Biofuels

Lec 3-Biogas: part 3

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Content

- **Upgrading techniques:**
  - **Chemical absorption**
  - **High pressure water scrubbing**
  - **Pressure swing adsorption**
  - **Cryogenic separation**
  - **Membrane separation**

Need for the Biogas Enrichment and Bottling

- Potential of biogas is not fully utilized and commercialized so far.
- For commercialization, its area of application may widen; from cooking fuel to vehicle fuel.
- For use as a vehicle fuel, it should be bottled like CNG.
- Before bottling, it should enriched in methane content from 55 % to 95 %; similar to NG.

Upgrading techniques

- Chemical absorption
- High pressure water scrubbing
- Pressure swing adsorption
- Cryogenic separation
- Membrane separation

Process
  Input/output
Cost estimation
  Investment costs
  Running costs
Waste streams
Ease of operation

$$\text{Output} = \frac{\text{input} \cdot \%CH_4 \cdot \text{yield}}{\text{purity}}$$

$$\text{Price per Nm}^3 \text{ biogas} = \frac{\frac{\text{investment}}{\text{depreciation period}} + \text{investment} \times \text{interest rate} + \text{running costs}}{\text{Nm}^3 \text{ produced biogas per year}}$$

CO_2 & H_2S Removal Processes from Biogas:

S. No.	Method	Advantages	Disadvantages
1.	Absorption in Water	One of the easiest and cheapest methods for CO_2 removal. Recommended for rural application.	Water pumping load is high. CO_2 can not be recovered
2.	Absorption by Chemicals	The chemical absorbents are more efficient in low pressure and can remove CO_2 to low partial pressures in treated gas.	Regeneration of the solvent requires a relatively high energy input. Disposal of by-product formed due to chemical reactions is a problem.
3.	Pressure Swing Adsorption	By proper choice of the adsorbent, this process can remove CO_2, H_2S, moisture and other impurities.	Adsorption is accomplished at high temperature and pressure. Regeneration is carried out by vacuum. It is a costly process.
4.	Membrane Separation	Modular in nature and separate CO_2 and CH_4 effectively.	High pressure requirement. The processing cost is also high.
5.	Cryogenic Separation	Allows recovery of pure component in the form of liquid, which can be transported conveniently	High cost involved makes it impractical for Biogas applications.
6.	Chemical Conversion	Extremely high purity in the product gas.	Process is extremely expensive and is not warranted in most Biogas applications.

CO_2 & H_2S Removal Processes from Biogas:

- Among various methods of enrichment i.e. Chemical absorption, Pressure Swing Adsorption (PSA), membrane separation;
- Water scrubbing (the use of pressurized water as an absorbent liquid) is found to be a suitable method for biogas enrichment in rural areas.
- It is simple, continuous and cheap process compared to other processes and also absorb H_2S.
- Enriched biogas can further compress up to 20 MPa pressure for optimum gas storage in cylinders.
- It is essential to have more energy per unit volume of compressed biogas and to get rid of the corrosive effect of H_2S.

Biogas Enrichment and Bottling

- For economic viability of biogas bottling, its availability should be in large quantity.
- Plants linked with Dairy (350 cattle or more), sewage treatment plants are suitable for this work.
- Biogas bottling may start new business venture in villages. Thus, open up new era of employment and income generation for village people.
- Biogas manure enhances the organic content of soil, thereby increases water holding capacity of soil.

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High pressure water scrubbing

- Carbon dioxide is more soluble in water than methane.
- This phenomenon is employed to remove CO_2 from biogas in water scrubbing technologies.
- Biogas is fed to a column where it is "washed" with counter-current water that
- is sprayed from the top of the column.
- The column is normally filled with some material to enhance the interface area promoting CO2 absorption.
- The CO2 is dissolved in the water that is then pumped to a "regeneration column" where CO2 is released.
- The regeneration of the water scrubbing process can be carried out at higher temperatures or at lower pressures
- The solubility of CO_2 in water strongly increases at lower temperatures. In order to reduce pumping energy, the water should be available at low temperatures

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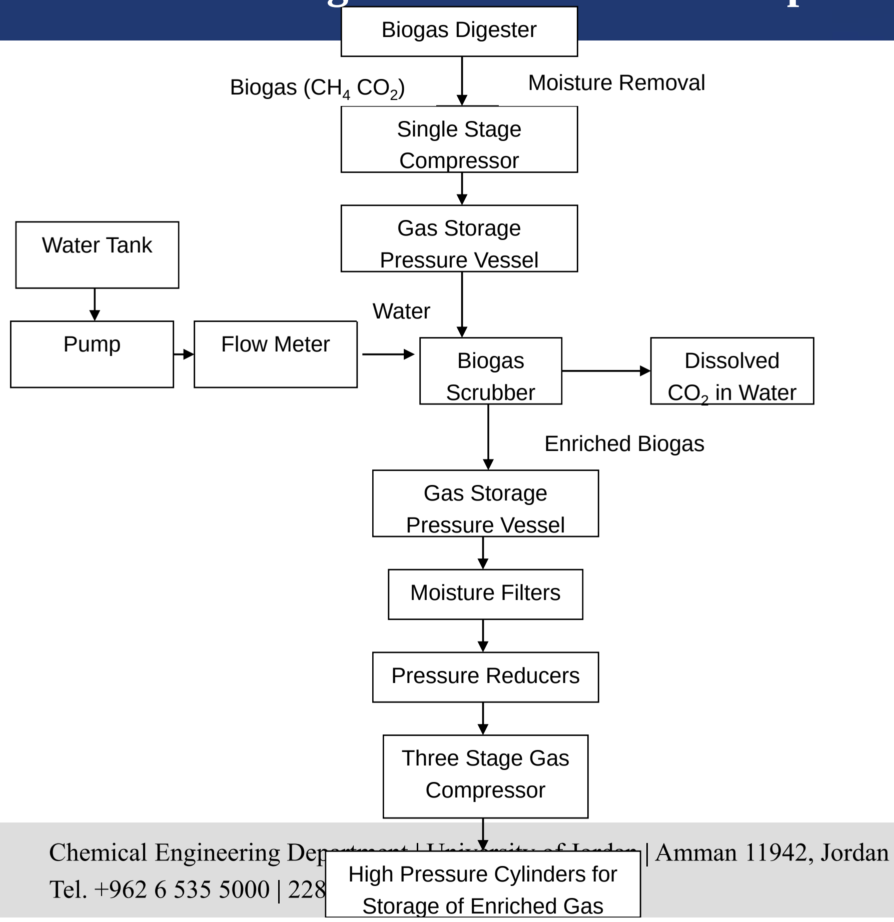
Design of Water Scrubbing System

