PG&E GAS R&D AND INNOVATION

Pressure Swing Adsorption Technical Analysis

7/2/2018

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Table of Contents

What is Pressure Swing Adsorption (PSA) 4
Drawbacks of PSA 6
Economic Benefits 7
Common Adsorption Materials 7
Companies that commercialize PSA technology 12
References 12

Table of Figures

Figure 1 Graph showing the relationship between adsorbed CO_2 and pressure 4
Figure 2 Illustration of the Skarstrom Cycle 6
Figure 3 Picture of zeolites 8
Figure 4 Picture of activated carbon 8
Figure 5 Picture of silica gel and aluminum oxide 9
Figure 6 Picture of molecular sieves 9
Figure 7 PSA process diagram 10
Figure 8 List of compounds and their adsorption force strength 10

Table of Tables

Table 1 Comparison of different biogas upgrading technologies 11

What is Pressure Swing Adsorption (PSA)

A technology used to separate and purify components of a gas mixture under pressure according to each component's molecular characteristics and affinity for a specific adsorbent material. Specific adsorptive materials preferentially adsorb a target gas at pressure. The pressure is then swung low to desorb the adsorbed material, leaving a purer gas.

- Under high pressure, gases tend to be attracted to solid surfaces, a phenomenon known as adsorption. Gas components are separated because different gases are attracted to different solid surfaces at different intensities.
- Since heating and cooling is not part of the process, the cycle time can be in the range of minutes. The adsorbent material has a very long lifetime compared to other upgrading technologies.
- Flow rates range from small scale at 10 m^3/hr to larger scale at 10,000 m^3/hr. (Grande, 2011)
- An attractive gas upgrading technology due to compactness of the equipment, low energy requirements, low capital costs, and simple operation (Augelletti, 2017).

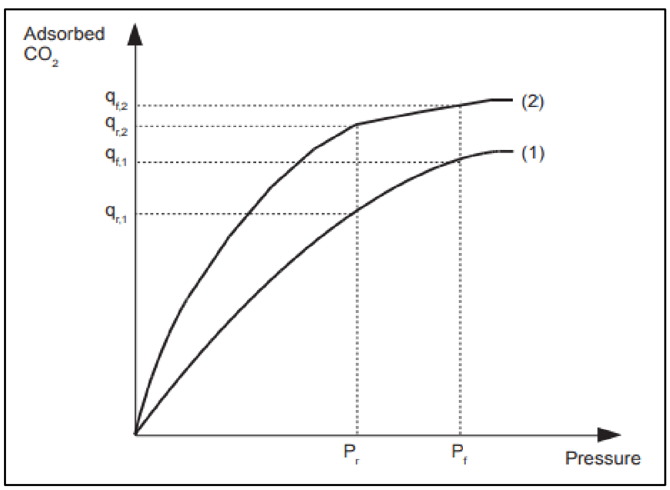

Figure 1 Graph showing the relationship between adsorbed CO2 and pressure (Bauer, 2012)

A methane recovery greater than 99% can be obtained with an energy consumption of 1250 kJ per kg of biomethane. Mixing blowdown gas with raw biogas, methane recovery can be increased by up to 5%. (Petersson, 2009)

There is a variant to PSA called rapid cycle PSA which will operate at a speed of 5-20 times conventional PSA. Rapid cycle PSA is carried out by using multi-port selector rotary valves and a many smaller adsorption chambers. These systems are typically smaller in size, have lower capital costs, lower pressure drops, and higher throughputs. The downside of rapid cycle PSA is the methane recovery rate. One of the largest suppliers of rapid cycle PSA systems is Xebec Inc. which can maintain a capacity of 150 to 5,000 Nm^3/hr of biogas. (Xebec Adsorption, 2017)

Four Steps (Skarstrom Cycle): (Bauer, 2012)

- **Pressurization:** The raw biogas is pressurized in the vessel to 4-10 bar.
- **Feed/Adsorption:** The raw biogas is fed into the tank and the targeted compounds start to become attracted to the solid adsorption surface as the methane flows through the column. When the adsorption bed is saturated, the feed is closed and the blowdown phase is initiated.
- **Blowdown:** Once the adsorption bed is saturated, and the upgraded methane was moved through, the feed is close. The pressure inside the vessel is lowered considerable to desorb the carbon dioxide from adsorbent and the carbon dioxide rich gas is pumped out of the vessel.
- **Purge:** At the lowest column pressure, the purge is initiated.

