CO_2 CAPTURE BY PRESSURE SWING ADSORPTION USING MOF: FROM THE LAB SCALE TO THE INDUSTRIAL SCALE EVALUATION

G. De Weireld[(a)], N. Heymans[(a)], A. Henrotin[(a)], G. Mouchaham[(b)], F. Nouar[(b)] C. Serre[(b)], N. Garcia-Moncada[(c)], M. Daturi[(c)], K. Amro[(d)], F. Martin[(d)], J. Casaban[(e)], S. Krishnamurthy[(f)], R. Blom[(f)], A. Wakaa[(g)]

[(a)]University of Mons, Belgium; [(b)]Institut des Matériaux Poreux de Paris, ESPCI, CNRS Paris, France; [(c)]Normandie University, CNRS-Caen, France; [(d)]SIKEMIA, Montpellier, France; [(e)]MOFTECH, Belfast, UK; [(f)]SINTEF Industry, Norway; [(g)]TCM, Mongstad, Norway

Corresponding author's e-mail address: guy.deweireld@umons.ac.be

Keywords: Post-combustion capture, adsorption, international R&D activities including pilot activities

ABSTRACT

At the present time, power generation and carbon-intensive industries (steel plants, cement plants, lime plants, waste incinerators…) are responsible of a large part of anthropogenic CO_2 emissions to the atmosphere and then contribute to global warming. Thus, the reduction of CO_2 emissions from industries is crucial. Since more than 25 years, CO_2 capture techniques were investigated to envisage CO_2 storage and chemical reuse. Absorption-regeneration amine-based process, the actual benchmark solution, suffers from high energy penalties and high environmental impacts. Thus, this makes of adsorption-based processes a promising alternative thanks to the improvement of process design and the development of new materials. Among the latter, Metal Organic Frameworks (MOFs) appear as promising materials for both gas separation and purification. However, the performances of these hybrid materials in carbon capture technologies have not been fully evaluated for adsorption processes at large scale in real industrial conditions, while fine-tuning is still needed.

In this context, the H2020-MOF4AIR project (https://www.mof4air.eu/) purposes to develop and demonstrate TRL6-reliable solution adsorption technology using MOF-based sorbents meeting end users' needs. The project has started in July 2019 and was initially planned to last 4 years. It should be extended by one year in order to complete all the on-site tests.14 partners are involved in the project, to develop the process of CO_2 capture with MOFs from the material synthesis to an industrial pilot scale.

After a screening of (27) samples at the gram-scale (a set of seven MOF samples have been selected and synthesized at the scale of few hundred grams. Various binders and binder loadings were studied to obtain the target crush strength of 20 N (without a significant sacrifice of CO_2 uptake). All samples have been fully characterized, and their quality has been verified. The stability of samples under a gas flow and conditions simulating their use in the industrial process (in presence of water, NO_X, SO_2) has been checked. The, different kinds of measurements have been carried out: (i) pure CO_2 and N_2 adsorption isotherm experimental measurements; (ii) influence of water on MOFs' CO_2 adsorption performance investigated by experimental measurements (different concentration of water have been tested 0.2%, 2%, 4%); (iii) stability in presence of contaminants was investigated in the dedicated *operando* IR/MS/NOx analyzer system under real conditions and (iv) breakthrough curve measurements.

That led to the identification of the best candidates and especially to the selection of shaping conditions to produce them.

MIL-160(Al) (fumarate-based MOF family) [1-2] was the first MOF chosen. MIL-160(Al) synthesis in powder form by mecanosynthesis was successfully upscaled to 5 kg quantities without any detrimental effect on the sorption properties (*i.e.* surface area and CO_2 uptake). Afterwards, the shaping methodologies (extrusion techniques) were successfully upscaled to produce 3 kg of MIL-160(Al) in 2 mm pellets form with suitable crush strength (>20 N).

MIL-160(Al) has been used in lab-scale pilot (3 columns of 1.1 L each). Based on the results obtained with the laboratory Vacuum Pressure Swing Adsorption (VPSA) pilot scale, a complete simulation of VPSA process using the Linear Driving Force (LDF) model and IAST was performed on Aspen Adsorption® software to evaluate the performances of a VPSA process with MIL-160(Al) on an industrial TRL6 pilot (100 Nm^3/h of flue gas). The flue gas specification (14.7%mol of CO_2 in wet conditions) comes from a fluid catalytic cracking system in Technology Centre Mongstad pilot plant which is one of the three demonstration sites of the MOF4AIR project. Three different configurations were simulated for this study: a 2-stage VPSA process with 2 columns (Skarstrom cycle with 5 steps including pressure equalization), and a 1-stage VPSA process with 3 columns (with 5 or 6 steps including rinse and purge) [3-5]. These configurations have been investigated and optimized to study the influence of operating conditions and reach the targets of such a process: CO_2 purity of 95% and recovery of 90% with the lowest energy consumption (below 0.14 electric kWh/kgCO_2 captured). To reach at same time CO_2 purity of 95% and recovery of 95%, a 2-stage VPSA process with 2 columns is need with important energy consummation increase.

After a first optimization of both processes based on a design of experiments (adsorption time, purge time, purge flowrate, rinse time, rinse flowrate, pressure levels, column volume, L/D ratio, *etc.*), the best results were obtained with the 1-stage VPSA process with 6 steps where the targets were reached with a lower energy consumption than the 5 steps configuration for which the targets are not reached. These results confirm the promising potential of MIL-160(Al) for the use on an industrial scale.

The results are under verification on the pilot unit with 3 columns of 41 L each fill with shaped MIL-160(Al) produced at the scale of 60 kg. Pilot have been installed on the Technology Centre Mongstad in early February 2023 to treat a fraction of flue gas coming from fluid catalytic cracking (FCC) unit.

REFERENCES

[1] A. Cadiau et al., “Design of Hydrophilic Metal Organic Framework Water Adsorbents for Heat Reallocation,” Adv. Mater., vol. 27, no. 32, pp. 4775–4780, Aug. 2015.

[2] D. Damasceno Borges et al., “Gas Adsorption and Separation by the Al-Based Metal–Organic Framework MIL-160,” J. Phys. Chem. C, vol. 121, no. 48, pp. 26822–26832, Dec. 2017.

[3] C. A. Grande, “Advances in Pressure Swing Adsorption for Gas Separation,” ISRN Chem. Eng., vol. 2012, pp. 1–13, 2012.

[4] L. Wang, Z. Liu, P. Li, J. Wang, and J. Yu, “CO_2 capture from flue gas by two successive VPSA units using 13XAPG,” Adsorption, vol. 18, no. 5–6, pp. 445–459, 2012.

[5] S. Krishnamurthy et al, “Post combustion carbon capture with supported amine sorbents: From adsorbent characterization to process simulation and optimization,” Chem. Eng. J., vol. 406, p. 127121, 2021.

ACKNOWLEDGEMENT

This project has received funding from the European Union’s Horizon 2020 research and innovation program under grant agreement No. 831975 (MOF4AIR project).