Abstract

Climate change is one of the major challenges of the twenty-first century and requires rapid reductions in greenhouse gas emissions. Although the transition from fossil fuels to renewable energy is essential, several industrial sectors, particularly cement production, generate unavoidable process-related CO_2 emissions. Carbon capture is therefore necessary to decarbonize hard-to-abate industries. Among available technologies, adsorption is promising for post-combustion capture because of its moderate energy demand, limited environmental impact, and applicability over a wide range of CO_2 concentrations.

This thesis evaluates vacuum pressure swing adsorption (VPSA) for CO_2 capture through an integrated approach combining experimental characterization, pilot-scale testing, detailed modeling, process optimization, and industrial-scale extrapolation. A fully instrumented laboratory VPSA pilot comprising three 1.1 L adsorption columns was designed and built to perform breakthrough experiments and two- or three-bed cyclic tests while varying pressure levels, step durations, feed flow rate and composition, and reflux conditions.

Three adsorbents were investigated: benchmark zeolite 13X and two aluminum-based metal-organic frameworks, MIL-160(Al) and MIL-120(Al), selected within the MOF4AIR project. After adsorption-isotherm and breakthrough characterization, the materials were tested in a three-bed, six-step VPSA cycle operated at a practical evacuation pressure of 0.1 bar. At 1 Nm^3/h with a 15/85 CO_2/N_2 feed, both MOFs achieved CO_2 purity and recovery above 90%, whereas zeolite 13X reached 79.7% purity and 85% recovery. These results highlight the limitations of conventional adsorbent screening indicators and demonstrate the importance of kilogram-scale cyclic testing.

A one-dimensional adsorption-bed model was developed and validated against breakthrough and cyclic experiments, reproducing purity, recovery, pressure, flow rate, and concentration profiles. Model analysis identified adsorption-isotherm shape, heat of adsorption, and mass-transfer kinetics as key performance determinants. Simulations covering 5–15% CO_2 and feed flow rates of 0.5–1.5 Nm^3/h showed that MIL-160(Al) provided the lowest energy consumption, especially for dilute feeds, while MIL-120(Al) achieved comparable productivity with intermediate energy demand.

Finally, the validated simulation models were extrapolated to industrial scale by studying a hybrid unit composed of a VPSA unit as the first stage and a cryogenic carbon purification unit (CPU) as the second stage. This configuration was used to produce a high-purity CO_2 stream suitable for transport or utilization, with a final purity higher than 99.999%. The hybrid unit was studied for flue gas containing 5 to 20% CO_2 and a flow rate of 70,000 Nm3/h, by testing the three adsorbents studied in this thesis and two VPSA cycles: a 2-bed 5-step cycle, used as a reference cycle for VPSA, and a 3-bed 6-step cycle. The results showed that the 3-bed 6-step cycle can reduce energy consumption compared with the 2-bed 5-step cycle, especially for diluted flue gas. However, the economic optimum depends strongly on the feed CO_2 concentration, electricity price, and carbon tax, since the process complexity of the 3-bed cycle and the production cost of MOFs can make some configurations uneconomical. Overall, this work demonstrates that MOFs, especially MIL-160(Al), are promising adsorbents for VPSA-based CO_2 capture, and that the combination of pilot-scale experiments, validated simulation, and techno-economic optimization is an efficient methodology for the development of adsorption processes for industrial CO_2 capture.