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MOF4AIR project (H2020): Metal Organic Frameworks for carbon dioxide Adsorption processes in power production and energy Intensive industries

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Abstract

Power generation and carbon-intensive industries are responsible of a large share of the anthropogenic CO₂ emissions into the atmosphere and play an important role in the greenhouse effect and global warming. Shifting towards a low-carbon economy needs, in addition to reductions at source and use of renewable energy, cost-effective novel carbon capture solution to be conceived, tested and deployed. Current mature solutions either suffer from elevated energy penalties and environmental impacts like in amines-based adsorption and lot of other solutions simply cannot offer sufficient performances. Adsorption processes are promising alternatives for capturing CO₂ from power plants and other energy intensive industries as cement, steel or petrochemical industries. In this regard, Metal Organic Frameworks (MOFs) are a widely studied class of porous adsorbents (recent crystallized porous materials) that offers tremendous potential, owing to their large CO₂ adsorption capacity and high CO₂ affinity (MOFs can be tuned to create specific adsorption sites associated for trapping CO₂). However, the performances of MOF-based carbon capture technologies have not been fully evaluated with flue gases on industrial sites.

In this context, the MOF4AIR project (H2020 LC-SC3-NZE-1-2018) gathers 14 partners from 8 countries and aims to develop, validate and demonstrate the performances of MOF-based CO₂ capture technologies (VPSA and MBTSA) in power plants and energy intensive industries. The developed capture solutions will be demonstrated in real environment (TRL 6) on 3 demonstration sites. MOF4AIR aims to foster the uptake of CCUS technologies by providing a TRL6-reliable solution matching end users' needs. The solutions developed will be highly replicable thanks to the consideration of a wide range of carbon intensive sectors and clusters.

Keywords: adsorption processes, MOF, pilot units, CO₂ capture

1. Introduction

Now, it is currently commonly assessed that greenhouse gases (GHG) emissions are major challenging environmental issues and that carbon dioxide is the largest anthropogenic source of GHG.

Based on economic and environmental considerations, it is required to apply efficient and suitable technologies for the separation and recovery of industrial CO₂ with low operating costs and energy consumption. In this perspective, different technologies can be considered according to the CO₂ content of the industrial flue gas to be treated.

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At present, the only carbon capture technology at the highest level of maturity (TRL9) is the post-combustion CO₂ capture using amine-based solvents in an absorption/regeneration process [1]. Unfortunately, such process involves a high energy consumption (e.g. 3.5 GJ/tCO₂ captured in monoethanolamine (MEA) 30 wt.% which is the reference case, to 2.2 GJ/tCO₂ captured for innovative blends amines/demixing amine solvents [2] using alternatives configurations [3]), related mainly to the solvent regeneration step and environmental impact due to the daily amines consumption and degradation [4]. In order to reduce the energy consumption, the environmental impact and the operating cost of CO₂ capture processes, other technologies are needed.

One of the most promising alternative technologies for CO₂ capture is based on the adsorption process using solid sorbents with the most important advantage being the energy penalty reduction during the regeneration step [5, 6].

Adsorption processes are well-established and used at industrial level for air separation (production of O₂ or N₂), gas drying, and hydrogen purification [7]. In all these processes, the adsorbent material is used in a cyclic mode, switching between adsorption and desorption steps, where adsorbent regeneration is performed either by a change in pressure (Pressure Swing Adsorption (PSA) or Vacuum Pressure Swing Adsorption (VPSA)) or by a change in temperature (Temperature Swing Adsorption (TSA)) [7].

In several detailed reviews on CO₂ capture by adsorption [8], it can be understood that developing a suitable CO₂ capture adsorbent should satisfy (1) high CO₂ adsorption, (2) high CO₂ selectivity, (3) low heat for regeneration, (4) fast kinetics, (5) thermal, chemical, and mechanical stabilities under extensive cycling capacity and (6) obviously low cost green synthesis procedures.

