Design and Optimization of a Steam-assisted Adsorption Process for Direct Air Capture

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Abstract

Purification of CO2 from atmospheric air via a steam-assisted temperature-vacuum swing adsorption (S-TVSA) process is a promising approach for efficiently achieving greenhouse gas removal. In this work, we present a computational framework for design and optimization of S-TVSA direct air capture processes by employing detailed numerical simulations, variance-based sensitivity analysis, and black-box optimization. We develop a numerical simulation platform for S-TVSA processes through solution of the governing dynamic material, momentum, and energy balance equations via a finite volume approach. We then use the developed simulator to conduct variance-based sensitivity analysis to quantify the influence of each process operating condition on all key process KPIs, in terms of both first and second order effects. Further, we conduct constrained multi-objective optimization to maximize the efficiency of S-TVSA direct air capture in terms of maximum productivity and minimum energy usage, while achieving high CO2 purity. The results show that the system performance is strongly non-linear with respect to the operating decisions, and that process design by rigorous optimization is central to obtaining near-optimal performance. Further, we identify that under optimal operating conditions, the energy usage of S-TVSA direct air capture is not prohibitively large for wide-scale deployment – but the system productivity is low. This challenges the emerging view of co-locating direct air capture to low-carbon electricity and heat provision without consideration of the available land footprint in the vicinity of such resources. Results recommend that significant future research efforts should be dedicated towards enhancing the productivity of S-TVSA direct air capture processes to enable their deployment at climate-relevant scales.

**Keywords**: Direct air capture, process simulation, process optimization, global sensitivity analysis, temperature-vacuum swing adsorption

* 1. Introduction

Greenhouse gas removal (GGR) is to play a critical role in achieving net-zero carbon emissions by mid-century, in-line with international climate commitments (IEA, 2022). GGR allows handling of residual CO2 emissions for which there are few other decarbonization options, as well as addressing historical emissions. A leading technological solution for providing GGR is the direct removal of CO2 from atmospheric air by chemical separation in a direct air capture (DAC) process (Deutz & Bardow, 2021). Among the available options for DAC, chemical adsorption onto the surface of solid adsorbents in a steam-assisted temperature-vacuum swing adsorption (S-TVSA) process is a promising approach. An S-TVSA process operates in a complex sequence of steps where CO2 is adsorbed from the air at ambient conditions and is subsequently recovered from the sorbent at high purity by heating the sorbent under vacuum using a steam purge.

The design of environmentally effective S-TVSA DAC processes is very challenging owing to several key factors, including the complexity of the process cycle, the presence of multiple conflicting performance targets, and the large number of operating decisions (step durations, operating pressures/temperatures, gas flow rates). To date, S-TVSA processes have been designed according to heuristic guidelines (Stampi Bombelli et al, 2020; Young et al, 2021). Owing to the highly non-linear nature of the system, we can anticipate that such an approach does not yield a near-optimal process. Further, there has been very little published work which aims to quantitatively understand the relationship between the operational decisions and the performance of the system (Young et al, 2023).

In this work, we present the development and application of a mathematical model to enhance the understanding of S-TVSA DAC via a rigorous computational operational assessment. We deploy dynamic numerical process simulation, variance-based sensitivity analysis, and black-box optimization to model, design, and optimize an S-TVSA process with the aim of better understanding the system operation and the reasonable limits of process performance for the current state-of-the-art technology.

* 1. Methods
		1. Temperature-vacuum swing adsorption process

We consider a 5-step steam-assisted temperature-vacuum swing adsorption (S-TVSA) process for purification of CO2 from humid ambient air comprising CO2/N2/H2O using a fixed bed of APDES-NFC adsorbent (Stampi-Bombelli et al, 2020). The cycle steps are 1) adsorption, 2) blowdown, 3) heating, 4) desorption, and 5) pressurisation and cooling (Young et al, 2023). In the adsorption step, ambient air is fed to the column and CO2/H2O are selectively adsorbed onto the surface of the adsorbent. In the blowdown and heating steps, the pressure in the column is reduced using a vacuum pump and the temperature is increased using a heating jacket to remove residual N2 from the system, and to prepare optimal conditions for efficient desorption of CO2 in the following step. In the desorption step, the column is further heated using a direct steam purge under vacuum to collect a high-purity CO2 product. Finally, in the pressurization and cooling step, the column is returned to ambient pressure by introducing air, and the temperature is reduced by flowing cooling water in the column jacket. The sequence of cycle steps is then repeated, with CO2 being captured and recovered in a semi-batch fashion.

