOV	XACZEH	QUGNOV
NICJUG	LUMZUO	QUFFED
VODPOU	QUGNOV	TIVFEK
CAYDOX06	NICJUG	YERJEL
OKILEA	VODPOU	IFENOY02
KENJEU	IWEPUW	VODPOU
ICEGED	FUFREE	XACZEH
NINHOH	ESUMOU	WAJHIA
	*9/20 are common	*10/20 are common

(c)

Figure 1: Top 20 best-performing MOFs obtained using MAPLE, MEM, and ROKM screening methodologies for (a) 7.5% (b) 13%, and (c) 20 % CO_2 compositions in the flue gas. The common materials found in MAPLE, MEM, and ROKM are highlighted in green. The orange highlighted materials in MEM and ROKM were found in the Top 50 MOFs from MAPLE screening. The red ones were not found in the Top 50. Note that the MOFs are denoted with their index number in the list.

to be common for both MAPLE and ROKM. The MOFs highlighted in orange indicate that they appeared in the top 50 of the MAPLE-based ranking. This indicates that some of the top 20 MOFs from MEM and ROKM methodologies were also good-performing MOFs in the MAPLE-based screening. The red-shaded materials were not found in the top 50 of the MAPLE-based ranking. It is worth mentioning that the percentage differences in the minimum CO_2 avoided cost between the top-ranked and the 50^{th}-ranked MOF in the MAPLE-based ranking for 7.5%, 13%, and 20% CO_2 composition cases are 94%, 39%, and 31%, respectively. Similarly, the analysis is extended to 13% and 20% CO_2 composition cases, and the common materials between MAPLE and ROKM approaches were found to be more than the matched materials between MAPLE and MEM approaches. The addition of simplified mass transfer kinetics in ROKM compared to MEM, which was only based on the equilibrium-based description of physics, could possibly be the reason for the improvement in the number of common materials. Note that the MAPLE model was trained on the data generated by the detailed process model that described the complete physics of adsorption column dynamics.

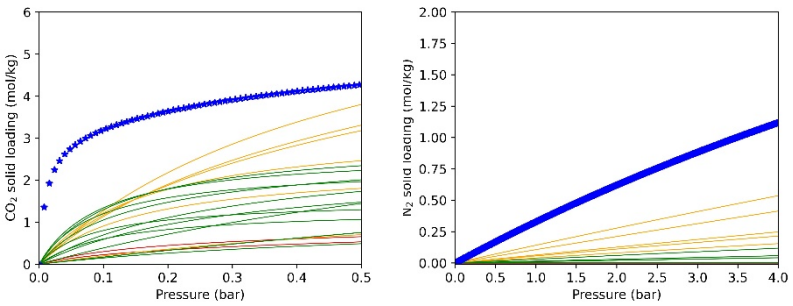

Figure 2: CO_2 and N_2 isotherms of the materials in the top 20 of the ROKM approach for the case of 13% CO_2 composition, out of which 12 were found in the MAPLE-based top 20 (green), 6 MOFs in the MAPLE-based top 50 (orange), and the remaining ones (red). Blue markers represent CO_2 and N_2 isotherms on zeolite 13X.

The CO_2 and N_2 isotherms of the top 20 MOFs from the ROKM-based screening approach for the case of 13% CO_2 composition are illustrated in Fig. 2. For comparison, CO_2 and N_2 isotherms of zeolite 13X are also shown as a reference. In Fig. 2, the green lines indicate CO_2 and N_2 isotherms of those MOFs that were found in the top 20 of both ROKM- and MAPLE-based screening. The orange lines represent the CO_2 and N_2 isotherms of the MOFs in the top 20 of the ROKM-based ranking that were also found in the top 50 of the MAPLE-based ranking. The red line isotherms are those MOFs in the top 20 of the ROKM-based ranking that were not found in the top 50 of the MAPLE-based ranking. It is interesting to notice that the best-performing materials have fairly linear CO_2 isotherms and very low N_2 adsorption. This observation remains consistent with several previous studies [1][13][14]. Finally, these common MOFs in the top 20 along with their normalized costs are tabulated in Table 2. It must be stressed that the main objective of the models presented, especially the simplified physical models, is to rank adsorbents rather than provide precise cost figures. Hence, this comparative analysis focused on the relative performances among the adsorbents.

Table 2: List of top-performing MOFs common in all three methodologies with normalized minimum CO_2 avoided cost for 13% CO_2 composition case. Note that the normalized CO_2 avoided cost was obtained by scaling the min. CO_2 avoided costs between the CO_2 avoided costs of the top-ranked MOF and the 20th-ranked MOF in each category.

MOF	Normalized minimum CO_2 avoided cost (-)		
	MAPLE model	MEM model	ROKM model
CUGLTM01	0.00	0.47	0.28
ARIBOS	0.05	0.57	0.31
MEHPAQ	0.11	0.14	0.18
CUGLTM02	0.39	0.16	0.37
QUFFED	0.73	0.81	0.53
CUGLTM	0.74	0.17	0.49
QUGNOV	0.79	0.71	0.53
QEYWUN	0.88	0.40	0.00

4. Conclusions

Two types of computationally inexpensive modelling and optimization frameworks are assessed to enable rapid screening of adsorbents for post-combustion CO_2 capture using a four-step PVSA cycle. On the one hand, the data-driven-based MAPLE model was coupled with the cost model and NSGA – II optimizer to minimize the CO_2 avoided cost for the set of 369 MOFs to evaluate their techno-economic performance. On the other

hand, simplified physical models, MEM and ROKM, both with simpler descriptions of the physics of adsorption columns, were combined with Bayesian optimization to rank the set of MOFs in terms of minimum CO_2 avoided cost. The results showed that almost 60% of the MOFs in the top 20 best-performing materials ranked by each of these approaches were found to be common. The validation of these screening approaches against the detailed process simulation and optimization approach is currently ongoing.

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