Flexible operation assessment of adsorption-based carbon capture systems via design space identification

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Abstract

Post-combustion CO2 capture by pressure-vacuum swing adsorption (PVSA) is gaining increasing interest due to the evolving energy landscape and the industry's decarbonization efforts. Within a hybrid energy system composed of conventional fossil-fuel-based power generation balancing renewable electricity sources, PVSA systems must be able to accommodate for transient conditions arising from intermittent operation. In this work, a model-based approach to investigate the operational flexibility of a PVSA unit applied to a 1,000 MW coal power plant is presented. The comparative analysis of two distinct adsorbents reveals a clear trade-off between operability and economics. Specifically, Zeolite-13X exhibits a lower capture cost, while ZIF-36-FRL demonstrates more flexibility in the ranges of high- and low-pressures at which the unit can be operated. The most flexible nominal operating point was successfully identified for each adsorbent using the developed framework, highlighting the importance of incorporating into the design process operational robustness. The latter is represented by a novel metric of normalised space size (NSS). This work demonstrates that significant improvement in NSS can be achieved, while increasing capture cost only marginally. This result highlights that optimal adsorbent selection for CO2 capture should account for operational flexibility.

**Keywords**: global sensitivity analysis, design space, pressure-vacuum swing adsorption

* 1. Introduction

The energy landscape is gradually shifting towards more environmentally friendly and renewable energy sources to substitute conventional fossil-fueled power generation. As a result, a hybrid energy system is emerging that combines both technologies in a load-balancing modality, which ensures a steady supply of power irrespective of the intermittency of renewable resources (Wilkew and Brown, 2022). In this context, fossil fuel combustion methods, extensively used for energy generation, must be redesigned and retrofitted to reduce their carbon emissions. To this end, these technologies can be integrated with post-combustion carbon capture, with amine-based absorption being widely employed on an industrial scale. However, this leading technology faces challenges, including thermal and chemical instability of the solvent.

An alternative approach for post-combustion carbon capture is adsorption, particularly pressure-vacuum swing adsorption (PVSA). While prior research has predominantly focused on developing novel adsorbent materials, the process-level assessment of the same materials presents significant challenges due to high number of design parameters involved (Ward and Pini, 2022). The arising hybrid fossil-and-renewable operation scheme of the energy system also adds complexity, demanding a highly flexible adsorption process design that remains viable under strict output constraints, such as the purity and recovery of CO2. This scenario calls for an integrated framework to screen adsorbents, encompassing both design performance and operational flexibility considerations (Grossmann et al., 2014).

In this study, an approach that combines global sensitivity analysis with design space analysis (Sachio et al., 2023) for assessing the flexibility and feasibility of the design of a PVSA process for CO2 capture is presented. This work also contributes to the formulation of a comprehensive adsorbent screening framework that takes into account both performance considerations and the critical aspects of process flexibility and robustness (Pistikopoulos et al., 2021).

* 1. Computational framework

This study implements a computational framework utilizing the direct sampling method to describe the design space (Sachio et al., 2023). The design space problem is formulated by defining the process model, the relevant input variables (i.e., the process parameters), the key performance indicators (KPIs), and associated constraints. A general flowchart of the methodology applied herein is depicted in Figure 1.

Global sensitivity analysis (GSA) was utilized to determine the most relevant process parameters in design space analysis (Kotidis et al., 2019). In the context of a PVSA process, the KPIs are influenced by various process parameters, broadly categorized into three main groups. First, “design parameters” are decided during the initial design phase and remain fixed throughout its operation. Second, “operational parameters” are expected to remain constant over time but can be adjusted based on the evolving conditions of the

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| **Figure 1.** General flowchart of the framework. |

PVSA process. Lastly, “material properties parameters” are associated with the physical properties of the adsorbent material employed and remain constant post-design.

