Introduction
Direct Air Capture (DAC) is the extraction of CO₂ directly from the atmosphere. It is considered an essential technology to keep the temperature rise well below 2°C. Adsorption via solid supported-amine sorbents is a promising method that is being applied on increasingly larger scale. This is a two-step process. First, CO₂ is adsorbed by the porous solid material. Once the sorbent is saturated it requires regeneration. This desorption step is carried out at increased temperature and reduced (partial) pressure (temperature-vacuum swing adsorption or TVSA). In this step, the CO₂ product gas is collected. A complete optimization of such process is not straightforward due to the many operational parameters present in the process. Furthermore, constantly changing ambient conditions generates additional complexity to the system since reaction kinetics, CO₂ equilibrium capacity, water co-adsorption and with these, the energy consumption and system productivity, depend heavily on temperature and humidity. This study provides an optimization framework to determine the optimal operational parameters for a minimum cost of capture (€/ton CO₂) for a TVSA process in a fixed bed reactor. The results are subsequently used to assess the effect of ambient conditions on the viability of such process. In addition, the consequences for process control are evaluated, since the optimal set of operational parameters might also vary.

Model
An accurate numerical model of the complete adsorption-regeneration cycle is essential for process optimization. Furthermore, sorbent characteristics such as adsorption isotherm for CO₂ and H₂O, reaction kinetics, heat transfer properties and mass transfer properties are required. For a more detailed explanation of the adsorption model and its validation, we refer to a previous study [1]. In that study also an initial sensitivity analysis is reported, identifying which of the parameters and choices made have the largest impact on the system performance.

Optimization framework
The goal of the current optimization study is to minimize the costs of capture for a given set of ambient conditions. This requires an analysis of both capital costs as well as operational costs. For the capital costs, the actual equipment cost of a novel (2021) 0.5 tpa TVSA R&D pilot unit, using fixed bed technology with four parallel reactors, is taken and scaled up to a capacity of 10 kton per annum. The operational costs include, among others, energy costs (thermal and electrical), sorbent costs and labour costs.

Figure 1 shows a schematic of the TVSA process (per reactor). In the modelling framework, the temperature and
relative humidity of ambient are fixed (constant) input parameters, which are of course changing when evaluating operation at different weather conditions. The varied parameters (for optimization of the DAC unit operation) included the gas velocity during adsorption, lean sorbent loading, adsorption time, desorption temperature, desorption pressure and purge gas flow rate. Note that lean sorbent loading and adsorption time are equivalent to the working capacity and desorption time. For these parameters, a large set of simulations of the process was carried out and the performance of the process was evaluated by the daily system productivity, the specific energy consumption and the overall cost of capture.

**Figure 1:** A schematic of a TVSA process and its operational parameters are shown. These parameters are gas flow rate during adsorption, adsorption time, desorption time, desorption temperature, desorption pressure and purge gas flow rate. Adsorption and desorption time can be substituted with lean sorbent loading and working capacity.

**Results**

The typical result of the simulations, using many combinations of various operational parameters, is shown in Figure 2. This gives a clear trade-off between system productivity and energy requirement, where, in an ideal world, the operation point would be somewhere in the ‘Utopia’ region. Intuitively, the point with the minimum costs of capture will be somewhere on the pareto front, which is indicated with the black line. Furthermore, the working capacity of each simulation is presented. In general, a low working capacity gives a high productivity with high energy consumption and vice versa for a high working capacity. This is due to the amount of temperature swings that is required to capture the same amount of CO₂. The minimum costs of capture is then determined via an economic analysis of the points on the pareto front.

**Figure 2:** Combinations of productivity and energy duty for different sets of operational parameters, the black line indicates the Pareto front. The productivity is down-scaled to a kg-scale TSVA reactor.
This optimization analysis is performed for three sets of ambient conditions. These are labelled ‘cold’, ‘moderate’ and ‘hot’ with a temperature and relative humidity of respectively 10°C and 80%, 20°C and 50%, and 30°C and 30%. Figure 3 shows the total costs of capture as well as the distribution over the cost categories. It is clear that ambient conditions make a significant difference with a total cost of capture of €686/ton for the ‘cold’ scenario and €516/ton for the ‘hot’ scenario. Especially the sorbent costs and thermal energy costs are higher for the ‘cold’ scenario. The former is due to the lower productivity, since the sorbent lifetime is assumed unrelated to operation conditions. The latter is mostly due to water co-adsorption, since the affinity of the sorbent towards water rapidly increases at these conditions.

Future work will use this optimization framework to assess the viability of DAC using weather data of several locations. Furthermore, the implications on process operations will be evaluated. For example, the adsorption time decreases from 165 min to 90 min from the ‘cold’ scenario to the ‘hot’ scenario. Finally, sensitivity analyses are envisioned to assess the influence of uncertain input parameters or parameters that are sensitive to fluctuation.

Figure 3: Costs of capture for three different weather conditions: cold (10°C/80% RH), moderate (20°C/50% RH) and hot (30°C/30% RH)

**Keywords:** Direct Air Capture; Supported-amine sorbents; Process optimization; Temperature-vacuum swing adsorption