* + 1. Process simulation

The dynamics of the S-TVSA process have been simulated using a detailed 1D adsorption column model (Ward & Pini, 2022). The model equations are comprised of material, momentum, and energy balances. The material balance equations describe axially dispersed plug flow of a mixture of ideal gases in a packed bed of adsorbent pellets, as well as the transfer of mass between the gas-phase and the adsorbed-phase in the column. The momentum balance is Darcy’s law for the pressure drop inside a packed-bed column. The energy balance equations describe several important mechanisms of heat transfer, including conduction, convection, heat released by adsorption, and heat exchanged with the heating jacket.

The resulting model equations are a system of partial differential equations (PDEs), which we provide in Table 1. The model equations are first discretized with respect to space by applying a weighted essentially non-oscillatory (WENO) finite volume scheme using *N* = 10 volume elements to yield a system of ordinary differential equations (ODEs) (Haghpanah et al, 2013). The system of ODEs contains 60 equations, describing the evolution over time of pressure, composition, temperature, and adsorbed amount at all locations in the column. The system of ODEs is integrated with respect to time using the variable-order stiff *ode15s* solver in MATLAB. The equations are integrated subject to cyclic boundary conditions representing the 5-step temperature-vacuum swing adsorption process, described in Section 2.1, until the attainment of cyclic steady state (CSS). Once CSS is achieved, the process performance is evaluated in terms of the following key performance indicators (KPIs): CO2 purity, productivity, electrical energy usage, and thermal energy usage.

Table 1. System of non-dimensional material, momentum, and energy balance equations for simulation of adsorption column dynamics.

|  |  |
| --- | --- |
| Overall material balance: | $$\frac{∂\overbar{p}}{∂τ}-\frac{\overbar{p}}{\overbar{T}}\frac{∂\overbar{T}}{∂τ}=-\overbar{T}\frac{∂}{∂Z}\left(\frac{\overbar{p}\overbar{v}}{\overbar{T}}\right)-ψ\overbar{T}\sum\_{i=1}^{n\_{c}}\frac{∂x\_{i}}{∂τ}$$ |
| Component material balance: | $$\frac{∂y\_{i}}{∂τ}+\frac{y\_{i}}{\overbar{p}}\frac{∂\overbar{p}}{∂τ}-\frac{y\_{i}}{\overbar{T}}\frac{∂\overbar{T}}{∂τ}=\frac{1}{Pe}\frac{\overbar{T}}{\overbar{p}}\frac{∂}{∂Z}\left(\frac{\overbar{p}}{\overbar{T}}\frac{∂y\_{i}}{∂Z}\right)-\frac{\overbar{T}}{\overbar{p}}\frac{∂}{∂Z}\left(\frac{y\_{i}\overbar{p}\overbar{v}}{\overbar{T}}\right)-\frac{\overbar{T}}{\overbar{p}}ψ\frac{∂x\_{i}}{∂τ} $$ |
| Solid-phase material balance: | $$\frac{∂x\_{i}}{∂τ}=α\_{i}\left(x\_{i}^{\*}-x\_{i}\right)$$ |
| Pressure drop: | $$-\frac{∂\overbar{p}}{∂Z}=\frac{150}{4r\_{p}^{2}}\left(\frac{1-ϵ}{ϵ}\right)^{2}\frac{v\_{0}L}{p\_{0}}μ\overbar{v}$$ |
| Column energy balance: | $$\frac{∂\overbar{T}}{∂τ}+Ω\_{2}\frac{∂\overbar{p}}{∂τ}=Ω\_{1}\frac{∂^{2}\overbar{T}}{∂Z^{2}}-Ω\_{2}\frac{∂}{∂Z}\left(\overbar{p}\overbar{v}\right)+\sum\_{i=1}^{n\_{c}}\left[\left(σ\_{i}-Ω\_{3}\overbar{T}\right)\frac{∂x\_{i}}{∂τ} \right]-Ω\_{4}\left(\overbar{T}-\overbar{T}\_{w}\right) $$ |
| Wall energy balance: | $$\frac{∂\overbar{T}\_{w}}{∂τ}=Π\_{1}\frac{∂^{2}\overbar{T}\_{w}}{∂Z^{2}}+Π\_{2}\left(\overbar{T}-\overbar{T}\_{w}\right)-Π\_{3}\left(\overbar{T}\_{w}-\overbar{T}\_{a}\right) $$ |

