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CO_2 removal by PSA: an industrial view on opportunities and challenges

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Abstract CO_2 removal from gaseous streams is one of the most important separation tasks in this decade. Adsorption processes can contribute in a wide range to this topic, thus an enormous effort is performed respectively in research and industry. In two scenarios the competitiveness of pressure swing adsorption (PSA) and vacuum pressure swing adsorption technology is assessed: Carbon capture from hydrogen production by steam methane reforming for enhanced oil recovery and CO_2 removal from direct reduction processes for iron making. Additionally, industrial requirements, project as well as operation driven, have to be considered. Robustness and stable operation is as important as optimized captial expenditure and operational expenditure. Considering economical and operational aspects PSA processes are the most attractive alternatives in the presented scenarios.

Keywords PSA · VPSA · CO_2 removal · Carbon capture · EOR

Abbreviations

CAPEX	Captial expenditure
EOR	Enhanced oil recovery
OECD	Organisation for economic co-operation and development
OPEX	Operational expenditure
PSA	Pressure swing adsorption
SMR	Steam methane reformer
VPSA	Vacuum pressure swing adsorption
EOR	Enhanced oil recovery

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1 Mega trend clean energy

While the energy demand of the OECD countries is assumed to be stable up to 2030, the demand of the non-OECD countries will dramatically increase by 65 % from 2010 to 2030.[1] In the energy mix fossil fuels will continue to dominate in the medium term.[2] Efficiency improvement, renewable energies and CCS/CCU (carbon capture and storage/carbon capture and utilization) are the key factors for CO_2 emission reduction schemes.[3]

2 H_2 production and carbon capture options

Traditionally, processes for synthesis gas generation use fossil coal or hydrocarbon based fuels. With the addition of air, water (steam) and energy synthesis gases and CO_2 containing waste streams are produced. Applying renewable primary feeds based on biomass, the CO_2 loop may be closed. Otherwise sequestration (e.g. by utilisation in EOR—enhanced oil recovery) is needed to remove CO_2 from emission as greenhouse gas.

In externally fired SMR based hydrogen production plants three CO_2 containing streams can be identified:

- Stream 1: Shifted synthesis gas upstream the H_2 PSA, low CO_2 content, elevated pressure
- Stream 2: H_2 PSA tail gas, medium CO_2 content at low pressure
- Stream 3: Flue gas from steam reformer burner system, low CO_2 content at low pressure

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[1] US Energy Information Administration.

[2] US Energy Information Administration.

[3] International Energy Agency.

The process conditions of stream 1 allow the application of amine based scrubbing systems and pressure swing adsorption (PSA) or vacuum pressure swing adsorption (VPSA) processes. Due to the high CO_2 concentration of stream 2 only PSA/VPSA systems are applicable, while for stream 3 amine based systems are preferred, but PSA/VPSA systems are under development (Fig. 1).

2.1 CO_2 removal or recovery from shifted synthesis gas by PSA or VPSA

The application of PSA/VPSA systems in the shifted synthesis gas stream (1) is obvious, because this stream is pressurized and therefore additional installation and energy for feed gas pressurization can be avoided.

Figure 2 illustrates the two options PSA or VPSA for CO_2 recovery for EOR application at 150 bar. There is no generally agreed standard for the composition of the CO_2, but CO_2 concentration itself must be above or equal to 95 mol% (Melzer 2007).

With the VPSA option the required CO_2 concentration (on a dry basis) might be directly obtained but only with intolerable H_2 losses. To minimize the H_2 losses a process modification by executing rinse (CO_2 preloading) step(s) is mandatory. It is part of the process optimization from which step the rinse gas is taken, usually it is taken from a medium or low pressure step of the VPSA cycle.

