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Overview on Pressure Swing Adsorption (PSA) as CO_2 capture technology: state-of-the-art, limits and potentials

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Abstract

This paper provides an insight on state-of-the-art, limits and potentials of pressure swing adsorption (PSA) as CO_2 capture technology into power plants. To get a complete picture both post- and pre-combustion cases are considered. The expertise developed with modeling and simulation of PSA processes in power plants stressed the need of a holistic approach to the analysis. The different domains which determine the viability of the technology are taken into account, together with their mutual influence. Accordingly, adsorbent materials characteristics, process configurations and integration strategies are investigated and discussed, in order to provide a general evaluation. In post-combustion applications, PSA has been widely assessed with regard to adsorbent materials and processes. The integration into power plant does not entail significant issues, with a good potential for retrofitting old plants. An excessively large footprint of the separation unit has been reported, which seems to question the feasibility of PSA. In pre-combustion applications, prospects for improving adsorbent materials and processes are noticed. Good potential for PSA is envisaged whit hot gas separation processes, especially with sorption-enhanced processes. Furthermore, the complexity of the arrangements in pre-combustion cases may open room for interesting alternative system configurations, like power and H_2 coproduction layouts.

Keywords: Pressure Swing Adsorption; CO_2 capture; power plants; technology review; holistic approach.

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1. Introduction

Carbon capture and storage (CCS) is a key tool in the global commitment to tackle climate change. Absorption, whether chemical or physical, is commonly regarded as the most mature technology for CO_2 capture. Nevertheless, absorption suffers from some drawbacks, such as high energy requirements and corrosion of process equipment. Adsorption is considered a promising alternative, especially when the regeneration process is carried out through a pressure reduction (i.e. pressure swing adsorption - PSA), with potential for reducing energy penalty, environmental impact [1] and cost of CO_2 capture [2,3]. A significant research effort has been already undertaken in order to develop PSA technology for CO_2 capture applications. A wide range of adsorbent materials has been synthesized and studied [4–7]. However, material science is still very active and newly-discovered adsorbents are currently under investigation. With regard to the engineering of the process, PSA cycles have been studied in depth [8,9]. Some key criteria to define the most efficient way to use and regenerate adsorbents can be already pinpointed. Further work is ongoing, focusing on decreasing the relative energy consumption and on the process optimization. The literature is less comprehensive with regard to the integration of PSA processes into the power plants and the relative system performance. Some analyses at a system level have been published lately [10–14], touching upon these topics and giving some indications on strengths and weaknesses of PSA in the contexts investigated.

This work aims to wrap up all this information, so to provide a thorough insight on the current viability of PSA as CO_2 capture technology into power plants. The analyses presented are based on the expertise gained with modeling and simulation of those systems [15] and include considerations on the adsorbent materials, the process configurations and the integration strategies. Such holistic approach, taking into account different domains and their mutual influence, is missing in the literature and provides a systematic overview on the topic, putting in the right context the specific advancements achieved. The analyses encompass both post- and pre-combustion process frameworks. The final outcome is an evaluation on the current status and the prospects of PSA for CO_2 sequestration in power plants.

2. Post-combustion analysis

The first case analyzed is post-combustion CO_2 capture in thermal power plants. The focus is mainly on coal-fired power plants.

2.1. Adsorbent materials

Zeolites are the natural candidate adsorbents for a PSA process in a post-combustion process framework. Zeolites exhibit good CO_2 adsorption capacity and selectivity at low pressures and moderate temperatures, and demonstrated to outperform activated carbons in post-combustion operating conditions [16,17]. For the typical CO_2 partial pressures of flue gases, zeolite 13X and NaY showed to be the most effective [18]. Some studies suggest to use zeolite 5A because of its higher volumetric capacities and less severe heat effect of adsorption [19], although these advantages may apply more to thermal swing processes [20]. A main drawback of zeolites is linked to their hydrophilic nature. The presence of water vapor, an inevitable component of flue gas, negatively affects the capacity of these adsorbents and reduces the availability of the active surface area. Metal organic frameworks (MOFs) are a potential alternative. Extremely promising CO_2 adsorption capacities have been demonstrated in the MOFs with the highest surface area, even in the presence of water vapor [21]. High adsorptive selectivity has also begun to emerge in materials MOFs furnished with functionalized surfaces [22]. However, additional research effort needs to be undertaken to ensure the MOFs applicability. Many issues are yet to be addressed, including: the effect of impurities components (O_2, CO, CH_4, SO_x, NO_x) in the feed, the practical aspects of employing a PSA process [22], the stability over multiple adsorption/desorption cycles [4] and the material formulation and mechanical stability [23]. Amine-functionalized adsorbents display large CO_2 adsorption capacity at low pressure levels, high CO_2 selectivity (especially over N_2) and robustness toward water. These characteristics make them promising candidates for post-combustion applications. However, issues like very sharp adsorption isotherms, high energy requirement for regeneration and possible amine degradation at high temperature question their actual applicability in common PSA-based systems [8].