Next to a lot of VPSA studies where it is difficult to reach targeted CO₂ recovery (at least 90%) and purity (95%) without using two VPSA units, TSA could be a credible alternative [9]. However, the main issue with conventional TSA processes, where the adsorbent is packed in large columns, is the long cycle time associated to the heating (by hot gas [e.g. water vapour or nitrogen]) and cooling steps, which can take between several tens of minutes and several hours [10]. One interesting way to overcome this issue and improving the efficiency (increasing the productivity by a drastic decrease of the cycle time), is using the Moving Bed Temperature Swing Adsorption (MBTSA) concept [11] in which the adsorbent flows through different sections, always running at the same operational conditions for their specific purpose: adsorption, desorption or cooling. The great interest of MBTSA is that moving adsorbent enables a fast heat transfer and increases the retention time of the solid into the column ensuring that a CO₂ equilibrium capacity higher than 90% is achieved [12]. Once the solid cannot adsorb more CO₂, it must be regenerated.

Hybrid porous solids represent a new class of crystalline porous materials, commonly named Metal–Organic Frameworks (MOFs) or Porous Coordination Polymers (PCPs). These materials are highly tunable and offer quasi-infinite possibilities of crystal structures and chemical compositions, which can be easily tuned to offer an extremely broad range of pore sizes/accessible surface areas and diverse nature of specific adsorption sites which, associated with a low framework density, make them attractive candidates for trapping gaseous species [13]. The capture of CO₂ from flue gas in post-combustion processes using MOFs has been extensively studied [14–18], especially concerning the materials characterisation and associated thermodynamics data (CO₂ uptake, selectivity and/or heat of adsorption). However, the performances of MOF-based carbon capture technologies have not been fully evaluated with flue gases on industrial sites.

In this context, the MOF4AIR project (H2020 LC-SC3-NZE-1-2018) gathers 14 partners from 8 countries and aims to develop, validate and demonstrate the performances of MOF-based CO₂ capture technologies in power plants and energy intensive industries (<https://www.mof4air.eu>). The MOF4AIR carbon capture system combines these promising sorbents with two different advanced capture processes: VPSA and MBTSA that are highly promising for carbon capture. The developed capture solutions will be demonstrated in real environment (TRL 6) on 3 demonstration sites. MOF4AIR aims to foster the uptake of CCUS technologies by providing a TRL6-reliable solution matching end users' needs. The solutions developed will be highly replicable thanks to the consideration of a wide range of carbon intensive sectors and clusters.

2. Overall concept of the project

The main concerns on MOF-based carbon capture are two-folds. Regarding the MOF material used, the main question is to know if there is any potential degradation when exposed to the different components of the post flue gases. And, regarding the adsorption processes, various steps to achieve high efficiency carbon capture are still needed

in order to decrease the capture costs and to reach an overall energy penalty that would be acceptable for the carbon intensive industries.

The overall concept of MOF4AIR is thus to combine carbon capture processes: VPSA and MBTSA, and innovative highly efficient MOFs in a tailored carbon capture solution adapted to energy intensive industries and their varying composition of off-gases including contaminants.

2.1. Decarbonisation of industrial processes

CO₂ can be captured in power plants and other energy intensive industries mainly in three configurations: precombustion, post-combustion, and oxy-combustion and the MOF-based adsorption capture systems investigated in MOF4AIR can be implemented in all these configurations [14]. As the post-combustion configuration is the only one that can be easily retrofitted to existing plants, including low adaptation costs, it is seen by MOF4AIR partners as the most relevant to focus on. The post combustion off-gas usually contains many different gases and particulate matter: CO₂ (usually 3-33% depending on the process producing the flue gas), N₂ (typically more than two-thirds of the flue gas), particulate matter, sulfuric oxides (SO_x), and other nitrogen oxides (NO_x), carbon monoxide (CO) and water (H₂O) that are released into the atmosphere. Some of these components can lead to corrosion that can hamper the performance of the capture system and that can even deteriorate the transport and storage/utilization systems. MOF4AIR will thus review a wide range of conditions and gas concentration in lab and thanks to the different end-users.

MOF4AIR will address the following issues when it comes to MOFs and capture processes: the potential degradation of MOFs when exposed to the different components of the flue gases and the energy required by the capture process. The impact of contaminants on the stability of these MOFs has in some cases been evaluated [19, 20]. However, the resistance of some promising MOFs towards several contaminants is still unclear, particularly when mixtures of several contaminants are considered (e.g. SO₂ or NO_x combined with water). In addition, to our knowledge, no testing under ‘real conditions’ (i.e. with water and selected contaminants) using larger scale pilot systems together with repetitive cycling as well as an optimization of the process conditions has been reported to date.