Since this cycle contains four phases, it is common for PSA units to have four columns. The PSA cycle usually lasts between 2-10 minutes long.

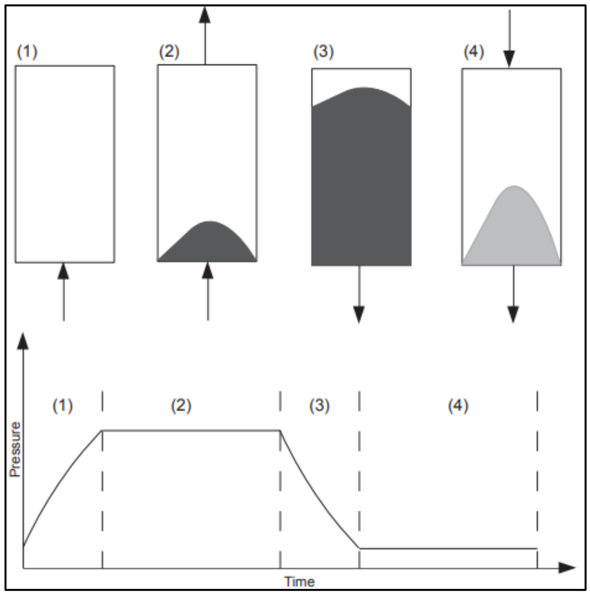

Figure 2 Illustration of the Skarstrom Cycle (Bauer, 2012)

The vent gas can be torched (if the methane content is high enough), or it can be catalytically oxidized in a special vessel to prevent methane leakage. Another option is for the vent gas to be combined with the raw biogas to be combusted to produce heat to be used locally.

Typically, multiple vessels are used in parallel to improve energy efficiency and to smooth gas production rate.

Drawbacks of PSA

Compared to other upgrading technologies, there is a relatively high amount of methane that is captured in the off gas rather than the captured gas. This off gas with require further upgrading if you are looking for a pure CO_2 stream. Methane recovery rates can range from 60 to 80%. The balance of methane leaves the system in the tail gas with the desorbed CO_2. This tail gas can be upgraded further by recycling back into the PSA system.

Moisture will need to be removed prior to biogas entering PSA system because water can block the adsorbent's micropores, reducing system performance. Could require high levels of electricity to achieve high pressure levels used in the process. (Grande, 2011)

Economic Benefits

- Low energy consumption, does not consume water or create contaminated waste water. Does not require any heat.
- High purity levels
- Relatively low investment and maintenance costs

Common Adsorption Materials

Adsorbents are usually very porous materials because of their large surface areas. Adsorbent material will need to be replaced once it is filled or when it has reached its regenerated limit. In general, adsorbent material require minimal maintenance and are inexpensive. The setup is simple: adsorbent material is place in a drum with a gas inlet and an outlet.

The two main criteria for an attractive adsorption material:

- Have a high selectivity to CO_2. We want the material to have a higher affinity towards CO_2 than methane.
- Be of a material that has pores that CO_2 can penetrate their structure, while larger CH_4 molecules have size limitations to diffuse through them. These materials are called kinetic adsorbents because their selectivity mechanism is through diffusion constraints.

Zeolites:

- One of the most common adsorbents used in PSA
- Naturally occurring or synthetic silicates with uniform pore size and dimensions.
- They work best with polar compounds such as H2S, SO2, NH3, carbonyl sulfide, mercaptans

Figure 3 Picture of zeolites

https://www.igb.fraunhofer.de/en/research/competences/physical-process-technology/heat-and-sorption-systems/sorptive-heat-storage/projects/hipel.html

Activated Carbon:

- Most commonly used adsorbent due to low cost, widespread availability, high surface area, and adsorptive affinity to hydrogen sulfide, carbon dioxide, moisture, VOCs, halides, and siloxanes.
- Surface area of 500 – 2500 m^3/g (usually 1500)
- Capacity of 20-25% loaded by weight of H_2S

Figure 4 Picture of activated carbon

https://www.hmicronpowder.com/industries/chemical/activated-carbon

Silica Gel and Aluminum Oxide:

- These can remove siloxanes and moisture by trapping them within their crystalline structure.
- Regenerate by exposing to high temperature and high pressure.

Figure 5 Picture of silica gel and aluminum oxide

http://www.preservationcare.com/shop/silica-gel

Molecular Sieves:

- Carbon molecular sieves are kinetic adsorbents that have micropores allowing contaminant molecules to penetrate faster than methane.
- Note that activated carbon and zeolites can also act as molecular sieves.

