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Addressing the criticalities for the deployment of adsorption-based CO₂ capture processes

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Abstract

Adsorption-based separations are a promising alternative for CO₂ capture, for both pre-combustion and post-combustion applications. The desirable characteristics of solid sorbents and the flexible cyclic nature of the processes operated with fixed beds open the doors for potential improvement over the most established technology, which is represented by amine-scrubbing systems. Two main routes are available for the regeneration of the sorbents, i.e. either pressure-driven (PSA/VSA cycles) or temperature-driven desorption (TSA cycles) respectively. A series of criticalities are encountered in the implementation of both solutions: They prevent adsorption-based separations to reach breakthrough performances, in terms of energy consumption and plant productivity. To tackle these issues, research should address different aspects: Besides the development of innovative sorbents, the fine-tuning of both unit operation and cycle design is believed to be the key to advancing this technology towards commercial success.

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1. Introduction

Adsorption-based processes have been widely employed in industrial processes for separation of gas mixtures. Solid physisorbents have several desirable properties: They are non-volatile and non-toxic; solid particles are rather

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simple to store and to displace; moreover, in some cases, they are associated to a smaller energy penalty as compared to liquid absorbents, thanks to the lower sorption enthalpy.

The easiest and most established way to operate adsorption-based processes makes use of fixed bed reactors, in which the solid sorbent beads or pellets are packed into columns. Solids remain stationary, whereas the gas flows through the bed and the operating conditions in the columns change following a pre-set sequence, undergoing a series of steps, e.g., adsorption, depressurization, purge, repressurisation. The cyclic nature of the process allows for a high degree of flexibility, a feature that makes this technology highly adjustable to the specifications of the feed or to the minimum desired separation performance.

More recently, adsorption-based separations have attracted the interest of many research groups within the context of CO₂ capture technologies. Some issues concerning the deployment of these processes have not been fully solved. Furthermore, the achievable separation performance comes at a high cost, in particular in terms of energy consumption. This is one of the reasons that prevent this technology from prevailing over other more established technologies and attaining commercial maturity.

Two main options, different in terms of regeneration methodology, have been mainly investigated: pressure swing adsorption (PSA) and temperature swing adsorption (TSA). PSA systems are best suited for pre-combustion CO₂ capture applications, where the gas flow comes to the adsorption unit already at high pressure. The low temperatures required for thermal regeneration combined with the possibility of using available waste heat, suggest the use of TSA processes for post-combustion capture. Vacuum swing adsorption (VSA), which is commonly referred to as a PSA with a regeneration pressure that is significantly below ambient, has also been considered in this context. All of these technologies share the common principle, that the separation of the species in the feed is driven by a solid medium undergoing alternating loading and regeneration phases. As a consequence, they share criticalities related to the properties of the sorbent and to the cyclic nature of the process. At the same time, the implementation of each process solution raises specific questions and problems. In order to drive the development of the adsorption-based CO₂ capture technologies towards commercial competitiveness, multiple factors must be taken into account. This proceeding identifies and discusses six major criticalities for the deployment of adsorption-based CO₂ capture processes.

2. Handling of impurities

In both pre-combustion and post-combustion CO₂ capture applications, the gas mixture to be separated is composed predominantly of CO₂/H₂ and CO₂/N₂, respectively. However, the presence of other secondary species is inevitable and can significantly affect the separation, even if present in dilute concentrations. The sorbent material, in fact, might show high selectivity towards one of those secondary compounds, and the competition with CO₂ for the adsorption sites can in some cases not be neglected. A technology proposed to treat multicomponent mixtures consists of combining layers containing different sorbent materials within a single fixed-bed, i.e. layered beds. A fair amount of research has already been dedicated to developing solid understanding of the interactions between gas mixtures and different material [1]–[7]. The results provide clear indications about the most relevant trends characterizing multicomponent adsorption equilibria and have helped explaining the most evident heat and mass transfer phenomena.