2.2. MOF-based carbon capture

MOFs are hybrid porous solids representing a new class of crystallized porous materials (Fig. 1). They combine inorganic and organic moieties and build 3D networks exclusively through strong bonds. The inorganic parts (usually labeled ‘bricks’ or Secondary Building Units (SBU)) can be simple polyhedra, clusters, chains layers or even inorganic 3D arrangements; the organic linkers are mainly anionic oxygens (polycarboxylates, polyphosphonates) and nitrogens (imidazolates, polypyrazolates, polytetrazolates) donors. These materials have well crystalline nanoporous or mesoporous frameworks.

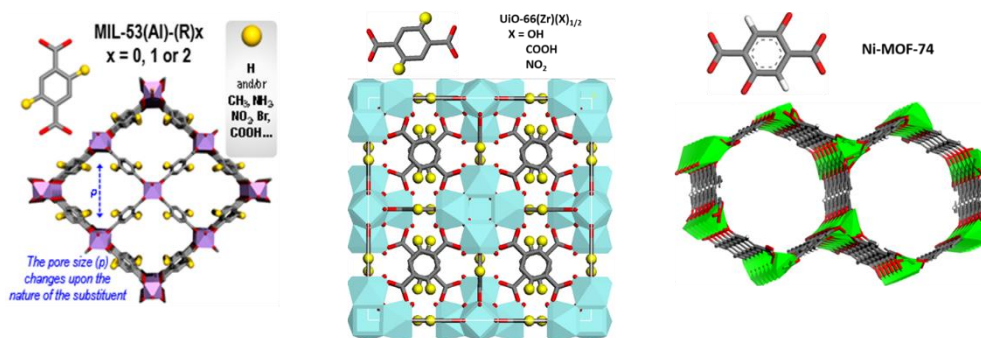


Fig.1. Some examples of potential MOFs structure for CO₂ capture.

These porous materials could have large surface area values typically ranging from few hundreds to 7,000 m²/g, thus exceeding those of traditional porous materials such as zeolites and carbons. Porous solids like zeolites and activated carbons are usually employed in adsorption processes for gas purification and/or separation. However, in CO₂ capture context, these materials are difficult to regenerate without heating, have decreasing of adsorption performances due to moisture (zeolites) and/or exhibit poor selectivity (often below activated carbons), which induces a low productivity and high energetic costs [21].

MOFs represent alternative solids for these applications and area potential technological breakthrough with respect to the conventional materials used so far. Their considerable advantage, compared to zeolites, is to accept in their skeleton almost all the cations of the periodic table. Their combination with the huge number of possible organic linkers offers quasi-infinite possibilities of crystal structures (flexible or rigid character) and chemical compositions (metal, ligand, functional group, which can be easily tuned by playing both on the nature and coordination of the metal centres (Lewis acidity) and the length and/or the functionalization of the organic linker). Consequently, they offer an extremely broad range of tunable pore sizes, polarity and specific surface areas which, associate to a low framework density, make them attractive candidates for trapping gaseous species [13].

Indeed, their structures can be adjusted to capture preferably CO₂ molecules rather than other components in combustion exhaust gases (e.g. N₂) while their moderate hydrophilic character allows even in some cases an increase of selectivity for CO₂ towards N₂ in the presence of a reasonable amount of moisture [19,22]. Moreover, the thermal and chemical stabilities of many MOFs have made them more serious candidates for CO₂ capture. Their variability offers tailoring possibilities to the capture processes foreseen in MOF4AIR thus creating an optimised MOF/capture process couple.

To achieve a low energy penalty for the capture solution, MOF4AIR will aim for materials stable in operating conditions, offering the best compromise between a high selectivity, a high working capacity (difference between the amount adsorbed under the feed condition and the residual amount adsorbed at the end of the purge step) and a low regeneration energy. The cost of the materials as well as their environmental impact were also considered in the selection of the foreseen materials.