* + 1. Variance-based sensitivity analysis

We have conducted a variance-based sensitivity analysis of the process KPIs (CO2 purity, productivity, electrical energy usage, and thermal energy usage) with respect to all the operational decisions of the S-TVSA process (cycle step durations, operating pressure/temperature, gas flowrates). Sensitivity analysis has been conducted in this work by coupling the process simulator described in Section 2.2 to the SobolGSA software package (Kucherenko, 2013). To apply the SobolGSA software to our system, we have supplied the software with the process KPIs corresponding to 4,096 operating points determined by quasi-random sampling via the Sobol sequence. The bounds applied to the process operating conditions for quasi-random sampling are provided in Table 2.

Table 2. Upper and lower bounds of process operating conditions used for variance-based sensitivity analysis and process optimization.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | $t\_{ads}$ [s] | $t\_{heat}$ [s] | $t\_{des}$ [s] | $p\_{L}$ [bar] | $T\_{H}$ [K] | $v\_{F}$ [m/s] | $v\_{s}$ [m/s] |
| Lower bound: | 1,000 | 500 | 1,000 | 0.05 | 363 | 0.003 | 0.0015 |
| Upper bound: | 15,000 | 1,500 | 40,000 | 0.5 | 373 | 0.01 | 0.005 |

* + 1. Process optimization

The performance of the S-TVSA process has been optimized to maximize the efficiency of the process in terms of maximum productivity and minimum energy usage. The design is conducted subject to the requirement that the CO2 product gas should have a purity of at least 95%. The optimization problem is formulated as a constrained multi-objective optimization with the following form:

$$\min\_{θ}\left[-Pr, W\_{eq}\right]$$

$$s.t. θ\_{L}\leq θ\leq θ\_{U}$$

$$Pu\_{CO\_{2}}\geq 95\%$$

where $Pr$ is the productivity, $W\_{eq}$ is the specific equivalent work, $Pu\_{CO\_{2}}$ is the CO2 product purity, and $θ$is the vector of process operating conditions. $θ\_{L}$and $θ\_{U}$are the lower and upper bounds, respectively, applied to the operating conditions for optimization. The concept of the specific equivalent work has been adopted to combine the electrical and thermal energy usage into a single value for the purposes of conducting multi-objective optimization. The bounds used for optimization are identical to those used for variance-based sensitivity analysis (Section 2.3) and are provided in Table 2. The implicit constraint on the CO2 purity is handled using a penalty function approach. The constrained multi-objective optimization problem has been solved using the non-dominated sorting genetic algorithm II (NSGA-II). We run the algorithm for 100 generations with a population size of 140. The NSGA-II algorithm has been widely applied to the design of adsorption-based processes and has been previously shown to be effective at identifying optimal process performance (Ward & Pini, 2022).

* 1. Results & Discussion
		1. Variance-based sensitivity analysis

Variance-based sensitivity analysis has been conducted to quantify the influence of each process operating condition on each process KPI. The most significant interactions between the operating conditions and the process KPIs are presented in Table 3 $\left(S\geq 0.1\right)$. We can see that the influence of the operating conditions on the process performance is predominantly controlled by first order effects, with at least $≈50\%$ of the oberseved variability in each KPI being attributed to significant first order effects. However, there are also significant second order effects for the CO2 purity, electrical energy usage, and thermal energy usage. We can see that the most important operating conditions for optimizing the process performance are the duration of the adsorption $\left(t\_{ads}\right)$ and desorption $\left(t\_{des}\right)$ steps, and the desorption pressure $\left(p\_{L}\right)$. Particularly, the adsorption step duration and desorption pressure have a significant effect on all the conflicting process KPIs. This result underlines the need to apply rigorous optimization

Table 3. First and second order Sobol indices for the effect of operating conditions on the process KPIs. Only significant effects are presented in the table ($S\geq 0.1$).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **KPI** | CO2 purity | Productivity | Electrical energy | Thermal energy |
| 1st order effects: | $$t\_{ads} \left(0.44\right)$$$$p\_{L} \left(0.23\right)$$ | $$t\_{ads} \left(0.33\right)$$$$t\_{des} \left(0.42\right)$$$$p\_{L} \left(0.11\right)$$ | $$t\_{ads} \left(0.43\right)$$$$p\_{L} \left(0.13\right)$$ | $$t\_{ads} \left(0.19\right)$$$$p\_{L} \left(0.24\right)$$ |
| 2nd order effects: | $$t\_{ads}, p\_{L} \left(0.16\right)$$ |  | $$t\_{ads}, p\_{L} \left(0.15\right)$$ | $$t\_{ads}, p\_{L} \left(0.13\right)$$ |

to such a system design, as the non-linear interactions between the decisions and the process performance will yield heuristic process design extremely challenging, and likely sub-optimal.