The length of each layer has to be calculated in order to allow for simultaneous breakthrough of the different compounds at the end of their dedicated section, so that the productivity of the process can be maximized and contamination of the product is minimized. Such fine tuning of the process is not trivial. An even harder aim is that of developing optimization tools, suited to the definition of all lengths of the different layers, in such a way that they apply to a wide range of operating conditions. A good understanding of the multicomponent equilibria, together with a large amount of experimental data, is needed for this purpose. Some PSA plants for hydrogen purification employ layered beds: Up to four adsorbents are utilized, i.e. silica gel or alumina for water, zeolites for CO and CH₄ and activated carbon for CO₂ [8]. These systems can provide high H₂ purity, but the recovered CO₂ stream is usually around 50% pure (on volumetric basis). A different design is required to obtain both pure H₂ and CO₂.

In flue gases, water commonly amounts to a volumetric fraction comparable to that of CO₂. This poses a major challenge since most commercially available highly CO₂-selective sorbents feature a higher selectivity for H₂O than

for CO₂. Frequently, adsorption-based PCC systems must be preceded by a drying unit, or else the presence of water must be managed with a dedicated adsorption cycle.

Besides the well-known possibility of cryogenic dehydration, drying of the feed can also be achieved by adsorption. Materials like alumina and silica show high selectivity towards water and a high adsorption capacity [9]. Since the same principle can be applied, integrating drying into the adsorption process appears to be a viable alternative, potentially minimizing capital expenses. In principle, the problem can be approached as a multicomponent separation, for which layered beds can be employed [10]. A first layer at the entrance of the column, i.e. the guard layer, serves the purpose of removing the water vapor from the flue gas so as to avoid impairment of the CO₂ capacity in the subsequent layer(s). Contamination between water and carbon dioxide is tolerable in most applications. Compared to the flue gas, the stream of recovered CO₂ has a significantly reduced flow rate, hence further purification of the product can easily be accomplished.

On top of the already discussed complexity associated with the design of the layered beds, a major issue arises from the particular behavior of water adsorption: On certain sorbents, capillary condensation may occur within the range of temperatures and pressures at which the CO₂-separation process is operated. Because of that, regeneration of the adsorbent material may prove difficult, giving rise to hysteresis and requiring long desorption times and critical operating conditions.

3. Use of new materials

A spread field of research about adsorbent materials is dedicated to the development of new tailor-made porous media, which could offer high adsorption capacities and high CO₂/N₂-selectivity. Thanks to available knowledge of material structures and molecular dynamics, many of them can be extensively adjusted in order to properly fulfill the task of specific applications. For example, some metal-organic framework (MOF) compounds arouse great interest as they show great potential to perform well in the context of CO₂ capture, because of their large adsorption capacities and high selectivity [11].

The diamine-appended MOF materials developed by McDonald et al. [12], for instance, feature step-shaped CO₂ isotherms, where the position of the step changes depending on temperature. The choice of the metal ions in the structure also affects the shape of the isotherm, so that a series of analogous materials can be created, each of them featuring the step transition at a different pressure for a given temperature. In this way, the most suitable sorbent can be identified in order to pursue significant enhancement of the effectiveness and of the overall efficiency of the separation process.

In a recent work by Hefti et al. [13] the materials characterized by McDonald et al. have been, for the first time, investigated to present a quantitative assessment of the process performance achievable in the case of a 4-step TSA cycle for post-combustion capture. The results obtained through simulations have been compared to those of a common, commercially available and well-performing CO₂ sorbent, i.e. zeolite 13X. Five different MOFs materials have been tested and one of them has achieved the desired separation specifications (90% recovery, 96% purity) under the operating condition tested. The outcome of the study highlights the potential of this class of adsorbents, whose use could lead to substantial (around 20%) reduction of the energy requirements for regeneration and to an increase in the productivity of the system.

A comparison to the established amine-scrubbing technology draws the attention to the uncertainties associated with large scale employment of these materials. While they are undoubtedly well performing and could represent a key solution for adsorption-based processes to overtake other separation technologies, there is currently no data on their usability on a larger-than-laboratory scale. Whether these materials can be produced in large quantities at an industrially attractive cost and in an environmentally sustainable way, and whether they remain stable under cyclic operation over a long period of time, are questions that still need to be answered.