Quasi-random Sobol sequence was employed to sample the process model, thereby establishing the knowledge space. Within this space, the design space containing all sample points with feasible output was defined. Subsequently, flexibility regarding prospective optimal operating points within this design space was assessed using a so-called acceptable operating region (AOR). In the context of a three-dimensional scenario, the AOR is visualized as a cuboid. The lengths of the cuboid's edges along each axis reflect the allowable operational range within the model parameter represented by the corresponding axis that guarantee process feasibility. Based on this information, a novel performance index called the normalized space size (NSS) has been applied to quantify and compare process flexibility across various adsorbents at different candidate optimal operating points. The formulation for the NSS is presented in Eq. (1).

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|  | (1) |

Here, includes all manipulated parameters (), represents the length of the AOR edge along axis , while and are the upper and lower bounds of .

* 1. Process model

In this study, a cyclic PVSA operation designed for post-combustion CO2 capture from a 1,000 MW coal power plant (Ward and Pini, 2022) has been examined. A feed gas mixture composed of 15% CO2 and 85% N2 (on a molar basis) available at 298.15 K and 1 bar was assumed. Two distinct adsorbent materials were assessed: Zeolite-13X, a benchmark material for post-combustion carbon capture, and ZIF-36-FRL, known for its high CO2 adsorption productivity and superior energy efficiency (Khurana and Farooq, 2016). This selection aligns with a previous study comparing their capture costs for industrial-scale application, facilitating a comprehensive extended comparison considering capture costs and operational flexibility of the PVSA unit.

A process model based on a rigorous dynamic simulation of an adsorption column has been employed, capturing non-isothermal and non-isobaric conditions. The process model is constructed through a set of PDEs describing mass, momentum, and energy balance within the column, discretized into 10 volume elements using the finite volume approach. In general, a cyclic PVSA operation is comprised of four stages, repeated cyclically: feed pressurization, adsorption, forward blowdown, and reverse evacuation. During feed pressurization, the column is charged with feed gas, elevating the system's pressure to the desired pressure level. In the adsorption stage, the CO2 content of the feed gas is adsorbed into the stationary phase (the adsorbent surface), producing a N2-rich effluent stream and a CO2-rich adsorbed phase. In the blowdown stage, the pressure is reduced to the pre-determined level , allowing the bulk gas to be released from the column. In the evacuation stage, the column pressure is further reduced to to produce a high purity CO2 stream upon desorption of the adsorbed phase.

The performance indicators considered in this study are the CO2 productivity, CO2 purity, CO2 recovery, and CO2 capture cost. For the latter, a techno-economic analysis by scaling up a single adsorption column to handle industrial-scale flue gas flow rate has been considered. The adsorption column model and the formulation of the KPIs are based on prior research within our group (Ward and Pini, 2022).

* 1. Results and Discussion
     1. Global sensitivity analysis (GSA) on PVSA model

For this task, Zeolite-13X, which is widely acknowledged as the benchmark adsorbent for this application, was used as the adsorbent material. To reduce the dimensionality of the problem prior, the single-site Langmuir adsorption model has been chosen to describe the isotherms. For all parameters, the range of uncertainty incorporated for GSA was set at ±40% of the previously reported optimal operating point (Ward and Pini, 2022).

The analysis indicates that “material properties parameters” – more specifically the temperature-dependent adsorption isotherm parameters – play a substantial role in driving the variation of all KPIs. It is noted here that parameters describing the saturation limit of the adsorption isotherm exert the weakest degree of influence, further indicating that the adsorbent bed might not achieve complete saturation during the adsorption step, nor full desorption during the evacuation step — a subject meriting further investigation in subsequent studies. GSA also indicates that “design parameters” primarily affect the capture cost and that “operational parameters” exhibit lower sensitivity relative to the “material properties parameters”. Nevertheless, these operational parameters still contribute to process feasibility (CO2 purity and CO2 recovery) and affect capture cost. Considering their significance in the PVSA design phase and their impact on these critical factors, they have been included in the design space analysis. The relatively low total sensitivity index values of these parameters underline the relative nature of GSA results: highly influential parameters tend to reduce the sensitivity indices of other parameters.