2.2. PSA process configurations

A variety of PSA cycle configurations have been developed for concentrating CO_2 from stack and flue gases. Given the atmospheric pressure level of these gases, the most common PSA processes in post-combustion applications rely on sub-atmospheric adsorbent regeneration (vacuum pressure swing adsorption – VPSA). As an alternative to vacuum pressures, an upstream flue gas compression has been studied but this approach demonstrated to be unfeasible due to the large energy requirement involved [10,24]. Many combinations of process steps may be able to meet the targets in terms of CO_2 purity and recovery, so the primary factor to optimize becomes the energy consumption for implementing the gas separation process. A 2-stage PSA system is likely necessary to efficiently meet the requested separation performance, i.e. 90% CO_2 recovery (R_{CO2}) and 95% CO_2 purity (ϑ_{CO2}) [19,25,26]. Commonly, the first stage provides high CO_2 recovery, while the second stage achieves the CO_2 purity level desired. Some studies seem to show that a single stage process may become able to reach similar performance with competitive energy consumption [27,28] but would require high vacuum conditions, which are not simple to implement on large systems [8]. Moreover, experimental results on the same PSA system arrangements not always fully agree with the simulation outputs [29], stressing the degree of complexity of these systems and the necessity of further results validation. Table 1 gives an overview of the current status, reporting some of the most meaningful significant results from the literature.

Table 1. Performances of various PSA arrangements for CO_2 capture from flue gas. The nomenclature used refers to CO_2 mole fraction in the feed gas stream (y_{CO2}), feed pressure (PF) and regeneration pressure (PR), CO_2 purity (ϑ_{CO2}) and CO_2 recovery (R_{CO2}). The energy term reported refers to ideal processes, unless stated differently.

No. PSA stages	Cycle configuration	Adsorbent	y_{CO2}	PF/PR (bar)	ϑ_{CO2}*	R_{CO2}*	Energy (kJ/kg$_{CO2}$)	Ref.
2	3-bed 5-step 2-bed 5-step	zeolite 5A	15 %	1.0/0.1 2.0/0.1	95.1 %	90.1 %	561	[10]
2	3-bed 5-step 2-bed 6-step	zeolite 5A	15 %	1.5/0.1 1.5/0.15	96.1 %	91.1 %	646	[19]
2	2-bed 4-step 2-bed 5-step	AC	15 %	1.3/0.1 3.5/0.1	95.3 %	74.4 %	724	[25]
2	3-bed 5-step 2-bed 6-step	zeolite 13XAPG	15 %	1.5 /0.1 1.5 /0.1	96.5 %	93.4 %	528	[26]
2	3-bed 9-step 3-bed 9-step	zeolite APGIII	15 %	- /0.1 - /0.1	95.3 %	98.2 %	551	[30]
1	3-bed 12-step	AC	13 %	1.0/0.02	93.8 %	91.3 %	331	[27]
1	4-step**	zeolite 13X	15 %	1.0/0.03	> 95 %	> 90 %	399	[28]
1	4-step**	zeolite 13X	15 %	1.0/0.03	94.8 % ± 1 %	89.7 % ± 7 %	1710 ± 132***	[29]