4. Design of the cycle

Despite some skepticism on the potential of commercially available sorbents, many studies so far conducted for PSA applications have already demonstrated how the identification of a viable and effective cycle design is key for the development of an operable technology.

The most traditional cycle for gas mixture separation by adsorption was developed by Skarstrom [14]; it consists in a four step cycle, in which the adsorption step is conducted at high pressure and is followed by depressurization, a purge step and the re-pressurization of the system. This first-concept PSA technology was meant to enable the purification of the light (i.e. less retained) component. Similar procedures are suitable for those applications where the desired product is the less adsorbing compound. In the case of CO₂ capture, the strong quadrupole of the CO₂ molecule makes its interaction with current sorbents stronger as compared to the compounds from which it must be separated, e.g. N₂, H₂, CH₄ and O₂. Moreover, even if a sorbent were available where CO₂ is the light component, for post-combustion capture the CO₂ content is relatively limited (4%–15%), so that it appears disadvantageous to adsorb all other species, leaving the CO₂ flow through the system as light component. For these reasons, new cycle designs are being investigated so as to deliver the heavy component at high purity. As a result, coproduction of high purity CO₂ and H₂ by PSA represent a commercially ready technology, whose improvement pace has been continuously increasing since its first deployment [15]: modifications as the introduction of pressure equalization, multiple column setup and the use of purge and rinse streams have improved the performance of conventional PSA remarkably. New process concepts have been proposed by Sircar and Kratz [16] and by Grande et al. [17], [18] considering solutions that make use of two different units.

Limiting the adsorption-based separation to a single step could provide a substantial reduction in capital expenditures. Decisive improvement, in this sense, has been achieved by means of a reconsideration of the step sequence of the process: the introduction of both light product reflux and heavy product reflux has delivered the concept of double reflux PSA cycles (DR-PSA)[19], [20], expressly conceived to serve also the purpose of rectification for heavy component production, instead of stripping for purification of the light component only. In this new configuration the gas is fed at an intermediate position of the fixed bed, so to operate a double stripping-rectifying process within each column.

Further improvement is expected from the optimization of this configurations, a task that requires adequate tools and reliable modeling [21], [22]. Adapting the cycle to specific operating conditions and characteristics of the sorbent opens the way to minimize energy consumption for compression and enhance process productivity.

While for PSA technology the evolution of cycle design (either to simply increase efficiency, like for the introduction of pressure-equalization steps [23], or the effectiveness of a specific separation, like for the DR-PSA technology) has been a discussed topic in the last decades, on TSA applications fewer studies have been conducted. Nevertheless, the introduction of some modifications may indeed increase the separation performance and the process efficiency.

The simplest TSA cycle one could imagine consist of 4 steps, in analogy with the Skarstrom cycle. The pressure changing step are in this case replaced by a heating and cooling steps: heating drives the desorption, whereas a cooling phase substitutes the pressurization step. Possible modifications of the cycle may be operated by introducing closed heating or cooling steps and interconnecting different units via recycled fluxes, with or without the need for buffer tanks, depending on the configuration. Recent work done by the authors [24] demonstrates how such expedient changes can produce significant reduction of the energy consumption and enhance the plant productivity, while maintaining separation performance within the optimal constraints for CCS (90% recovery, 96% purity).

Another possible upgrading solution that has recently been proposed by Ntiamoah et al. [25] tackles a series of different issues which are commonly encountered in TSA processes for recovery of the heavy component. In usual cycles for CO₂ capture the bed is eventually swept, after a first regeneration phase, using a N₂-rich purge, whose product though has low CO₂ content. During the recovery of the CO₂-rich product, heat is provided to the fixed bed indirectly, usually by letting a thermovector fluid flow on the external side of the column walls. The efficiency of this heat exchange method depends on the size of the system, as thermal gradients might be negligible on a lab-scale column, while they are likely to significantly affect the operation of a full-scale plant. A possible solution to both problems might come from the introduction of a direct regeneration, where a flux of hot CO₂-rich product is fed to the column during the regeneration step, satisfying the thermal duty required for desorption. The disadvantage of desorbing at high CO₂ concentrations, as the loading capacity of the sorbent cannot be fully exploited, is though inevitably translated into lower-than-usual productivity.