Although different structures of MOFs have been studied for CO₂ capture, it has been confined to a few grams and mostly in powder form. One challenge is thus to synthesize them in large batches and formulate them into useable spheres/pellets. MOFs are indeed first produced in powder assembling the metal ions or clusters of metal ions with the organic ligands and then shaped into larger bodies like pellets or beads. Common ways to produce these powdered materials are:

- hydro-/solvo-thermal synthesis: solution synthesis either in batch or continuous tubular reactors [23,24,25];
- mechanosynthesis: chemical synthesis straight from starting materials in solid form by direct adsorption of mechanical energy; avoiding or dramatically reducing the use of toxic and harmful solvents;
- synthesis optimisation and scale-up of non-commercially available ligands.

Once the powder is obtained, the powder can be shaped into pellets/beads using different processes:

- extrusion: formation of tubular shaped beads by extruding a MOF/binder/water paste [26];
- wet granulation [27]: formation of spherical MOF particles by agglomeration with solvent and binder;
- alginate bead formation: formation of well-shaped spherical MOF beads by spraying/dripping a MOF/alginate/water slurry into a Ca²⁺ containing water solution [28].

The cost of production of the foreseen materials depends on raw material sources, availability and existing (or not) synthesis process. According to previous experiences and estimations, current MOFs can be produced in a pilot plant at an approximate cost of 17 €/kg, which is high respect to inefficient carbon, but much cheaper than zeolites. Scaled up production is supposed to decrease costs. The MOFs considered in MOF4AIR can be produced by the partners as they have both the needed patents and the means.

2.3. Enhanced capture processes

MOF4AIR will fine-tune 2 different capture processes that are highly promising for carbon capture in combination with MOFs:

- one pressure swing adsorption process (PSA): Vacuum Pressure Swing Adsorption (VPSA);
- one temperature swing adsorption process (TSA): Moving Bed Temperature Swing Adsorption (MBTSA).

These capture processes are distinguishable by their regeneration process: VPSA uses vacuum to regenerate the adsorbent, while MBTSA uses heating.

PSA is a well-established technology and is based on a physical binding of gas molecules to a solid adsorbent material. The attractive forces between the gas molecules and the adsorbent material depend on the gas component, the type of adsorbent material, the partial pressure of the gas component and the operating temperature.

The PSA process uses the effect of alternating pressure/partial pressure to perform adsorption and desorption. PSA process thus works between two pressure levels. Adsorption is carried out at high pressure to increase the partial pressure of the undesired gas, here CO_2 , and desorption, or regeneration, takes place at low pressure to reduce the residual loading of the undesired component as much as possible. If the desorption is achieved by the aid of vacuum, the process is called Vacuum Pressure Swing Adsorption (VPSA). With its low-pressure adsorption step (1-1.25 bars), VPSA avoids the high compression (around 5-6 bars in PSA) of flue gas. Moreover, the working capacity of the adsorbent is higher in this case, which ensures better performance of the adsorption process. The VPSA process is an adsorption/desorption cycle containing adsorption, rinse, blowdown, evacuation, purge, and product pressurization (Fig. 2).