- Water scrubbing method is found most suitable for biogas enrichment in rural areas.
- Water is good solvent for CO_2.
- The solubility of CO_2 in water is governed by variation in pressures and temperatures.

System Operation

- Raw biogas is compressed up to 1.0 MPa pressure to enhance solubility of CO_2 in water.
- Pressurized biogas is sent into bottom section of the scrubber.
- Packing material is used to enhance the contact time (interfacial area) between gas and water.
- Pressurized water is sprayed from top to absorb the CO_2 from pressurized biogas.

Process flow chart of biogas enrichment and compression system



Biogas Enrichment and Bottling System

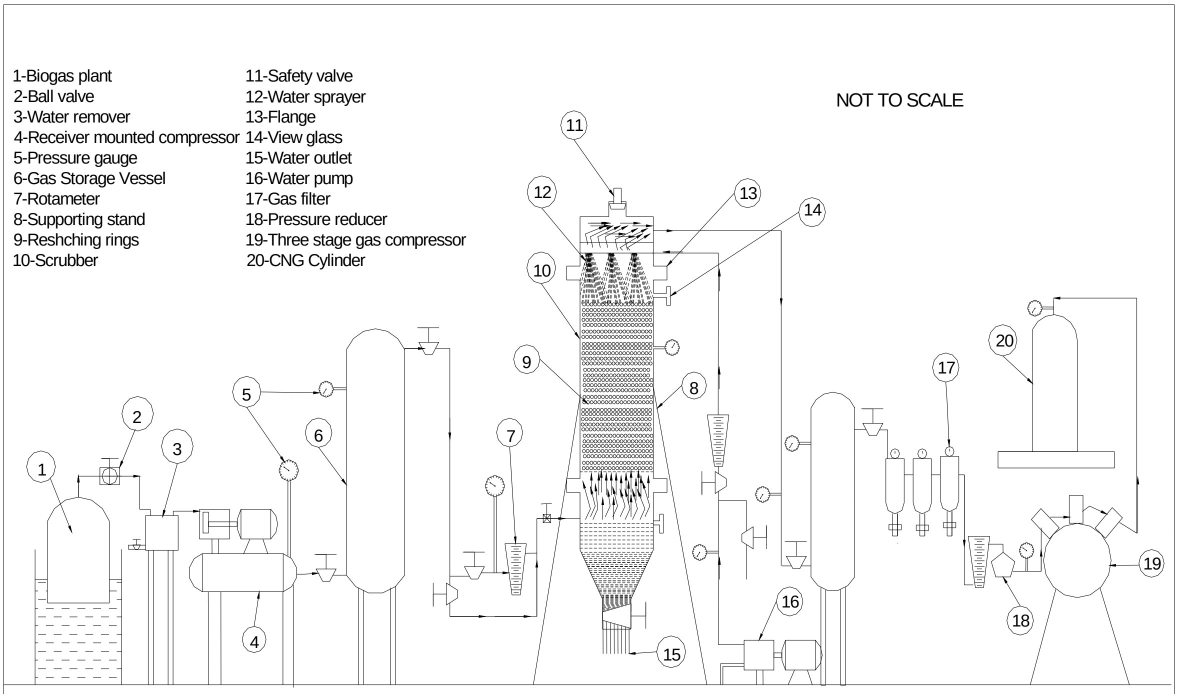


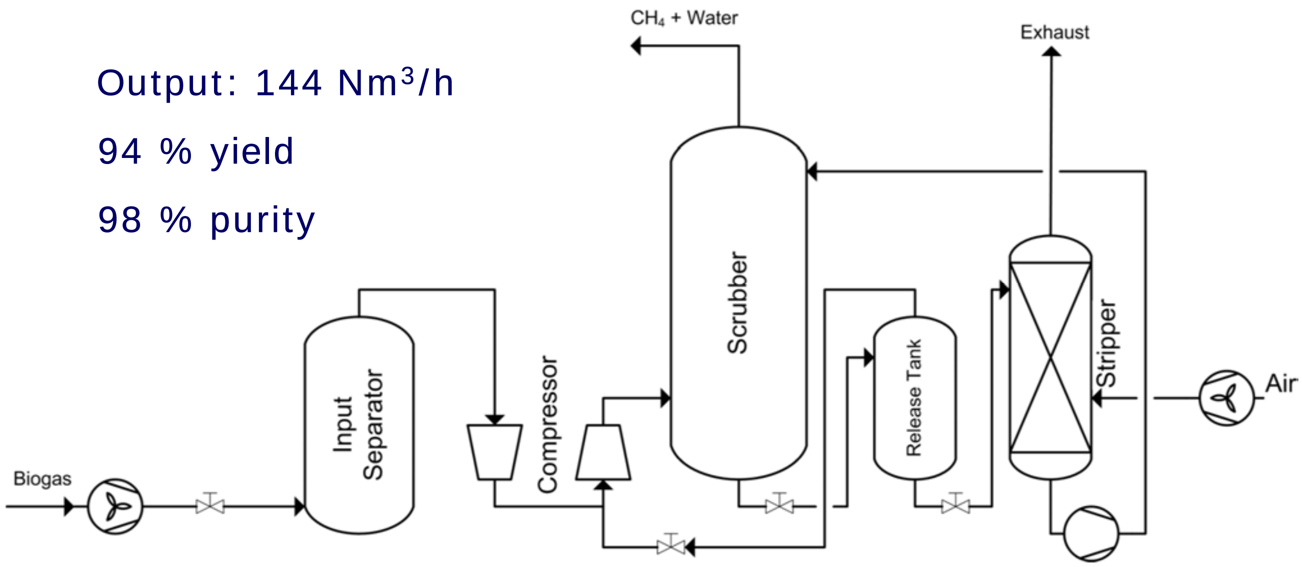
Fig.1: Experimental setup for biogas purification and bottling

High pressure water scrubbing

Output: 144 Nm³/h

94 % yield

98 % purity



High pressure water scrubbing

Cost estimation

	HPWS
Investment costs (€)	440,000
Running costs (€)	120,000
Price per Nm^3 biogas (€)	**0.15**

Chemical absorption (I)

- It is possible to use other chemicals to absorb CO_2
- The technology is also composed by absorption tower where the chemical solvent is flushed to selectively absorb CO_2
- The saturated absorbent is then heated in a regeneration tower, releasing CO_2
- The selection of the solvent for this process is quite important since the "energy" of CO_2 absorption dictates the final consumption of energy of the system.
- Chemicals which strongly absorb CO_2 (like amines) are more suitable to upgrade methane with relatively low content of CO_2 to a very high purity.