* + 1. Process optimization

The performance of the S-TVSA process has been optimized to maximize the system productivity and minimize the energy usage, while achieving a CO2 product purity of at

least 95%, as described in Section 2.4. The resulting Pareto front is presented in Figure 1(a). We can see that the minimum energy usage of the process,$W\_{eq,min}=1.66$ MJ/kg, is relatively low. Such an energy usage is comparable in magnitude to the energy usage of deployments of adsorption-based separations in other energy systems applications (*e.g.,* post-combustion CO2 capture) (Haghpanah et al, 2013). Therefore, despite previous literature having expressed significant concerns over the high energy usage of DAC processes, we find that the process is not prohibitively costly in terms of energy usage. We find that the total energy usage of the process is strongly dominated by thermal energy usage, emphasizing the need for co-location of DAC units to a supply of low-carbon heat to enable environmental effectiveness – such as geothermal heating or industrial waste heat. However, this need for co-location to particular resources is challenged by the very low productivity of the system at optimal operating conditions. We find that the maximum productivity, Prmax $=1.63×10^{-3}$ mol/m3/s, is very low. To contextualize the magnitude of this productivity, deployments of adsorption-based separations to post-combustion carbon capture typically yield a productivity of order $O\left(10^{0}\right)$ mol/m3/s (Ward & Pini, 2022). The productivity of the system is a strong indication of the required land footprint at climate-relevant scales. Therefore, we can anticipate that there is a significant practical conflict between the need to co-locate to specific energy resources to enable environmental effectiveness, and the large land footprint of the system. Development of design approaches to increase the maximum productivity of the system should form a central aspect of future work on S-TVSA processes for DAC to allow for practical deployment at the required scale.



Figure 1. (a) Constrained productivity/energy usage Pareto front for the S-TVSA process. (b) Comparison of process performance by formal optimization (orange circles) and heuristic design guidelines (blue star). The dashed lines in each panel correspond to the corresponding single-objective optima for each objective.

In Figure 1(b), we present a comparison between the Pareto front obtained in this work, and the process performance obtained by applying heuristic design guidelines suggested for S-TVSA processes for DAC in previous work (Stampi-Bombelli et al, 2020). We can see that application of rigorous process optimization using the NSGA-II algorithm has resulted in significantly improved process performance, as compared to the heuristic design. We find that the maximum productivity of the system is increased by +629%, and the minimum energy usage of the process is reduced by -90.2%. As anticipated in Section 3.1, this result underlines the critical need to apply rigorous computational optimization techniques when designing such a strongly non-linear system with multiple conflicting performance targets.

* 1. Conclusions

In conclusion, we have developed a computational simulation, sensitivity analysis, and optimization framework for the design and optimization of steam-assisted adsorption processes applied to direct air capture. We simulate the process performance by numerical solution of the governing material, momentum, and energy balance equations using a high-resolution finite volume scheme. The process simulator is coupled to both variance-based sensitivity analysis and rigorous multi-objective process optimization to allow for a comprehensive assessment of the system design. Sensitivity analysis reveals the strongly non-linear nature of the design problem, highlighting the influence of multiple process operating conditions on several conflicting process KPIs. Through optimization of the system performance, we find that the energy usage of the process is not prohibitively high. However, we find that the productivity of the system is very low, falling several orders of magnitude below benchmark applications of adsorption-based separations in other energy systems applications. This implies that the land footprint of such processes at climate relevant scales will be a significant deployment constraint. We therefore contend that a central aspect of future work on steam-assisted adsorption processes for DAC should be optimization of the adsorbent selection and contactor design to target enhanced system productivity. Finally, future work will aim to conduct techno-economic optimization of the system performance – accounting particularly for practical factors such as pressure drop, heat transfer, and flow non-idealities at large-scales.

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