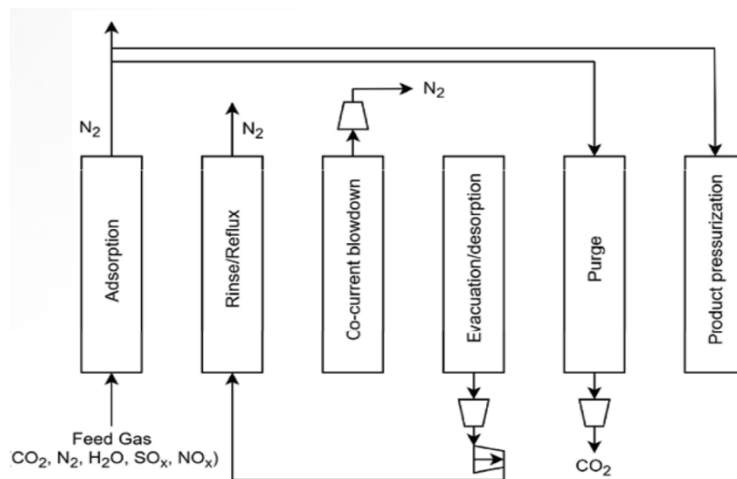


Fig. 2. Example of 6-step/two beds VPSA unit for CO_2 capture from flue gas

In an actual process, the steps are carried out for multiple cycles (typically >50 cycles) and to ensure continuous processing of the feed, multiple columns are used. Several studies with different configurations show the feasibility of CO_2 capture with VPSA processes essentially by simulation and sometimes with validation at lab scale [5, 6, 29, 30, 31]. MOF4AIR partners develop a model that will be used to optimize the variables (e.g. number of beds (2 or 3), number of steps (4, 5, 6, 9), the number of VPSA units (1 or 2), pressure levels, duration of the adsorption/regeneration cycle) necessary (Fig. 3) to obtain the maximum performance for a given application by minimizing the energy consumption and the footprint. The system will be validated in relevant environment (TRL 5) and finally, the whole system will be fine-tuned and demonstrated on 3 different sites (TRL6).

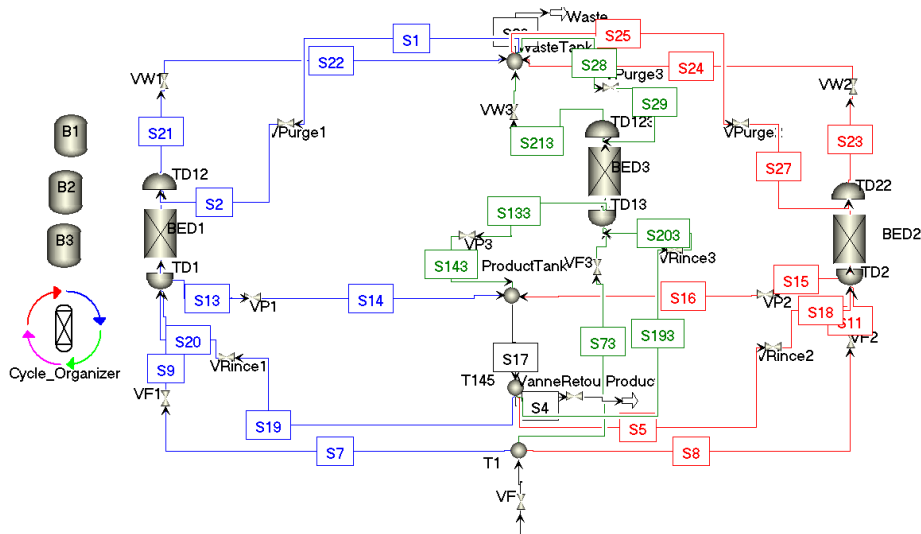


Fig. 3. ASPEN Plus flowsheet example of 3 beds CO₂/N₂ VPSA process

For the MBTSA process, adsorbent shaped spheres with diameters of 0.3-0.7 mm (versus 1-3 mm for VPSA) with good flow characteristics have to be used. In the process, the flue gas is stripped counter-currently in the "adsorption" section in contact with a descending solid adsorbent (Fig. 4) [32]. The great advantage of MBTSA is that moving adsorbent enables a fast heat transfer and increases the retention time of the solid in the column to ensure that CO₂ equilibrium capacity >90% is achieved. Once the solid cannot adsorb more CO₂ it should be regenerated. In the MBTSA process, regeneration and consequent recovery of CO₂ is performed at higher temperatures. By gravity, the adsorbent enters into the regeneration zone composed by an initial "pre-heating section" where the heat of the hot adsorbent leaving the regenerator is used to heat the adsorbent powder leaving the adsorption section, thus reducing the need for external thermal heat significantly [33].

The regeneration and cooling sections of the MBTSA system consist of heat exchangers that use different fluids: water in pre-heating, pre-cooling and cooling stages and hot flue gas or low-grade steam if available in the regeneration section. The vertical alignment of stripping and regeneration sections results in a significant reduction of the footprint of the capture plant. Spherical particles (0.3-0.7 mm diameter) significantly reduce the risk of attrition and system clogging, reason why generation of fines due to attrition should also be removed from the system. Such removal can be done using a filter prior or after the conveyor belt. The mathematical model developed in MOF4AIR will enable the optimization of all the process variables to obtain maximum performance for a given application. Fine-tuned system will be validated in relevant environment (TRL5). Combination of VPSA and MBTSA with adsorbents selected for their high CO₂ capacities and fast adsorption/desorption kinetics will allow efficient operation of the capture process. The other components of the capture process (e.g. filters, flue gas desulphurization unit, connectors, heaters and compressors) will be studied in the proposal as well.