- Different examples of physical absorbents are: methanol, Selexol, Rectisol, Genosorb, Morphysorb

Chemical absorption (I)

- The H_2S was removed by means of chemical absorption in an iron-chelated solution catalyzed by Fe/EDTA
- The process:
  - Has a high efficiency of H_2S removal,
  - the selective removal of H_2S and the low consumption of the chemicals because iron chelated solutions functions as a pseudo-catalyst that can be regenerated.
  - Convert the H_2S into a more stable or valuable product (into S).
  - The advantage of these processes is the conversion of a pollutant into a chemical product or at least a solid residue that can be disposed of easily and safely.

Chemical absorption (I)

- In processes based on iron chelating, H_2S is initially physically absorbed into water undergoing the dissociation according to reactions

$$H_2S\ (g) + H_2O \Leftrightarrow H_2S\ (aq) \qquad (1)$$

$$H_2S\ (aq) \Leftrightarrow H^+ + HS^- \qquad (2)$$

$$HS^- \Leftrightarrow H^+ + S^{-2} \qquad (3)$$

- The formation of S occurs by means of sulphide oxidation by the chelated iron according to the reaction described

$$S^{-2} + 2Fe^{+3} \Leftrightarrow S^0 + 2Fe^{+2} \qquad (4)$$

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- Regeneration of the aqueous iron-chelated solution occurs by means of its oxygenation, followed by conversion of the pseudo-catalyst into its active form Fe^{+3}

$$\tfrac{1}{2}\ O_2\ (g) + H_2O\ (l) \rightarrow \tfrac{1}{2}\ O_2\ (aq) \qquad (5)$$

- This is followed by conversion of the pseudo-catalyst into its active form Fe^{+3}