The result of GSA therefore highlights the importance of prioritizing comparisons between systems that employ different adsorbent materials. However, since the GSA results are not conclusive enough to pinpoint the most influential operational parameters, the three pressure set point parameters (, , and ) have been chosen as the manipulated variables in the design space, considering the possible operational disturbances that may occur during PVSA operation. This selection is also motivated by the fact that previous studies in this area have not explored the interaction between these three parameters and their simultaneous effects on the design space of a PVSA.

* + 1. Design space analysis on PVSA model

In this analysis, , , and were considered as the manipulated variables, while the other process parameters remained at their nominal operating point as reported by Ward and Pini (2022) using a black-box cost optimization method. For each investigated adsorbent material, a total of 4,096 Sobol sampling points is simulated that yield a minimum CO2 purity of 95% and CO2 recovery of 89% (feasibility constraints). The resultant of design spaces of both adsorbents are depicted in Figure 1.

Upon examining the design space visually, it becomes clear that Zeolite-13X exhibits a more constrained design space compared to ZIF-36-FRL, especially for the parameter. This outcome provides a novel perspective on comparing different adsorbents, such as the examined Zeolite-13X and ZIF-36-FRL herein. While Zeolite-13X does indeed offer a lower capture cost compared to ZIF-36-FRL (Table 1), the broader design space of ZIF-36-FRL highlights its enhanced process flexibility. In other words, ZIF-36-FRL's larger design space indicates increased adaptability and robustness in accepting process disturbances and uncertainties in PVSA operation, i.e., the flue gas (feed stream) condition, composition, and flowrate.

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| (a) | (b) |
| **Figure 1.** Feasible points (a) and design space analysis (b) of the PVSA process utilising two distinct adsorbents (Zeolite-13X and ZIF-36-FRL). | |

In line with the NSS definition, an exhaustive search-based optimization algorithm was used to identify the most flexible operating point, representing an operating point with the largest NSS. Surrogate modelling using Gaussian process (GP) was employed to predict the performance index of unexplored points within the design space. The Sobol sampling points were used as the training and test data set to mitigate overfitting of the surrogate model. Compared to artificial neural network (ANN) used in previous study (Sachio et al., 2023), the use of GP opens the possibility of considering the prediction’s uncertainty in future studies. Upon assessing the NSS of several operating points within the design space, it is observed that points with a minimal capture cost do not necessarily exhibit optimal flexibility. It should be highlighted that this observation does not imply that an operating point with a higher capture cost will automatically exhibit superior flexibility. The results, in fact, demonstrate that the candidate most-flexible optimal operating point lays within the design space somewhere between the minimum and maximum capture cost. Details of the largest NSS for each adsorbent and their feasible parameters ranges (calculated as relative deviation percentage from the optimal operating point) are available in Table 1. The feasible range of , , and are also illustrated in

**Table 1.** Feasible ranges of thenominal operating pressure points and the associated KPIs of the PVSA process accounting for operational flexibility (this work) and their comparison against cost-optimal operating points (Literature, Ward and Pini, 2022).

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| **Performance Indicator** | **Zeolite-13X** | | **ZIF-36-FRL** | |
| **Literature** | **This Work** | **Literature** | **This Work** |
| Feasible range of (bar) | 4.72 ± 3.0% | 5.28 ± 4.9% | 5.52 ± 0.0% *(a)* | 6.76 ± 12.5% |
| Feasible range of (bar) | 0.78 ± 2.9% | 0.92 ± 4.7% | 1.00 ± 0.0% *(a)* | 0.78 ± 19.6% |
| Feasible range of (bar) | 0.03 ± 3.0% | 0.03 ± 6.0% | 0.07 ± 0.0% *(a)* | 0.06 ± 18.2% |
| Normalised space size (NSS) | 0.04 × 102 | 0.26 × 102 | 0.00 | 5.61 × 102 |
| CO2 productivity (mol/m3s) | 1.13 | 1.23 | 0.92 | 0.95 |
| Capture cost (USD/tonne) | 41.55 | 44.07 | 54.46 | 54.65 |
| *(a)*The reported nominal operating point (Ward and Pini, 2022) is outside the design space | | | | |