* when two stages apply only the overall separation performance is reported

** number of beds not specified as a one-bed setup has been used

*** this term is an actual energy consumption being the output of experimental work

2.3. Integration strategies

The PSA unit in a common post-combustion layout has to process an atmospheric flue gas coming from a pulverized coal boiler or from a gas turbine. The content of CO_2 is rather low ($\approx$ 4% to 15% vol.) and is mainly diluted in N_2. Other components present are O_2 and H_2O. The separation unit is normally placed downstream the flue gas cleaning section of the plant. As previously mentioned, vacuum pressures are normally used for adsorption column regeneration. The vacuum level is an important optimization parameter, causing tradeoffs between CO_2 separation and energy consumption. The PSA regeneration process only necessitates of electric power, to drive vacuum pumps and fans. The avoidance of any thermal power duty simplifies the integration of this technology into thermal power plants (e.g. no steam extraction to design) and gives good potential for retrofitting existing plants. The units upstream PSA are basically unaffected by the following CO_2 separation process. When hydrophilic adsorbents (e.g. zeolites) are used, it is essential to remove water to large extents before the PSA unit. This may require a specific dehydration unit (e.g. a glycol-based process) or a tailor-made design of the PSA process (e.g. a pre-layer of selective adsorbents

like zeolite 3A [31]). Finally, an appropriate compression section has to be planned to compress the CO_2-rich gas stream for transport.

2.4. Performance, limits and potentials

The performance of a PSA-based plant demonstrated to be competitive with that associated with other decarbonization technology, chemical absorption in the first instance [10]. Table 2 reports the relative simulation outputs of a large advanced supercritical (ASC) coal-fired power plants implementing CO_2 capture by PSA. To the authors' knowledge, this is the only post-combustion full-plant analysis available in the literature. The performance is evaluated in terms of net electric efficiency (η_{el}) and CO_2 recovery (the CO_2 purity is not reported but it is implied that the systems achieve the 95% specification requested for safe transport and storage of CO_2). For comparison the simulation outputs of the same plant using a common amine absorption process as CO_2 capture technology are also shown. Steam is used for solvent regeneration in the absorption process, while only electric power needs to be supplied to the PSA process. In spite of the different energy consumption patterns, the final net electric efficiency is similar for the two cases tested, with PSA displaying a slightly lower energy penalty. Regarding the CO_2 separation performance, both technologies allow meeting the CO_2 separation targets (i.e. 90% CO_2 recovery and 95% CO_2 purity). A serious issue envisaged regards the size of the PSA unit. Common PSA processes would result in an unfeasible footprint. Taking into account some conservative design criteria, concerning the minimum fluidization velocity and the maximum pressure drop in the adsorption columns, the PSA unit would need an unacceptable number of columns to process the whole flue gas flow rate. Further studies must focus on an intensification of the process. Structured adsorbents, allowing higher superficial velocities with reduced pressure drops, are interesting in this perspective but necessitate further investigation [32–34]. Otherwise, different process frameworks are probably to be considered (e.g. moving bed adsorption reactors). Another issue, which has often been disregarded in the literature, concerns the detrimental effect of water on typical physisorbents, zeolites in the first instance. Since the presence of water is unavoidable in flue gases, methods for an effective removal must prove to perform satisfactorily integrated in the complex arrangement of a power plant, while keeping as low as possible the additional power consumption. The issue would no longer apply if water-resistant adsorbents demonstrate to be applicable.

Table 2. Performances of power plants implementing post-combustion CO_2 capture. The nomenclature used refers to CO_2 recovery (R_{CO2}) and net electric efficiency (η_{el}).

Case	CO_2 capture technology	R_{CO2}	η_{el} (LHV)	Ref.
ASC-absorption	Abs. (MEA)	90.0 %	34.2 %	[10]
ASC-PSA	PSA	90.2 %	34.8 %	[10]

3. Pre-combustion analysis

The second case analyzed is pre-combustion CO_2 capture in thermal power plants. Most of the considerations and results reported refer to integrated gasification combined cycle (IGCC) plants. However, some results are presented relative to natural gas combined cycle (NGCC) plants. Evaluations of PSA as a technology to produce H_2 are also presented, as this application is connected to some pre-combustion CO_2 capture cases.