$$\tfrac{1}{2}\ O_2\ (aq) + 2Fe^{+2} \rightarrow 2Fe^{+3} + 2OH \qquad (6)$$

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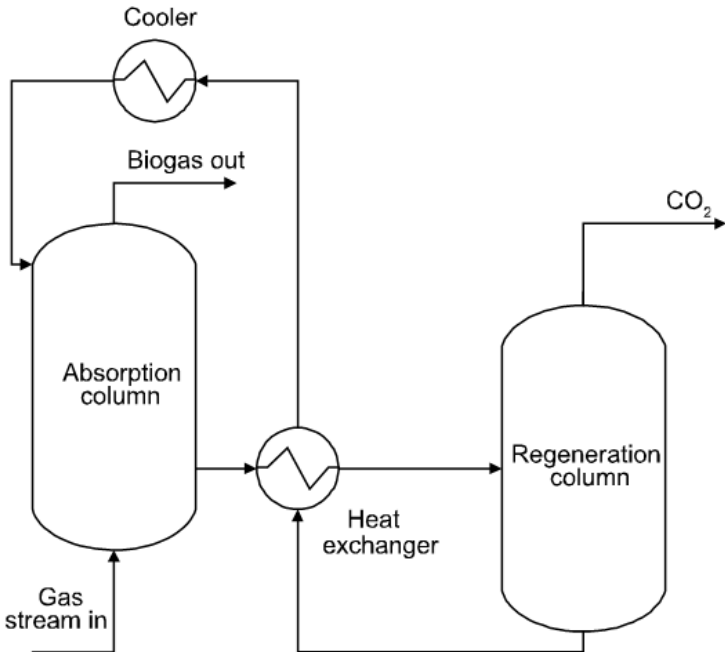
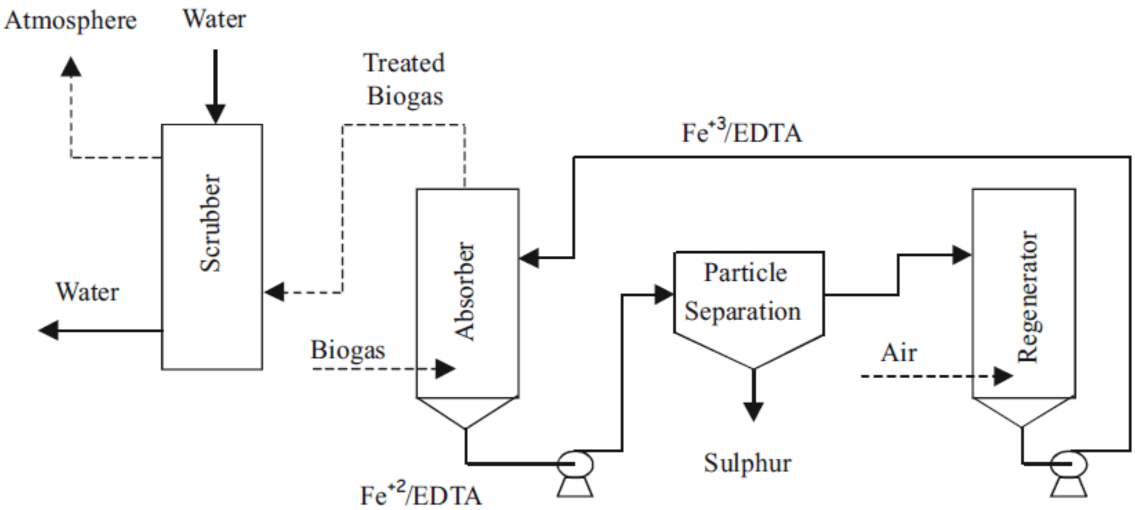
Chemical absorption (I)

Absorption of CO_2



Chemical absorption (I)



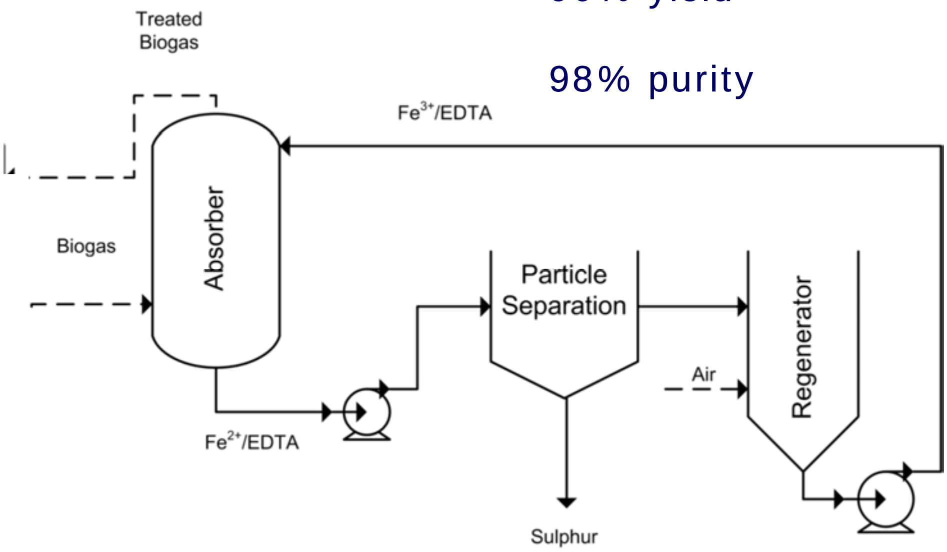
Chemical absorption (II)