Also in the case of post-combustion carbon capture, the effects of both pressure and temperature swings can be summed up in a single process design, creating hybrid cycles. Since the flow rates of the flue gas are in most cases

considerably large, compressing the gas during the adsorption phase would end up being too energy consuming. Therefore the pressure swing is usually achieved by drawing vacuum during the desorption step instead, which translates into the so-called VTSA (Vacuum-Temperature Swing Adsorption) process. This concept of hybrid cycles has already been applied for similar applications, for instance CO₂ capture from air [26]. When applied to post-combustion capture, such processes seem able to yield the desired performances. Moreover, it can be observed how the combination of both desorption strategies allows for gentler regeneration conditions [27]. This means that, in order to obtain the same performance, temperature does not have to be raised as high as in a TSA-only cycle and vacuum does not have to be drawn at as low pressures as in a VSA-only cycle.

5. Design of the bed system

One of the main issues that hinder the implementation of adsorption-based technologies to post-combustion capture is the relatively low productivity, in volumetric terms, that characterizes these systems. Most laboratory applications, if they were scaled up to treat flow rates as large as those expected at the stack of a power plant, would require enormous footprints, which would correspond to capital expenditures unaffordable within an industrial context. For TSA processes, in particular, the productivity is strongly affected by the long heating and cooling times required to operate the temperature swing. In order to reduce the total cycle duration, heat transfer from and to the bed must be enhanced. One possible solution for the heating phase is that of direct hot-gas regeneration, already previously mentioned; this cannot help though during the cooling phase, where an external indirect heat exchanging system is necessary. In order to improve heat transfer through reactor walls, some vessel configurations different from the standard column-shaped one might be taken into account.

Adsorbers consisting of radial beds, where the feed flows from the outermost section of the column inwards, have shown promising results for the treatment of gases at relatively large specific volume (i.e. ambient or vacuum pressure). Commercial applications (Linde and UOP) already exist for VPSA-based O₂ production and TSA-based gas drying (ASU): Radial beds are credited with reduced pressure drops along the bed, compactness and energy-saving effects on the large scale. There exist filed patents about the use of radial bed technology for separation of CO₂ by means of a molecular sieve bed; however, this technology is not broadly and systematically studied in the open literature. There are reasons to believe some new research could yield new achievements in the usage of this kind of reactors, which might represent an ultimate solution to the sizing issue connected to some adsorption-based capture technologies. Moreover, further improvement could derive from the possibility of combining the radial design and the layered disposition of different sorbents (previously discussed), something which to author knowledge has never been attempted in the field of CO₂ capture, but has already been proposed for similar applications, for instance for air purification [28].

6. Heat integration

The availability of waste heat in industrial and power plants is indeed one of the fundamental reasons that justify the interest into TSA-based processes for post-combustion CO₂ capture. From our modeling results, regeneration temperatures lower than 450 K are enough to reach breakthrough purity and recovery performance with commercial sorbents [24]; for such low temperature ranges, the recovery of the low-grade waste heat available in the plant (e.g. CO₂ compression and flue gas cooling) is perfectly suitable.

Furthermore, the cyclic nature of the process requires multiple units to operate in parallel. As a consequence, at any time during the operation of the system some of the reactors are being cooled while some others are being heated. This opens the doors to possible internal heat recovery, i.e. coupling vessels to transfer heat from cooled vessel to heated one, in order to partially avoid resorting to an external energy source.

Applying both strategies, a strong reduction in the overall energy consumption of the process can be expected. One of the most common techniques to evaluate the potential savings produced by heat recovery within a plant is to approach the issue by means of pinch analysis. For continuous processes, this procedure represents a quite established methodology, whereas for batch and other discontinuous processes major issues are encountered, so that it can only apply to them when strong assumptions are made [30], [31].