3.1. Adsorbent materials

Given the relatively high CO_2 partial pressures, adsorbents with high saturation capacity are desirable in pre-combustion applications. Activated carbons (ACs) demonstrated to perform effectively in relevant operating conditions. For instance, ACs outperform zeolites when CO_2 partial pressure overpasses a certain threshold (≈ 1.7 bar) [17]. A key challenge for the future could be to achieve higher selectivity. Further, the adsorbent should not saturate at too low pressures, because this would make the regeneration process more complex (although this issue can be mitigated to some extent by increasing the temperature). MOFs are gaining consensus as potential alternative [35] and

showed promising results [23]. As reported in the post-combustion section, additional research effort needs to be undertaken to assure the applicability of this family of adsorbents, especially with regard to particle shaping. However, the possibility to tune their structure and chemical composition in order to obtain desired properties makes these materials important candidates for pre-combustion CO_2 capture processes. The wide range of operating conditions and syngas compositions can be effectively addressed with tailor-made materials. For processes at elevated temperature (up to around 673 K [4]) the benchmark adsorbents seem to be potassium promoted hydrotalcites (K-HTC) [36,37]. These materials are positively affected by the presence of water [38], suitable for sour processes [39] and can be operated with a low steam feed. However, hydrotalcites generally display lower adsorption capacity than other common adsorbents.

When an additional objective is concentrating H_2 to very high purities, multi-layer bed structures are recommended [40,41]. The basic arrangement involves a first layer of ACs followed by a second layer of zeolites. According to their characteristics, the ACs remove the bulk CO_2 and CH_4 content, while the zeolites purify the gas from the remaining traces of CO and N_2. Additional layers can be added to further improve the separation performance (e.g. a silica gel/alumina layer for H_2O).

3.2. PSA process configurations

A single stage PSA process is normally considered sufficient for CO_2 separation in pre-combustion applications. On the other hand, complex PSA designs normally apply, involving many columns working in parallel and a complex cycle scheduling. This is mainly due to the large number of components present in the gas mixture and to the consequent introduction of non-standard PSA process steps. For example, a large number of pressure equalization steps increases the separation performance of the cycle but increases also its complexity. Normally a maximum of 4 equalization steps is envisaged [42]. An alternative approach could be to use a two-stage system or a dual PSA concept [43]. However, the literature generally focuses on single stage PSA designs [10,14,42]. Table 3 reports characteristics and performance of some PSA processes for separating CO_2 from a shifted syngas. One may notice that the energy consumptions involved are significantly lower than in the post-combustion cases. Pre-combustion cases are characterized by relatively high pressures at the inlet of the gas separation unit, which give a margin to operate the pressure swing process without using vacuum pressure levels. The avoidance of vacuum drastically reduces the energy demand of the process. The only energy consumption directly associated to the PSA process is that supplied to the fans to overcome the pressure drop in the column. The performance taken from [10] differs from the other cases because the system considered includes an additional double flash purification process downstream the PSA. This process increases the overall H_2 recovery and CO_2 purity, in order to comply with the requested process specifications.

Table 3. Performances of various PSA arrangements for CO_2 capture from shifted syngas. The nomenclature used refers to CO_2 mole fraction in the feed gas stream (y_{CO2}), feed pressure (PF) and regeneration pressure (PR), CO_2 purity (ϑ_{CO2}), CO_2 recovery (R_{CO2}), activated carbon (AC) and supported magnesium oxide sorbent (MgO/C).

No. PSA stages	Cycle configuration	Adsorbent	y_{CO2}	PF/PR (bar)	ϑ_{CO2}	R_{CO2}	Energy (kJ/kg$_{CO2}$)	Ref.
1	7-bed 12-step	AC	38 %	38.8/1.0	81.6 %	96.2 %	0.5	[10]
1	6-bed 10-step	AC	40 %	34.0/1.0	93.1 %	90.3 %	-	[42]
1	8-bed 11-step	MgO/C	31 %	40/1.0	93.0 %	92.7 %	-	[14]

Some studies investigated optimal cycles for sorption enhanced water-gas shift (SEWGS) processes. These processes combine the WGS reaction with the CO_2 separation pushing the reaction towards the product formation, hence increasing the H_2 production. The cycles are similar to common pre-combustion PSA cycles. A difference is the utilization of steam for the purge step and the introduction of a rinse step, again using steam. Accordingly, the steam to carbon feed ratio (S/C) in the purge and rinse steps is an important optimization parameter. Table 4 outlines the main characteristics and results of the cycles presented in the literature.