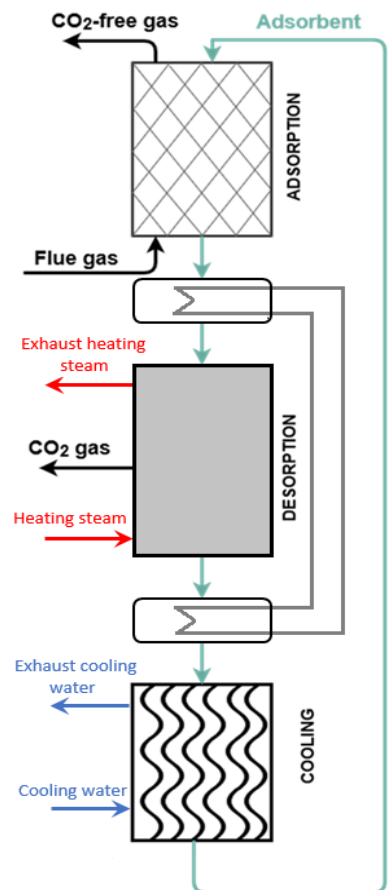


Fig.4. MBTSA unit for CO₂ capture from flue gas.

2.4. Process optimization and advanced CCU/CCS chains

The MOF4AIR consortium considers their performant capture solution as one brick of the global carbon chain. As compressing CO₂ at high CO₂ purity is needed for transport and utilization or storage and requires the use of energy, MOF4AIR will study the better integration of adsorption process with conventionally used Compression and Purification Unit (CPU). Compared to conventionally designed sorption systems consisting in a VPSA/MBTSA unit followed by CO₂ compression, improved overall performance (i.e. better recovery-purity front for given productivity) can be achieved by integrating the adsorption unit (either VPSA or MBTSA) with the CO₂ CPU. The idea here is to combine a process which is suitable for achieving high CO₂ purity but rather low CO₂ recovery (i.e. the CPU) with a sorption process tuned to achieve high CO₂ recovery with medium CO₂ purity.

In the MOF4AIR project, in addition to the conventional process optimization of stand-alone PSA/TSA processes, integrated sorption-CPU process configurations will be compared and systematically optimized from the techno-economic point of view using *ad hoc* numerical methods for the optimization of flowsheets [34] and adsorption cycles [35].

In addition to the key process design and operating variables (vessel/reactor sizes, pressures, temperatures, mass flow rates), also the cycle steps of the adsorption process will be optimized taking into account the integration with the CPU unit.

MOF4AIR will review the requirements of the use of their solutions in the global CCS and CCU chains.

3. Objectives of the MOF4AIR project

MOF4AIR overall objective will be achieved through 6 clear, measurable, realistic and achievable Specific Objectives (SOs).

3.1. SO n°1: Qualify and validate the most promising MOF materials or adsorption-based carbon capture

A list of 21 MOFs compositions under 8 structures have been identified for carbon capture applications. This list was established considering different parameters such as chemical stability, overall performance (selectivity and capacity), suitability to industrial processes and cost-effectiveness. MOF4AIR focuses on post-combustion processes where the CO₂ capture process can be integrated with the existing plant. In such processes, the CO₂ will be removed from nitrogen matrix containing impurities that can deteriorate the MOF materials: contaminants. As the current lack of visibility on the behaviour of the selected materials in relevant environment is a barrier for the progress of MOF-based CO₂ capture, MOF4AIR will bring an insight on the operational relevance of these materials particularly in the presence of humidity and diverse contaminants. MOF4AIR will test these materials and assess their performances in presence of such contaminants. These activities will include the scale up and shaping at large scale by various techniques as extrusion, wet granulation or alginate bead formation to minimize pressure drop inside of adsorption units.