The gaseous wet CO_2 fraction downstream of the vacuum pump has to be compressed from nearly ambient pressure to 150 bar in a multistage compressor. In addition

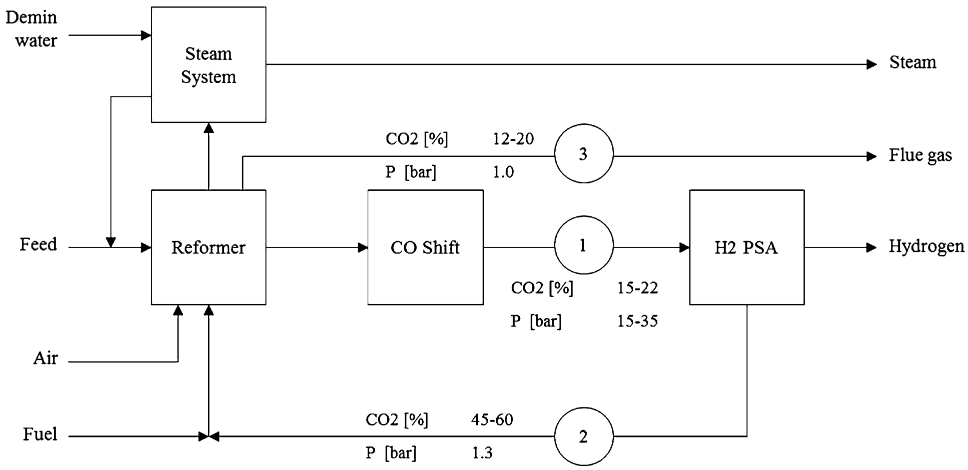


Fig. 1 Carbon capture in SMR (steam methane reforming) based hydrogen plants

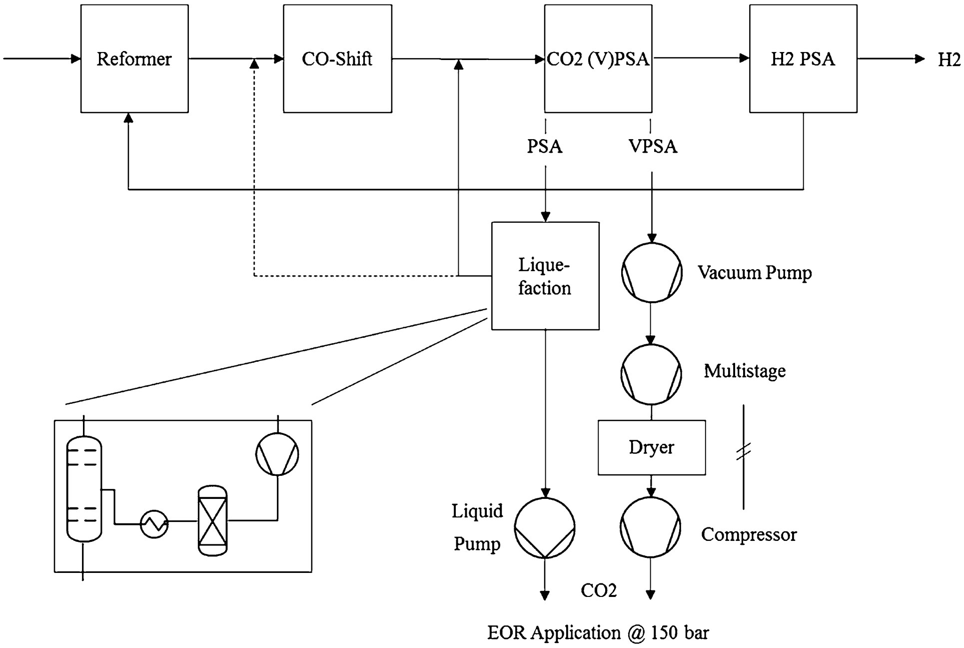


Fig. 2 CO_2 removal or recovery from PSA/VPSA in shifted synthesis gas

to the knock out system a dryer has to be installed to remove the remaining water. Due to the corrosive nature of the wet CO_2 stream, materials resistant to corrosion, e.g. stainless steel, have to be applied in a part of the plant.

The PSA option requires a subsequent liquefaction unit, because the achievable CO_2 concentration is below 95 mol%. The liquefaction unit operates at pressures between 20 and 35 bar. It consists of a compressor, a subsequent drying system, the heat exchanger and a flash drum. The liquefied CO_2 is pumped to the required pressure of 150 bar. In case the flash gases are recycled upstream of the shift reactor or the CO_2 PSA, no H_2 losses will occur.