Table 4. Performances of various SEWGS arrangements. The nomenclature used refers to CO_2 mole fraction in the feed gas stream (y_{CO_2}), feed pressure (PF) and regeneration pressure (PR), CO_2 purity (ϑ_{CO_2}), CO_2 recovery (R_{CO_2}) and potassium promoted hydrotalcite (K-HTC).

Cycle configuration	Adsorbent	y_{CO_2}	PF/PR (bar)	ϑ_{CO_2}	R_{CO_2}	Energy (kJ/kg$_{CO_2}$)	Ref.
8-bed 11-step	K-HTC	24 %	23.6/2	98.0 %	90.0 %	-	[44]
8-bed 11-step	sorbent α	24 %	24.1/1.1	99.0 %	95.0 %*	-	[11]
8-bed 11-step	sorbent β	24 %	24.1/1.1	99.0 %	95.0 %*	-	[11]
9-bed 11-step	K-HTC	24 %	24.0/1.1	99.0 %	95.0 %*	-	[45]

* carbon recovery

As anticipated, a short overview is provided also regarding PSA processes for H_2 purification. The PSA cycle has to be able to produce H_2 with high purity (i.e. up to 99.99+% vol.), while having the highest possible H_2 recovery. Generally, a trade-off can be observed between H_2 recovery and complexity of the PSA arrangement. Table 5 reports results from significant studies available in the literature.

Table 5. Performances of various PSA arrangements for H_2 production from different gas streams. The nomenclature used refers to feed pressure (PF) and regeneration pressure (PR), H_2 purity (ϑ_{H_2}), H_2 recovery (R_{H_2}), steam-methane reformer off-gas (SMROG), coal gasification off-gas (CGOG) and activated carbon (AC).

Cycle configuration	Adsorbent	Gas type	PF/PR (bar)	ϑ_{H_2}	R_{H_2}	Energy (kJ/kg$_{CO_2}$)	Ref.
10-bed 11-step	AC/zeolite 5A	SMROG	21.0/1.0	99.999 %	86.0 %	-	[46]
4-bed 8-step	AC/zeolite 5A	SMROG	7.0/1.0	99.996 %	52.1 %	-	[47]
4-bed 8-step	AC	SMROG*	7.0/1.0	99.999 %	62.7 %	-	[48]
10-step**	AC	SMROG	5.0/0.5	99.981 %	81.6 %	-	[49]
4-bed 8-step	AC/zeolite 5A	CGISP	8.0/1.0	99.430 %	71.2 %	-	[50]
12-bed 13-step	zeolite 5A	CGOG	34.0/1.0	99.993 %	92.7 %	-	[51]

* gas mixture saturated in water vapor

** number of beds not specified as a one-bed experimental set-up has been used

Few studies dealt with a set-up able to return multiple product streams, in particular high-purity H_2 and CO_2. Table 6 gives an overview of the available results.

Table 6. Performances of various PSA arrangements for contemporary CO_2 capture and H_2 production from different gas streams. The nomenclature used refers to feed pressure (PF) and regeneration pressure (PR), H_2 purity (ϑ_{H_2}), the overall H_2 recovery (R_{H_2}), CO_2 purity (ϑ_{CO_2}), CO_2 recovery (R_{CO_2}), steam-methane reformer off-gas (SMROG), coal gasification off-gas (CGOG) and activated carbon (AC).

No. PSA stages	Cycle configuration	Adsorbent	Gas type	PF/PR (bar)	ϑ_{H_2}	R_{H_2}	ϑ_{CO_2}	R_{CO_2}	Energy (kJ/kg$_{CO_2}$)	Ref.
2	7-bed 12-step 6-bed 11-step	AC/zeolite 5A	CGOG	38.8/ 1.0-1.8*	99.991 %	90.3 %	83.5 %	95.2 %	0.9	[52]
1	7-bed 13-step	AC	CGOG	38.8/1.0	99.983 %	85.8 %	79.8 %	97.7 %	0.7	[52]
2	6-bed 6-step 3-bed 7-step	Proprietary adsorbent	SMROG	17.2/-	99.999 %	87.1 %	99.4 %	94.0 %	-	[53]