3.2. SO n°2: Fine-tune adsorption processes for high performance MOFs

Carbon capture can entail high operational costs and difficulties to cope with operational variability. MOF4AIR will thus optimize the operational mode of selected adsorption systems, tailoring them to the selected MOFs and to the industrial application. The main improvement parameters foreseen are the duration of the adsorption/regeneration cycle (fast cycles are required), the operating pressure/temperature and the pressure/temperature swings throughout the cycle.

MOF4AIR will result in optimised systems guaranteeing high CO₂ capture performances (capture efficiency and CO₂ purity) with the highest productivity while coping with the variability of flue gas outputs. MOF4AIR partners will study two carbon capture processes (VPSA and MBTSA), validate both of them in relevant environment (TRL5) and will bring VPSA to demonstration in relevant environment (TRL6).

3.3. SO n°3: Increase the cost effectiveness of CCUS and decrease its energy penalty

The costs connected to the high energy penalty of carbon capture solutions is one of the main obstacles of a wider uptake of CCUS. This energy penalty depends on the industrial application targeted and on the capture technology used. As amine technologies are the most widely used carbon capture solutions due to the maturity level, they are often used as a benchmark to assess the performances of new carbon capture solutions. Depending on the sector/sub sector targeted, amines can reach an energy penalty of 15%.

MOF4AIR aims to bring the SPECCA (Specific Primary Energy for CO₂ Avoided) below 2.5 GJ_{LHV}/tCO₂ for all sectors and subsectors. To achieve this, the studied MOF-based capture technologies will be optimized from a techno-economic perspective. MOF4AIR will consider the integration of these technologies with the CO₂ Compression and Purification Unit (CPU) that is needed for the global CCS or CCU chain. This will indeed allow to achieve high CO₂ capture efficiency and purity (with purities even >99.9%) with energy penalty and costs lower than ever reported in the literature up to now for current sorbent systems.

With conventional technology the cost per ton of CO₂ avoided amount ranges typically from 40 to 60 €/tCO₂ for coal and lignite plants and up to 100 €/tCO₂ for natural gas-fired plants. A substantial reduction to 25 €/tCO₂ is expected, due to savings in capital as well as operating costs (no degradation and loss of amine solvents, reduction of energy consumption).

3.4. SO n°4: Demonstrate the performance of MOF-based carbon adsorption in real operation

The lack of visibility on MOFs performances with adsorption processes in relevant environment hampers research and the development on these promising carbon capture technologies. MOF4AIR consequently aims to validate and demonstrate a fine-tuned MOF-based capture system in real environment (TRL6). MOF4AIR will study their performance on three different demonstration sites to ensure smooth integration, productivity of existing processes, and minimal increase of expenses.

3.5. SO n°5: Ensure the technology replication in other CO₂ and energy intensive industries and its sustainability

With its flexible design and retrofittable post-combustion carbon capture systems, MOF4AIR targets a wide range of energy and CO₂ intensive industries. MOF4AIR aims for optimization from the techno-economic and environmental points of view and promotion of the developed system to all industries that have processes implying combustion (power plants, refineries, cement plants, iron and steel). The developed capture solutions will be demonstrated on the three demonstration sites. The partners will also study a variety of CO₂ emission sources originating from various combustion processes in the MOF4AIR Replicability Study, considering at least different processes, their energy consumption and the volume of CO₂ emitted. MOF systems will be optimized from technoeconomic point of view for the specific industrial application addressed, considering the different CO₂ concentration in the flue gases and the availability or absence of waste heat for thermal regeneration. The MOF4AIR Replicability Study will be achieved in close collaboration with the MOF4AIR Industrial Cluster Board (ICB that gathers industries from main CO₂ emission industrial sectors) that will help the consortium to consider the widest range of processes possible.

3.6. SO n°6: Increase stakeholder and public awareness of the challenges, benefits and issues related to carbon capture, transport, utilization and storage

MOF4AIR will study the societal readiness of various stakeholders to commit to CCUS in order to promote carbon capture, utilization and storage. Different tracks will be pushed forward in the project:

- Industrial stakeholders and solution providers should have a better insight on the risks and regulations regarding the share of responsibilities in the CCUS processes;
- Policy makers must be aware of the challenges of CCUS and that economic incentives might be needed to foster the wide commercial deployment of CCUS;

- The wider public must be involved in the industry and energy transition for a Near Zero Emission economy.