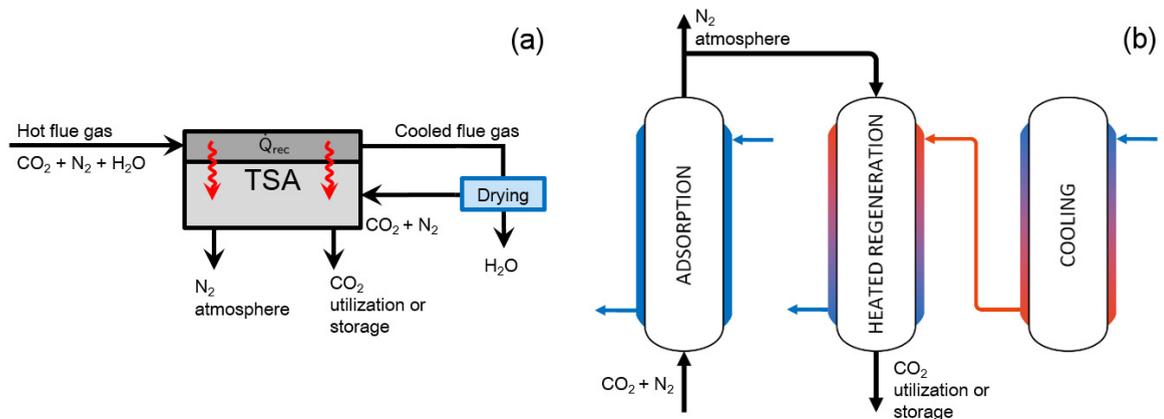


Figure 1: schematic example of heat recovery from the flue gas (a) and internal heat recovery (b)

According to preliminary calculations conducted by our laboratory [24], by summing both the recovery of the sensible heat stored within the flue gas and the transfer of heat from cooled vessel to heated ones, a reduction of about 25% in the overall energy consumption of the process may be expected. Nevertheless, this primary evaluation takes as assumption constant (in time) heat flux through vessel walls, a hypothesis which is clearly very strong for temperature dependent, strongly exo- or endothermal semi-batch processes, as the one occurring during a TSA cycle. A more detailed modeling of the heat transfer between the fixed bed and the external medium is the only way to assess the real potential of heat recovery by simulations. The first essential step towards this aim is a complete characterization of the heat transfer phenomena observed within packed sorbent beds, a prerequisite which is often not fully satisfied and which is subject to several problems connected with the scaling of the system from laboratory-scale to full plant-scale.

In fact, the modeling of fixed bed adsorption processes is usually confined to one-dimensional spatial discretization, a choice which implies the assumption of negligible gradients along any dimension other than the discretization one. Moreover, it is highly advisable to maintain this simplification, in order to allow for faster computation during the simulations. Therefore, the noticeable effects that derive from a scaling up of the simulated units must be considered by proper systematic adjustment of those parameters that regulate heat transfer. This can be done by developing sufficiently accurate correlations, able to predict the impact of these effects.

7. Process optimization

The optimal configuration of an industrial application corresponds to the minimization of its cost, which derives from the sum of capital costs (CAPEX) and operating costs (OPEX). For adsorption-based capture processes, the former are related to the size of the plant, which is directly proportional to the amount of adsorbent needed to capture a certain fraction of CO₂ out of a gas flow (i.e. productivity index); the latter are instead proportional to the amount of energy required to operate the separation (i.e. specific energy consumption).

Advanced tools are needed to deal with such a complex multi-object process optimization problem, where the objectives are the two mentioned performance indicators, the constraints are drawn by the desired separation performances (in terms of recovery and purity) and many different degrees of freedom may be considered. As long as the values of the two objective indexes are not translated into economic parameters, so that their impact over the total cost of the plant construction and operation can be assessed, the optimization remains double-objective and its solution does not consist of a single point, but rather of a set of separated points. These points can be displayed within a 'specific energy consumption-productivity' diagram, where they draw a Pareto front.