* the first and second PSA stages have different regeneration pressures

3.3. Integration strategies

In pre-combustion cases, the gas separation unit is normally located downstream a water-gas shift (WGS) process, which converts CO and H_2O into CO_2 and H_2 to large extent. WGS is essential to increase the CO_2 content in the syngas, which at the entrance of the gas separation units is composed mainly by H_2 and CO_2, with traces of other gases, such as CH_4, CO and N_2. This shifted syngas leaving the WGS process is cooled and desulfurized, normally

through an absorption process, before being routed to the PSA unit. An advantage of pre-combustion CO_2 capture is the high pressure at which the reforming/gasification occurs. It allows avoiding vacuum pressures for the PSA regeneration process. In addition, when common adsorbents are used, the water can be easily removed by condensation down to rather low levels (< 1 %) during the shifted syngas cooling process. This avoids issues with water accumulation in the adsorption columns. Albeit the relatively high CO_2 partial pressure, fully meeting the CO_2 separation targets can be somewhat challenging for a typical PSA process. An additional purification step may be advisable in order to reach higher CO_2 concentrations and, consequently, recovering more H_2. A double flash separation process or a separation by distillation have been proposed [54,55]. The integration of the flash separation has been evaluated through process simulations and demonstrated to be effective with regard to the energy performance of the plant. Even though increasing the compression power requirement, the additional H_2 recovered can be fed to the gas turbine. Such energy input balances out the increased auxiliary power consumption [56]. While the CO_2-rich gas stream leaving PSA is sent to the compression and further treatments section, a second product stream, rich in H_2, is sent to the power island as fuel gas. The power island consists of a gas turbine and a steam bottoming cycle. The composition of the fuel gas stream introduces challenges to the gas turbine operation. The low volumetric lower heating value (LHV), due to the high H_2 content, results in decreased air demand and may lead to compressor stall issues. When an air separation unit (ASU) is present, a convenient procedure involves taking a fraction of the air entering the ASU from the gas turbine compressor. A maximum of 50% integration is recommended, on grounds of reliability and availability [57]. The NO_x emissions need to be controlled with fuel dilution (the high flame speed of H_2 does not allow using air pre-mixing technologies). Common practice is to use nitrogen from the ASU, water (syngas saturation) or a combination of both. Additionally, the large fraction of H_2 in the fuel gas implies a large presence of water in the exhaust gas which in turn increases the thermal exchange coefficients. In order to keep the blades temperatures within the desired limits, a lower turbine inlet temperature has to be used, with adverse effects on the efficiency. It is worth mentioning that, while there is a good experience with gas turbines running on syngas (mixture of carbon monoxide and hydrogen), there are no existing turbines running on hydrogen as the only fuel. E-class gas turbines have been proven on hydrogen rich fuel streams and would probably be offered on commercial basis from various vendors, if asked. However, E-class gas turbines will result in a plant concept with ca. 3 %-points lower electrical efficiency compared to a state-of-the-art F-class machine.

The system integration strategies described refer to a PSA unit processing low temperature shifted syngas (i.e. cold PSA process). Interesting potentials are expected by PSA processes operating at higher temperature (i.e. hot PSA process). In such case, the process configuration remains rather similar, with some substantial differences. The main one consists in the avoidance of the syngas cooling upstream the gas cleanup section. This implies that, when sulfur compounds are present, a hot desulfurization process needs to be considered (e.g. ZnO-based sorbent process [14] or wet gas desulfurization [58]). Further, water cannot be removed effectively from the syngas by condensation. However, the adsorbents used in high temperature PSA processes are generally not negatively affected from the presence of water, which is often used for the regeneration of the adsorption bed. If regeneration using steam as purge gas applies, a proper extraction from the steam cycle has to be planned.