4. Demonstration of capture solutions

MOF4AIR ambition is to validate and demonstrate the interest of MOFs innovative porous materials combined with optimised capture processes on three demonstration sites.

4.1. TCM site

The TCM is one of the most advanced and the largest post-combustion CO₂ capture pilots, where several vendors have already qualified their CO₂ capture technologies. Onwards to 2020, TCM could play a key role by providing test campaigns for new and innovative post-combustion technologies that can realise the efficiency and cost-effectiveness of CO₂ capture technologies in full-scale plants' [36]. The MOF4AIR TCM pilot will enable the test of the project's fine-tuned solution on different flue gases: RFCC (Residue Fluid Catalytic Cracker - refinery) and CHP (Combined Heat and Power - power plant). The participation of TCM in this project is unique as it shows the common will to bring carbon capture solutions closer to the market from 4 major oil companies that collaborate at TCM: GASSNOVA, EQUINOR, SHELL and TOTAL.

4.2. TUPRAS site

TUPRAS has four refineries established in Izmit, Izmir, Kırıkkale and Batman with a total crude oil processing capacity of 30 million tons per year. TUPRAS is the largest industrial company in Turkey with the added-value and revenue that it creates. As Europe's 7th largest refining capacity, TUPRAS is one of the most complex refineries in the Mediterranean region with an average Nelson complexity index of 9.5. With the completion of the Residuum Upgrade Project (RUP), the Izmit Refinery now has the highest complexity of any refinery in the region. TUPRAS will host a pilot in its Izmit Refinery.

4.3. SOLAMAT site

SOLAMAT is part of the Marseille-Fos cluster and is part of SARP Industries (SARPI) group which is subsidiary of VEOLIA and leader for treatment and recovery of hazardous industrial waste. SOLAMAT owns and operates two industrial sites in Fos-sur-Mer and Rognac equipped with 60,000 tones/year incineration line on each site. The demonstration pilot will be installed in SOLAMAT Fos-sur-Mer site, operated by SOLAMAT with the help of its linked third party Veolia Research and Innovation Center (VeRI). The Fos-Berre/Marseille CCU cluster gathers industries and public sector (GPMM i.e. Port Authority). Soon, an important infrastructure component (pipeline collecting CO₂ from different sources and feeding different applications) will be set up. The main benefits for the territory are maintaining industries and reducing their CO₂ emissions at the same time by developing a circular approach (industrial symbiosis). The Fos-Berre/Marseille CCU cluster supports a wide range of CCU technologies from chemicals and biological transformation to produce chemicals, material and fuels. At SOLAMAT, the industrial process studied will be a waste incinerator.

5. State of progress

The project started in July 2019 with the identification of potentially most appropriate MOF candidates, in terms of foreseen performances (working capacity, selectivity), stability, cost, environmental impact and large-scale production possibilities. These MOFs were produced at small scale (some grams) and characterized by XRD, IR, BET, TGA techniques to check their quality and to validate their use in adsorption-based CO₂ capture technologies: working capacity above 1 mol.kg⁻¹ between 1 bar and 0.1/0.15 bar and 298-323 K, CO₂/N₂ selectivity > 30 at 1 bar, stable with

water, SO₂, NO_x (even in presence of water and heat of adsorption below 50 kJ.mol⁻¹. This work has been performed by experimental measurements and assisted, in parallel, by molecular simulations. That led to a first selection of 5 promising MOFs for which the scaling-up and the shaping has started as well as the first characterization of these materials.

Besides the adsorbent material development, the overall process has been investigated by simulation of adsorption-based CO₂ capture process and the required pre-treatment units for the demonstration plants. Moreover, methodologies have been developed to provide techno-economic assessments and verify the economic competitiveness of this adsorption-based CO₂ capture technology with other benchmark carbon capture technologies (MEA-based CO₂ capture plant).

Regarding the demonstration units, the selection of Engineering-Procurement-Construction (EPC) company subject to tendering process has been started. The pilots should be operational in summer 2022.

Finally, investigation of the legislative and regulatory framework in all participating countries and in EU level, concerning capture, transport, and storage of CO₂, have been performed. A literature review has been performed concerning the factors affecting acceptance and perceived risks/benefits of CCUS infrastructure.

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