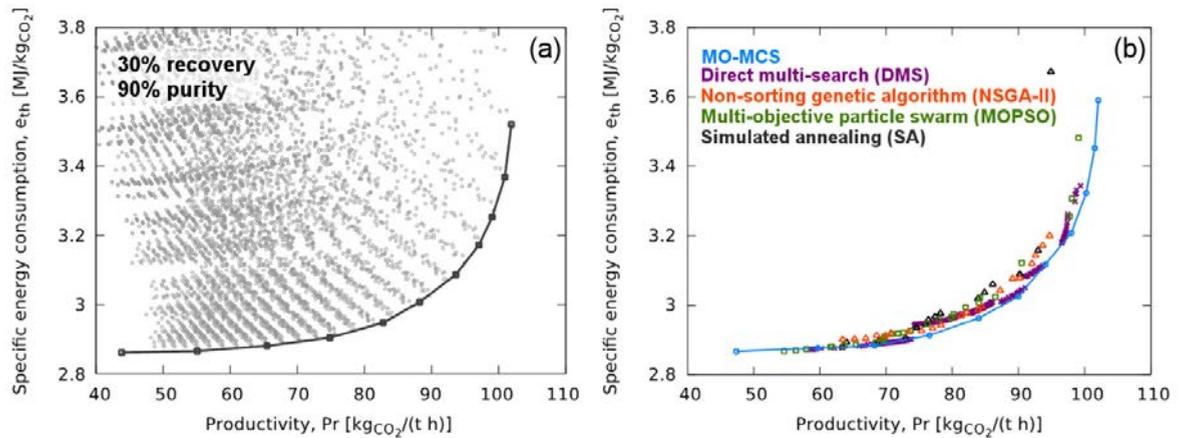


Figure 2: Example of Pareto front determined by detailed parametric analysis (a) and employing the multi-objective multi-level coordinate search (MO-MCS) optimization (b); the analysis has been performed over a 5-step TSA cycle for post-combustion CO₂ capture [24] under 30% recovery–90% purity constraints. Optimization variables: 5 step times.

As mentioned, the degree of freedom of the optimization problem can be identified with many different parameters, ranging from the adsorbent properties to the unit design specification, from the operating conditions to the configuration of the cycle. The effort required to densely scan the feasible ranges of many different parameters makes any sufficiently detailed parametric analysis excessively time- and effort-consuming. Efficient optimization methods are thus required.

Since multiple local minima are possibly present, given the non-linear and non-convex nature of the objectives and constraints, global optimization methods are necessary. Genetic algorithms are often used for this type of optimization problem and have already been applied to adsorption-based process for CO₂ capture [32]. Nevertheless, they do not guarantee any proof for convergence, and the results can strongly depend on the algorithm parameters. For these reasons our group, in collaboration with the GECOS group from Politecnico di Milano, has developed a new multi-objective optimization algorithm, based on multi-level coordinate search (MO-MCS) [33], which is both efficient (from a computational intensity point of view) and perfectly suitable for the study of adsorption-based technologies on a plant-wide scale. The results obtained from the testing show how computational times can be significantly reduced, while optimal points are found with the same precision of a highly detailed parametric analysis (see Table 1 and Figure 2).

Table 1: comparison between parametric analysis and MO-MCS optimization

Method	Parametric analysis	MO-MCS	MO-MCS parallel
Simulator calls	>14 000	1 153	1 253
Total time	1 300 min	120 min	50 min

8. Conclusions

Adsorption-based separations have been broadly investigated as a potentially competitive alternative to most established CO₂ capture technologies, mainly represented by absorption processes. The well-known advantages associated with the use of solid sorbents arouse interest for this separation technique, whose implementation at industrial level still encounters several issues though.

To overcome these hindrances, research must cope with a few different aspects, ranging from the properties of the sorbent to the design of the whole plant. At least partial resolution of each of these criticalities can produce slight improvements, which summed up together can drive this technology towards commercial success.

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