Combined output: 137 Nm^3/h

90% yield

98% purity

Absorption of H_2S



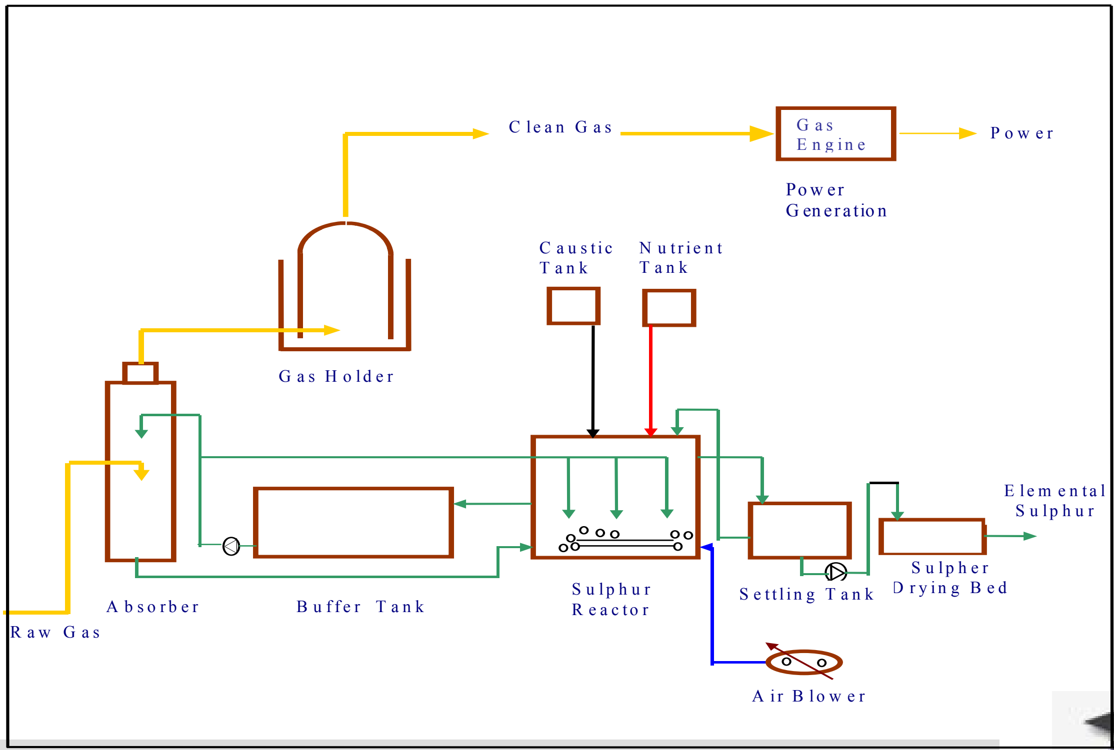
Chemical absorption (III)

Cost estimation

	CO_2 absorption	H_2S absorption	Total upgrading process
Investment costs (€)	353,000	516,000	869,000
Running costs (€)	134,500	99,500	179,500
Price per Nm^3 biogas (€)	0.17	0.16	**0.28**

Bioskrubber: Biological H_2S Removal System

Process Flow Diagram



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Bioskrubber: Biological H_2S Removal System

- Bioskrubber is a biological caustic scrubber to remove H_2S from biogas, in which the spent caustic solution is continuously regenerated in the bioreactor

Equation No 1

$$H_2S_{gas} + OH^- \longrightarrow HS^-_{liquid} + H_2O$$

Equation No 2

$$HS^- + 1/2O_2 \longrightarrow S^o \downarrow + OH^-$$

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Advantages

- Clean bio-technology for H_2S cleaning.
- Low operating cost of biogas – up to 92% caustic recycled.
- Successful commercially operating plants for last 8 years.
- Projects using BIOSKRUBBER PROCESS worth 30 MW of power successfully commissioned.
- Very high H_2S removal efficiency - over 99%.
- H_2S reduction to less than 250 ppm guaranteed.
- No expensive catalyst and chemical required.
- Operation at ambient temperature, pressure and PH between 8 and 8.5 .
- Elemental SULFUR as bi-product with 90% purity.

Additional benefits of H_2S removal

Impact On Surrounding air.

- H_2S is Highly Corrosive – Can damage other equipment's and expensive instruments in the vicinity.
- Health Hazard and odour nuisance.

Pressure swing adsorption (I)

- Pressure Swing Adsorption (PSA) is the second most employed techniques for biogas
- In a PSA unit for biogas upgrading, an adsorbent material is subjected to pressure changes to selectively adsorb and desorb CO_2
- biogas is compressed to a pressure between 4-10 bar and is fed to a vessel (column) where is putted in contact with a material (adsorbent) that will selectively retain CO_2
- The adsorbent is a porous solid, normally with high surface area.
- Most of the adsorbents employed in the commercial processes are carbon molecular sieves (CMS) but also activated carbons, zeolites and other materials (titanosilicates) are employed.
- The purified CH_4 is recovered at the top of the column with a very small pressure drop.

Pressure swing adsorption (II)

- After certain time, the adsorbent is saturated with CO_2, and the column needs to be regenerated by reducing the pressure (normally to vacuum for biogas upgrading).
- The adsorption of H_2S is normally irreversible in the adsorbents and thus a process to eliminate this gas should be placed before the PSA
- Alternatively, depending on the choice of the adsorbent, the humidity contained in the biogas stream can be removed together with CO_2 in the same unit.
- Multi-column arrays are employed to emulate a continuous process.
- For small applications subjected to discontinuities, a single column with storage tanks may be used.
- One of the most important properties of the PSA process is that is can be adapted to biogas upgrading in any part of the world since it does not depend on the availability of cold or hot sources

Pressure swing adsorption (II)

➢ The material selected should at least satisfy one of two criteria:

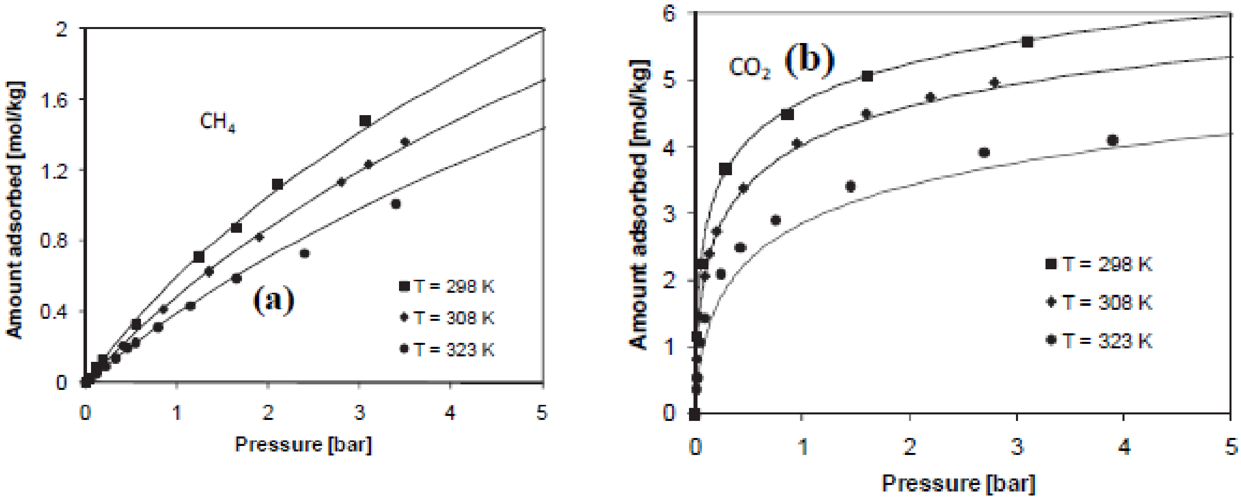
i. Have a higher selectivity to CO_2 :

- This gas should be more "attached" to the surface of the material than CH_4; in most solids CO_2 can create stronger bonds with surface groups than CH_4.
- This kind of materials will be termed as equilibrium-based adsorbents since its main selectivity is due to differences of interaction forces between CO_2 and CH_4 with and the surface.

ii. The pores of the adsorbent:

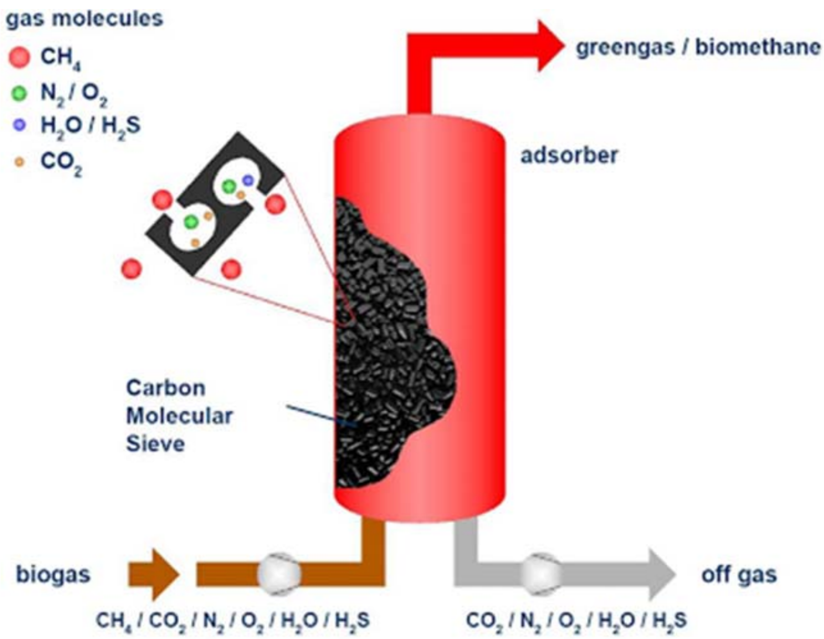
- It can be adjusted in such a way that CO_2 (kinetic diameter of 3.4 Ǻ) can easily penetrate into their structure while larger CH4 molecules (kinetic diameter of 3.8 Ǻ) have size limitations to diffuse through them.
- These materials will be termed as kinetic adsorbents since its main selectivity is due to diffusion constrains.

Pressure swing adsorption (II)