Figure 1(b). These new optimal operating points exhibit a marginal increase in capture cost when compared to the reported operating point in a previous study (Ward and Pini, 2022). It is noted here that the marginal increase in capture cost is compensated by a significant enhancement in process flexibility, as indicated by their corresponding value of NSS. Moreover, it's worth noting that under the proposed operating point, another crucial process performance metric, CO2 productivity, exhibits a subtle improvement. Consequently, for the studied PVSA system and adsorbent materials, the trade-off between an increase in capture cost and the process performance appears to be almost fully advantageous in favor of process flexibility rather than the CO2 productivity.

* 1. Conclusions

In this study, a comprehensive exploration of the design space and operational flexibility of CO2 capture via post-combustion PVSA has been performed. Through a combination of global sensitivity analysis and design space analysis, valuable insights into the complex interaction between process parameters, performance indicators, and the operational landscape of the system have been gathered. The framework began by utilizing GSA to help justify the choice of process parameters for consideration, thereby reducing the dimensionality of the design exercise. Using this choice of parameters, design space analysis was then conducted. This method successfully mapped out the operating parameter combinations yielding feasible results, given the CO2 purity and CO2 recovery constraints. This analysis emphasized the importance of considering not only performance metrics like CO2 productivity, CO2 purity, CO2 recovery, and the capture cost, but also the concept of normalized space size (NSS), which characterizes the flexibility of the operational space around an operating point. Using this technique, the operational robustness of two prominent carbon capture adsorbents, Zeolite-13X and ZIF-36-FRL, has been compared. Despite Zeolite-13X exhibiting a lower capture cost, it was found to possess a more constrained operational flexibility compared to ZIF-36-FRL. This dynamic highlight the complex balance between cost-effectiveness and operational flexibility when selecting optimal adsorbents for CO2 capture applications.

References

A. Ward and R. Pini, 2022, Efficient bayesian optimization of industrial-scale pressure-vacuum swing adsorption processes for CO2 capture, *Industrial & Engineering Chemistry Research*,**61**(36), pp.13650-13668.

E.N. Pistikopoulos, Y. Tian, and R. Bindlish, 2021, Operability and control in process intensification and modular design: Challenges and opportunities, *AIChE Journal* **67**, pp. 1-20.

I.E. Grossmann, B.A. Calfa, and P. Garcia-Herreros, 2014, Evolution of concepts and models for quantifying resiliency and flexibility of chemical processes, *Computers & Chemical Engineering*, **70**, 22-34.

M.D. Wilkew and S. Brown, 2022, Flexible CO2 capture for open-cycle gas turbines via vacuum-pressure swing adsorption: A model-based assessment, *Energy*, **250**, pp.123805.

M. Khurana and S. Farooq, 2016, Adsorbent screening for postcombustion CO2 capture: A method relating equilibrium isotherm characteristics to an optimum vacuum swing adsorption process performance. *Industrial & Engineering Chemistry Research*, **55**, pp. 2447-2460.

P. Kotidis, P. Demis, C.H. Goey, E. Correa, C. McIntosh, S. Trepekli, N. Shah, O.V. Klymenko, and C. Kontoravdi, 2019, Constrained global sensitivity analysis for bioprocess design space identification. *Computers & Chemical Engineering*, **125**, 558-568.

S. Sachio, C. Kontoravdi, and M.M. Papathanasiou, 2023, A model-based approach towards accelerated process development: A case study on chromatography, *Chemical Engineering Research and Design*, **197**, pp. 800-820.