Characteristics of the VPSA option are:

- For EOR application a subsequent purification process (liquefaction) is not necessarily required
- Reduction of intrinsic H_2 losses into the CO_2 product requires an additional rinse step
- Additional equipment: vacuum pump and an internal recycle compressor for rinse step
- Low pressure gaseous CO_2 product
- Extensive machinery and high energy consumption for compression of gaseous CO_2 to 150 bar

Characteristics of the PSA option are:

- Simple arrangement
- For EOR application a subsequent liquefaction process is required
- No H2 losses, if flash gases from liquefaction are recycled upstream the CO_2 PSA (or even upstream the shift unit)
- Medium pressure liquid CO_2 product
- Moderate energy consumption due to liquids pumping up to 150 bar

An evaluation of the two options reveals that in the present case the PSA is favourable because of the lower energy consumption and the H_2 savings. The following figure illustrates the pressure profile of both options. Finally the recovered CO_2 must be provided at 150 bar, while the CO_2 at the outlet of the PSA and VPSA unit has to be compressed starting from low pressure (Fig. 3).

For the determination of the operating cost for CO_2 compression the following aspects have to be considered:

PSA option:

- Increased flow of CO_2 rich stream by 10–12 % compared to VPSA option due to higher amount of non-CO_2 components
- Compression of gaseous CO_2 to pressure of shifted synthesis gas (pressure drop over liquefaction plant has to be considered)
- Pumping of liquid CO_2 to EOR pressure (150 bar)

VPSA option:

- Compression of gaseous CO_2 from low pressure to EOR pressure (requires extensive machinery)
- Internal recycle compression cost for rinse step has to be added

2.2 CO_2 removal or recovery from H_2 PSA tail gas by PSA or VPSA

While the CO_2 content in the H_2 PSA tail gas is high compared to the other CO_2 containing streams, the pressure is low and therefor a feed gas compression downstream of a PSA or VPSA CO_2 removal unit is mandatory. The additional CAPEX and OPEX do not justify this option compared to the CO_2 removal from the pressurized synthesis gas from economic aspects, but there are some conceptual advantages of this option: The impact on the hydrogen plant is lower, only the reformer burner management system is affected. Therefore it is comparatively easy to retrofit an existing plant.

The arrangement of a CO_2 removal unit downstream of the CO shift affects additionally the H_2 PSA. The required overall H_2 plant availability is 99+ %. As a consequence the plant must continue in operation in case of a failure of the CO_2 removal unit, therefore the adsorbent filling scheme of the layered bed of the H_2 PSA must be able to deal both with CO_2 reduced and the full CO_2 containing feed. In normal operation with CO_2 reduced feed the capacity of dedicated layer for CO_2 is not fully charged, this leads to an intrinsic loss in H_2 recovery in the range of 0.5–1 %-point.