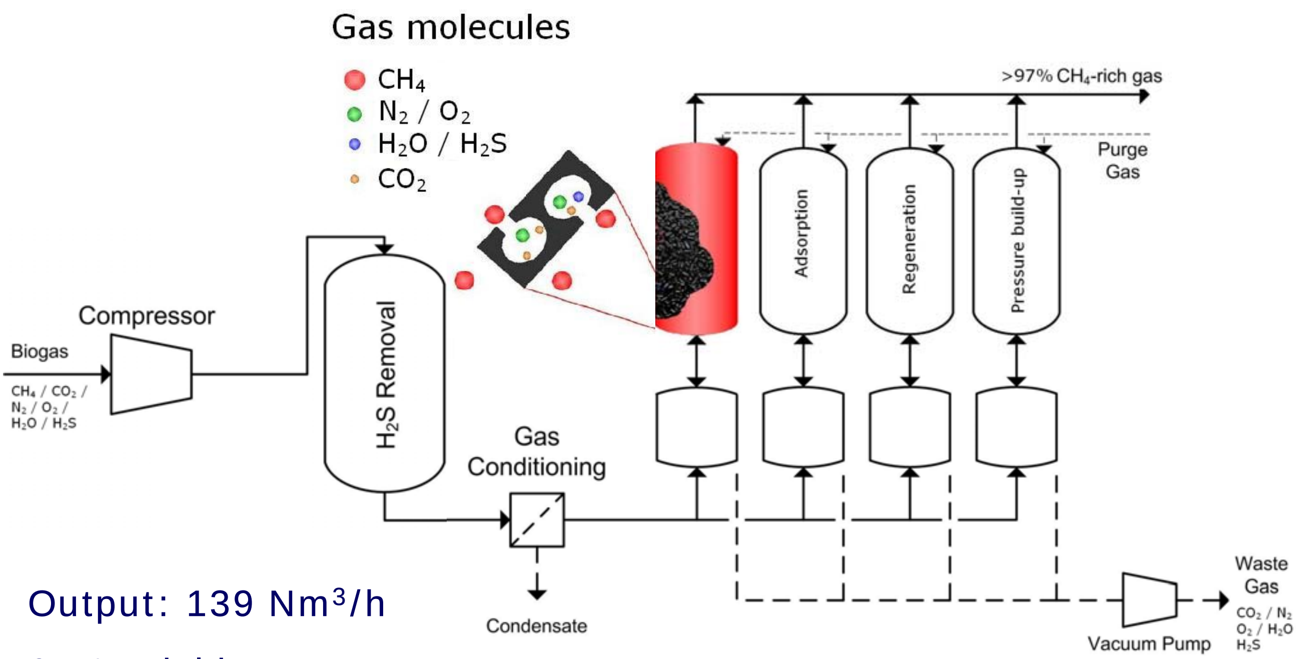


Adsorption equilibrium of CO_2 (a) and CH_4 (b) on zeolite 13X at 298, 308 and 323 K

Pressure swing adsorption (II)



Pressure swing adsorption (II)



Output: 139 Nm^3/h

91 % yield

98 % purity

Pressure swing adsorption (III)

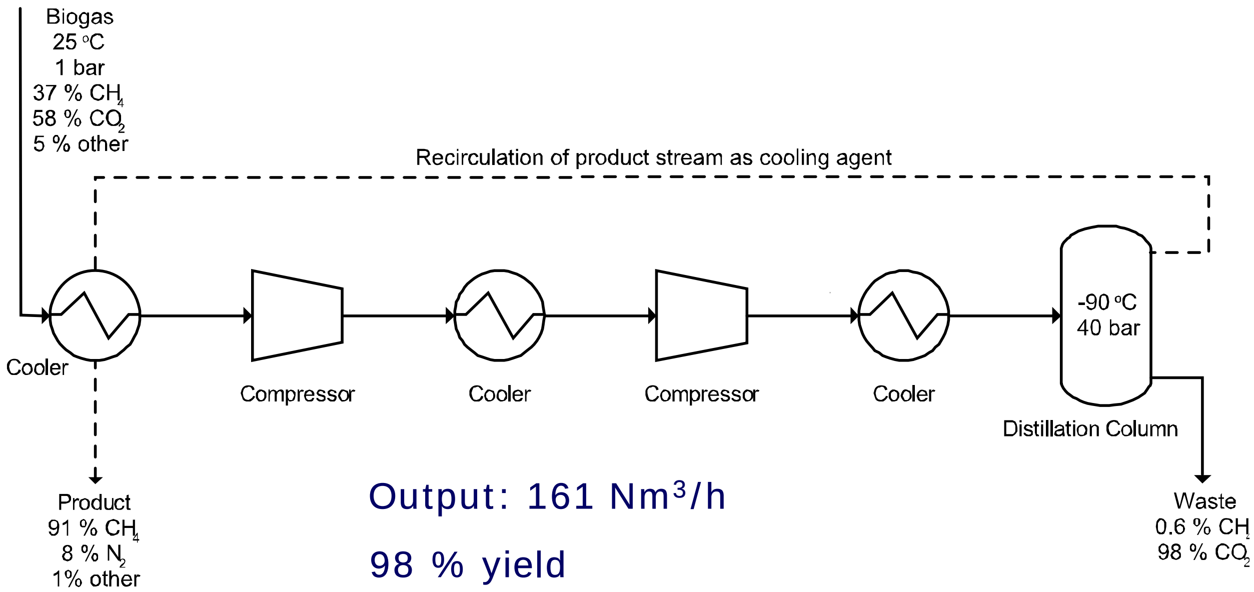
- Cost estimation

	PSA
Investment costs (€)	805,000
Running costs (€)	187,250
Price per Nm^3 biogas (€)	**0.26**

Cryogenic separation (I)

- Low temperature distillation (cryogenic separation) is a commercial process commonly used to liquefy and purify CO_2 from relatively high purity (> 90%) sources.
- It involves cooling the gases to a very low temperature so that the CO_2 can be liquefied and separated.
- Distillation generally has good economies of scale.
- This method is worth considering where there is a high concentration of CO_2 in the waste gas.
- The advantage is that it produces a liquid CO_2 ready for transportation by pipeline.
- The major disadvantages of this process are the amount of energy required to provide the refrigeration and the necessary removal of components that have freezing points above normal operating temperatures to avoid freezing and eventual blockage of process equipment.

Cryogenic separation (I)



Output: 161 Nm^3/h

98 % yield

91 % purity

Cryogenic separation (II)

Cost estimation

	Cryogenic separation
Investment costs (€)	908,500
Running costs (€)	397,500
Price per Nm^3 biogas (€)	**0.40**

Membrane separation (I)

- The use of membranes for gas cleaning is a well established technology in chemical industries.
- The membrane is a porous material that let some gases permeate through its structure.
- Employing an adequate material, it is possible to have selectivity between the gases of the mixture to be separated
- Two different streams are obtained: a permeate gas (mainly CO_2 water and ammonia) and the retentate (concentrated CH_2).
- The most commonly employed materials are hollow fibres made of different polymers.
- The biogas is compressed to 16 bars and then routed to a two-stage membrane process where methane with purity higher than 90% can be obtained.