Another option involves the utilization of sorption-enhanced processes (e.g. SEWGS). Within this process framework, the syngas cooling section is again unnecessary. Different degrees of integration between the process units and the power island are possible. The thermodynamic best would involve a tight integration but this penalizes the overall system flexibility [59]. In sorption-enhanced processes H_2S is separated together with CO_2. In order to comply with specification for CO_2 sequestration, H_2S content must be below 200 ppm. Thereby, a downstream desulfurization process should be designed (e.g. H_2S catalytic combustion [11]). Typically, the regeneration of adsorption columns is carried out by means of steam injection, implying the need of steam from the power island.

Only minor modifications in the plant layout are envisaged when PSA-based H_2 production is to be implemented alongside CO_2 capture. Depending on the process configuration selected, an additional PSA stage may be necessary. The system integration strategies of the PSA unit with the other process units of the plant remain quite the same as those previously outlined.

3.4. Performance, limits and potentials

Pre-combustion PSA technology is compared to absorption whether physical (i.e. Selexol solvent) or chemical (i.e. MDEA solvent). Table 7 sums up the outputs of the main studies present in the literature. For each PSA-based system,

the absorption-based counterpart is also reported, in order to allow fair comparisons of different technologies. The performance indicators reported are the net electric efficiency (η_{el}) and the CO_2 recovery (R_{CO2}) or, in some instances, the carbon recovery. The performance attained by the plant integrating a cold PSA process demonstrated to be slightly lower than that of the common absorption-based counterpart, both in terms of net electrical efficiency and CO_2 recovery [10]. This performance gap has some chances to be closed with targeted developments in materials and processes [60]. Table 7 reports a set of results (i.e. IGCC-PSA advanced) regarding a material with properties tailor-made on a specific process configuration. Those simulation outputs do not necessarily represent any existing adsorbent but rather aim to outline possible future advancements in the field. Tuning adsorbent material properties according to given process requirements demonstrated to be critical in order to enhance the plant energy performance on the same level as the absorption-based counterpart. However, the CO_2 recovery hardly meets the 90% target.

The possibility to implement adsorption processes effectively at elevated temperatures opens room for possible performance improvements. Gas cleanup at high temperature avoids the energy losses connected to syngas temperature swing. Net electric efficiencies similar to cold Selexol-based counterparts can be achieved [14] or even higher [61] when the PSA process reaches high levels of H_2 recovery. Sorption-enhanced processes demonstrated to be even more promising. In particular, sorption enhanced water-gas shift (SEWGS) showed to be able to outperform absorption [11,12] and is ready for being tested on a pilot plant installation [62] (with regard to this a SEWGS pilot installation is under construction in Luleå, Sweden, as part of the Stepwise project executed within the European H2020 LCE programme [63]). A comparison with other high-temperature gas separation technologies (i.e. palladium-based membranes) also revealed that SEGWS is the preferred technology for the production of decarbonized fuel, both from coal syngas and natural gas reformate [64]. Table 7 sums up the results from the studies available in the literature, with SEWGS analyzed both in an integrated gasification combined cycle plant and in a natural gas combined cycle. The potential of this innovative system is evident, especially for IGCC applications. Also an economic assessment returned encouraging results [65,66].

Table 7. Performances of power plants implementing pre-combustion CO_2 capture. The nomenclature used refers to CO_2 recovery (R_{CO2}), net electric efficiency (η_{el}) and cumulative energy efficiency (η_{tot}).

Case	CO_2 capture technology	R_{CO2}	η_{el} (LHV)	η_{tot} (LHV)	Ref.
IGCC-absorption 1	Abs. (Selexol)	90.9 %	37.1 %	-	[10]
IGCC-PSA	PSA	86.4 %	36.2 %	-	[10]
IGCC-PSA advanced	PSA	85.2 %	36.9 %	-	[60]
IGCC-absorption 2	Abs. (Selexol)	90.3 %	32.6 %[*]	-	[14]
IGCC-hot PSA	PSA	90.8 % ± 1.7 %	32.7 %[*]	-	[14]
IGCC-absorption 3	Abs. (Selexol)	87.5 %	31.5 %[*]	-	[61]
IGCC-hot PSA	PSA	90.5 %	32.1 %[*]	-	[61]
IGCC-absorption 4	Abs. (Selexol)	90.1 %[**]	36.0 %	-	[11]
IGCC-SEWGS	PSA	90.0 %[**]	39.3 %	-	[11]
NGCC-absorption	Abs. (MDEA)	94.3 %[**]	50.3 %	-	[13]
NGCC-SEWGS	PSA	90.0 %[**]	51.1 %	-	[13]
IGCC-Selexol coproduction	Abs. (Selexol)	92.4 %	31.1 %	36.2 %	[67]
IGCC-PSA coproduction 1	PSA	85.2 %	31.5 %	36.9 %	[52]
IGCC-PSA coproduction 2	PSA	85.7 %	31.3 %	36.6 %	[52]