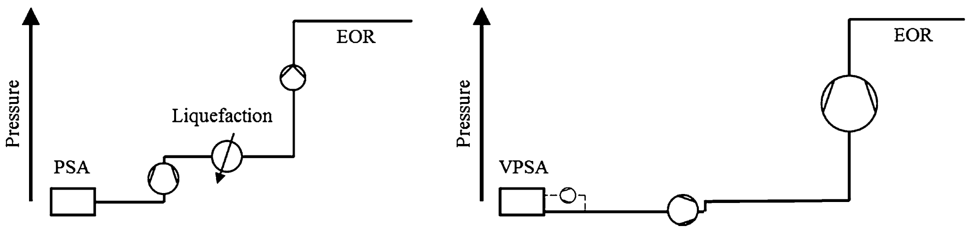


Fig. 3 Illustration of the pressure profile of PSA and VPSA option

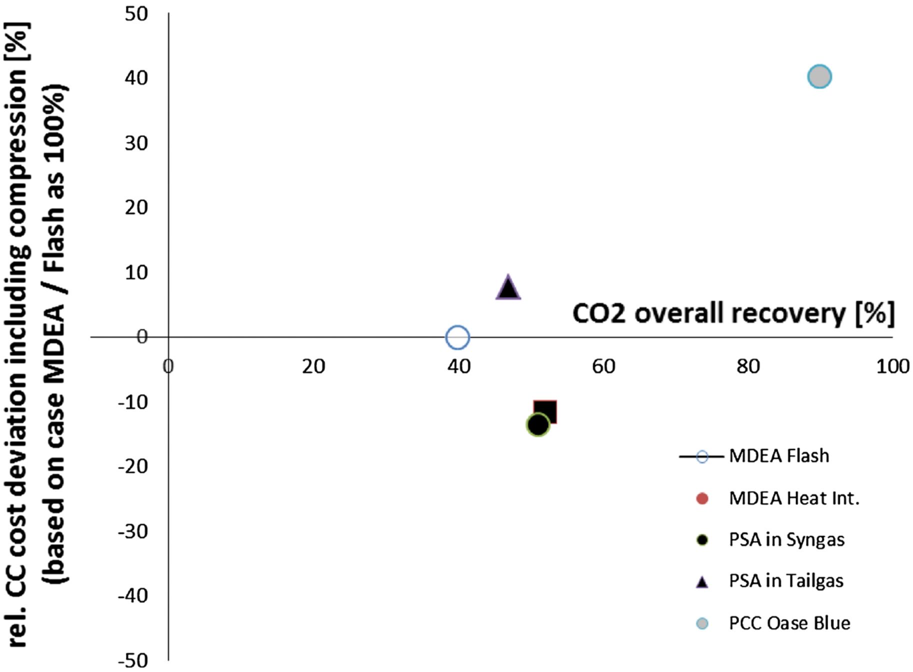


Fig. 4 Assessment of carbon capture costs (incl. compression) from synthesis gas production for enhanced oil recovery; *baseline* MDEA/flash

2.3 Assessment of adsorptive and absorptive processes for carbon capture from H_2 production by SMR

The assessment bases on a midsize 50,000 Nm^3/h hydrogen production plant which consists of a natural gas fed steam methane reformer. At position 1 of Fig. 1 (downstream shift reactor) two setups of amine scrubbing unit (with and without heat integration) and a PSA unit have been examined, at position 2 (H_2 PSA tail gas) a PSA unit and at position 3 (SMR burner system flue gas) a PCC amine system. At minimum 90 % of the contained CO_2 of the stream at the respective position has to be removed with a purity of min. 95 mol%. The CO_2 has to be compressed to 150 bar for EOR application. The synthesis gas composition is as follows:

Component	Concentration [mol%]
H_2	75
N_2	0.2
CO	4
CO_2	16
CH_4	4.5
H_2O	0.3

The assessment reveals that PSA technology is competitive even in comparison with sophisticated amine systems. Since the synthesis gas is pressurized, the operating costs of the PSA system are negligible compared to the effort of solvent regeneration and balance of solvent losses of amine systems. Additional costs for the PSA option have to be considered for the cold production in the subsequent liquefaction unit. The efforts for compression have been discussed in chapter 2.1; in this case the amine option is comparable to the VPSA option (compression of gaseous CO_2 from low pressure).

The competiveness of a PSA system depends mainly on availability of steam cost for solvent regeneration of the amine system. The recently developed amine system for post combustion capture (Kandziora 2012) yields the highest CO_2 recovery rates at extensive costs (Fig. 4).