Figure 6 Picture of molecular sieves

http://www.kuraray-c.co.jp/en/products/device.html

A "dry" method, meaning there are no solvents or washing liquid. Based on columns filling with adsorption materials which operate in a rotating/non-continuous mode.

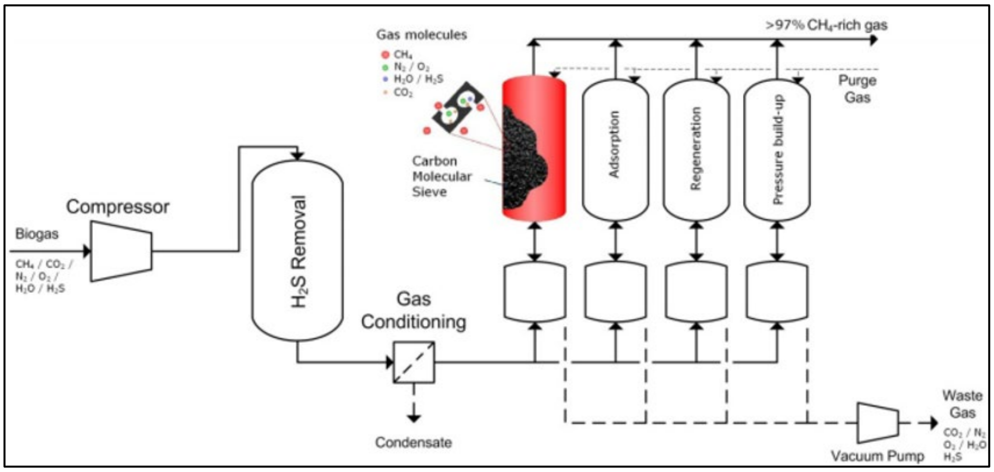

Figure 7 PSA process diagram (Kaffka, 2014)

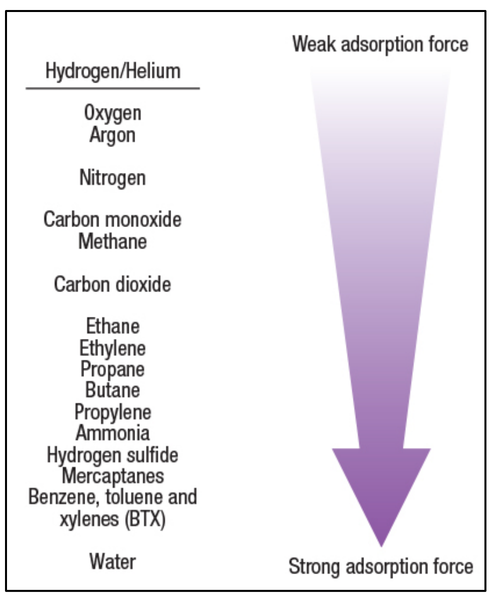

Figure 8 List of compounds and their adsorption force strength (Keller, 2016)

Table 1 Comparison of different biogas upgrading technologies (Langerak, 2018)

	Pressurized Water Scrubbing (PSW)	Catalytic Absorption	Pressure Swing Adsorption (PSA)	Membrane Separation (MS)	Cryogenic Liquefaction (CL)	Unit
Produced Gas Quality	98	99	97-99	99	99.5	% CH_4
Methane Slip	1	01 – 0.2	1 -3	0.3 – 0.5	0.5	%
Electrical Use	0.23 – 0.25	0.15 – 0.18	0.25	0.21 – 0.24	0.35	kWh/feed
Reliability/Up Time	96	94	94	98	94	kW/Nm^3 product
Turn Down Ratio	50 – 100	50 – 100	85 – 100	0 – 100	75 – 100	%
CAPEX	Medium	Medium	Medium	Low	High	%
Operations Cost	Low	Medium	Medium	Low	High	
Foot Print	Large	Large	Medium	Small	Large	
Maintenance Needed	Medium	Medium+	Medium+	Low	High	
Ease of Operation	Medium	Medium+	Medium	Easy	Complex	
Consumables/Waste Streams	AC*3/Water	AC*3/amines	AC*3/adsorbents	AC*3/none	AC*3/None	AC = Activated Carbon

Companies that commercialize PSA technology

- Carbotech (www.carbotech.de)
- Acrona (www.acrona-systems.com)
- Cirmac (www.cirmac.com)
- Gasrec (www.gasrec.co.uk)
- Xebec Inc. (www.xebecinc.com)
- Guild Associates (www.moleculargate.com)

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