[*] based on HHV

[**] carbon recovery

The complexity of the PSA arrangements in pre-combustion cases, normally seen as a drawback, may entail opportunities for alternative system configurations. For instance, a well-thought sequence of PSA steps could be able to efficiently produce H_2 with extremely high purity, besides the primary objective of CO_2 separation. A coproduction layout, producing power and pure H_2 with CO_2 capture, can be an option to improve the flexible operation of power

plants. PSA is already the benchmark for H_2 purification but, within this framework, it can be used also for CO_2 separation. Using PSA as the only gas separation technology demonstrated to be an attractive concept, as it can be argued by the system analysis outputs shown at the bottom of Table 7. For those sets of results, the performance is also reported in terms of cumulative energy efficiency, a term which takes into account the two different energy products of these plants. [52].

An issue related to the operability of PSA-based systems was noted. This has to do with the integration between the inherently dynamic PSA process and the other units of the system, especially the gas turbine. Even though proper scheduling of the PSA cycle is designed, some fluctuations of the PSA outlet gas streams characteristics (e.g. flow rate, composition, etc.) are unavoidable and potentially detrimental for some equipment (e.g. the gas turbine). Control strategies to smooth out those variations have to be carefully investigated [68].

4. Conclusions

A comprehensive analysis of PSA as CO_2 capture technology in power plants is carried out in the paper. The different domains that have an influence on the technology viability are taken into account. The analysis encompasses post- and pre-combustion CO_2 capture cases.

The post-combustion analysis revealed that good maturity has been reached in the development of adsorbent materials and separation processes. Zeolites are the current adsorbent of choice in many instances, while MOF and amine-functionalized adsorbents displayed interesting potentials but are still under development. Many processes have been proposed and the challenge is now to achieve the desired CO_2 separation performance with the minimum energy requirement. The integration of PSA into the plant is relatively straightforward and retrofitting of old plants is a viable option. The only system level analysis in the literature suggests that the energy and CO_2 separation performance may be competitive with chemical absorption. However, the the footprint of the PSA unit demonstrated to be much larger than that related to absorption and unlikely acceptable, neither practically nor economically. Further work is suggested to investigate new options to deal with this issue. It would be interesting to assess the advantages coming along with the utilization of structured adsorbents and the feasibility of alternative process frameworks (e.g. moving bed reactors).

The pre-combustion analysis revealed a margin for improvement in the adsorbent materials and in the separation processes. For cold PSA processes, activated carbons are feasible adsorbents, while MOFs are extremely interesting in prospect. Particularly, the possibility to tune their adsorbent properties on specific operating conditions could be critical in order to enhance the process performance. For hot PSA processes, potassium promoted hydrotalcites are the suggested adsorbents. However, the development of more effective adsorbents would be a key step forward. The gas separation process configurations should be developed in parallel to the advancements in the material science. The integration of PSA in the power plants is somewhat more challenging than in the post-combustion case. A higher complexity is involved and different degree of system integration are possible. The performance of cold PSA-based plants showed to be slightly lower than the absorption-based counterpart. However, if a hot gas separation process is demonstrated feasible, PSA may become advantageous in terms of energy efficiency. Sorption-enhanced processes are even more promising, as the available system analyses show a significant performance improvement in comparison with absorption-based systems. Further investigations of these systems are recommended. Additional assessments on the operability of the system need also to be undertaken, especially with regard to the integration between the inherently dynamic PSA process and the other process units. To complete the pre-combustion overview, an interesting concept could be a coproduction layout (i.e. power and H_2 as energy product), which could guarantee a higher degree of flexibility of the plant. In such process framework, preliminary analyses show the utilization of PSA technology as, potentially, the most advantageous option.

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