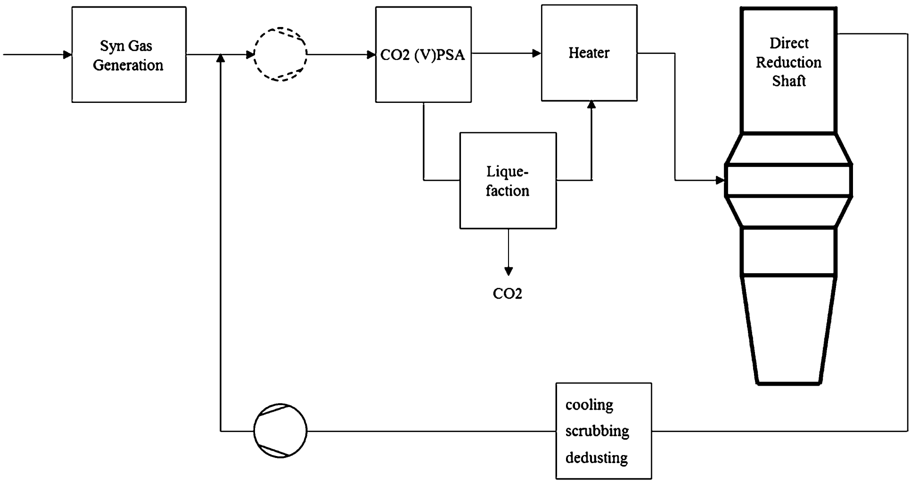
3 CO_2 removal from iron making processes

As an alternative to traditional iron making processes by blast furnaces direct reduction processes have been developed. The economic advantage of the direct reduction processes is the substitution of coke by less expensive coal. The reduction potential is provided by synthesis gas.

The conversion of the synthesis gas reduction components H_2 and CO in the shaft is comparatively low. Therefore, the top gas leaving the shaft is recycled and fed to the generated synthesis gas. The reduction products CO_2 and H_2O have to be removed down to a level of below 2 mol% and the reduction gas has to be heated to 800–900 °C before entering the shaft (Fig. 5).

The application of a PSA or VPSA system in comparison to amine based scrubber systems is advantageous because of the following reasons (Benkmann et al. 2005):

Fig. 5 Direct reduction process—gas treatment



- Simultaneous removal of CO_2 and H_2O
- Partial removal of inerts (N_2, Ar) decreases the recycle gas flow
- PSA or VPSA tail gas is used for reduction gas preheating
- Waste heat from reduction shaft top gas is used for additional reduction gas preheating instead of steam generation for solvent regeneration (usually no other steam source available)

In the rough and dusty environment of iron and steel production PSA technology is preferred compared to VPSA systems because no sensitive vacuum pumps are required.

This technology was recently extended to traditional, N_2 reduced and N_2 free blast furnace processes for partial substitution of coke by upgrading and recycling of the oven top gas (De Connick 2012).

4 Industrial requirements on CO_2 removal units

Project driven requirements on the design and optimization of CO_2 removal units are a high performance, both optimized CAPEX and OPEX and good product purity. Additionally—and not always 100 % aligned with project driven requirements—operational requirements have to be satisfied. The plant must operate with a high on stream factor, robust and stable during variable operating conditions, and be well prepared in case of wrong operation or upset conditions.

This means for the example of hydrogen production by SMR: In frequent cases there is no redundancy installed or hydrogen network available. If the H_2 plant fails the H_2 consumer (a hydrotreater or hydrocracker) may also get out of operation as a worst case scenario. It may take days until the respective product is according to specification after restart which results in a massive the loss of production. Since H2 PSA units usually have a 99+ availability, the CO2 removal unit may not decrease the availability number of the plant.

5 Conclusions

Pressure swing adsorption and VPSA technology represent a promising alternative for CO_2 separation. The processes are comparatively simple and flexible. They are favourable if the feed gas is pressurized, but there are applications, e.g. in iron making, where the technologies are competitive even if the feed has to be pressurized. In some applications the combination of CO_2 removal and drying is advantageous. Especially PSA processes are robust and do not need additional rotating equipment if feed gases are under pressure. This aligns with industrial requirements from project and operation.

References

Benkmann, C., et al.: DE 10 2005 010 050 A1 (2005)

De Connick, E., et al.: Presentation on ULCOS SC-21 meeting. Brussels (2012)

Kandziora, C.: New solvent based post combustion CO_2 capture in power plants: a joint development and commercial application. COAL-GEN EUROPE, Warsaw (2012)

Melzer, L.S.: CO_2 Transport—building on the current framework to meet the demands of widely deployed, commercial scale CCS systems, 6th annual conference on carbon capture and sequestration, Pittsburgh (2007)