Membrane separation (I)

- Compared to absorption separation, the advantages of the membrane process are

i. It does not require a separating agent, thus no regeneration is required;

ii. The systems are compact and lightweight, and can be positioned either horizontally or vertically, which is especially suitable for retrofitting applications;

iii. Modular design allows optimization of process arrangement by using multi-stage operation; and

iv. Low maintenance requirements because there are no moving parts in the membrane unit.

Membrane separation (I)

- A number of solid polymer membranes are commercially available for the separation of CO_2 from gas streams, primarily for natural gas sweetening.
- These membranes selectively transmit CO_2 versus CH_2.
- The driving force for the separation is pressure differential across the membrane.
- As such, compression is required for the feed gas in order to provide the driving force for permeation, and the separated CO_2 is at low pressure and requires additional compression to meet pipeline pressure requirements.
- The energy required for gas compression is significant when a very high pressure is required
- The commercial membranes for CO_2 separation are mainly prepared from cellulose acetate, polysulfone, and polyimide.

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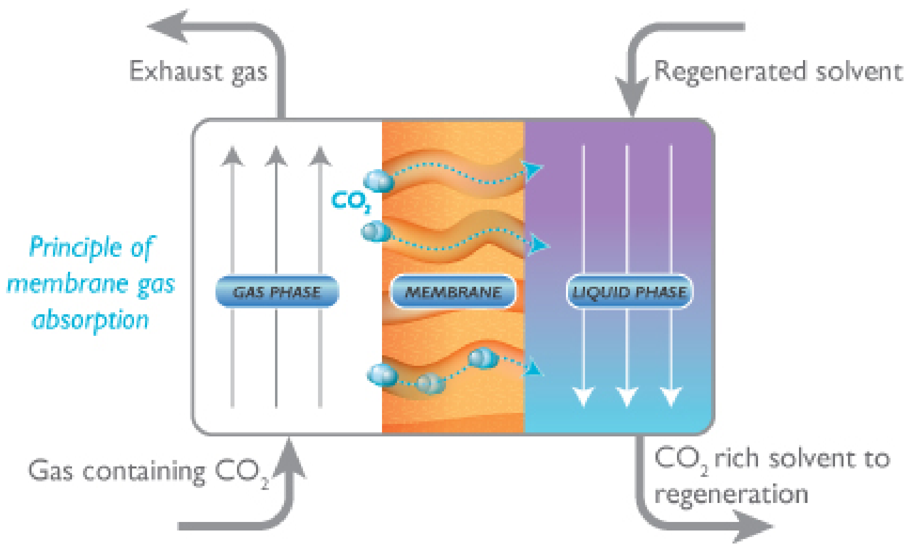
Membrane separation (I)



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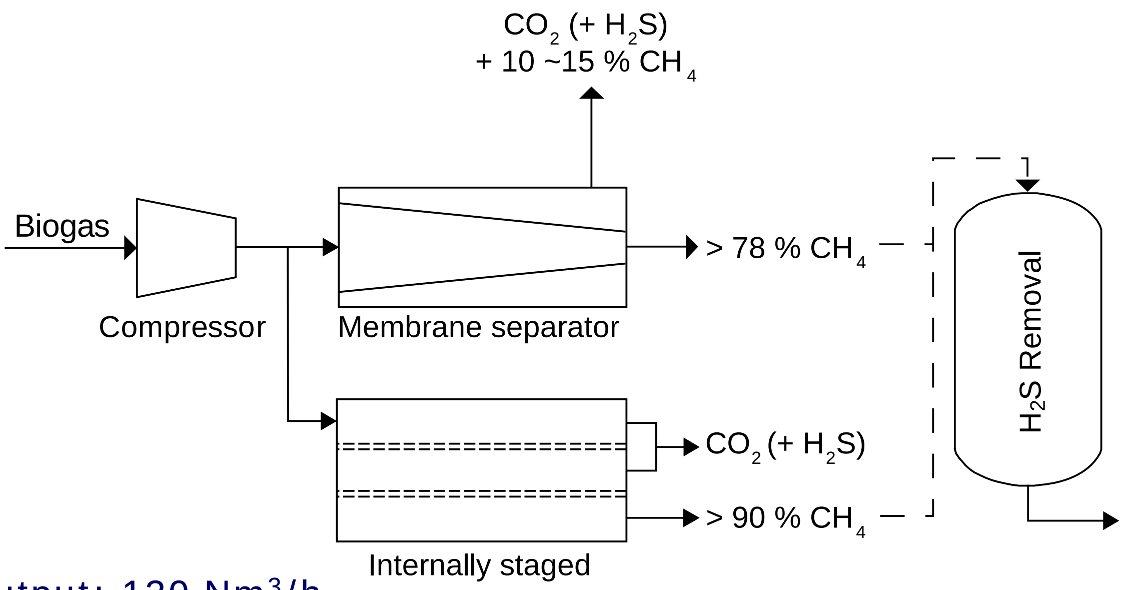
Membrane separation (II)



Output: 130 Nm³/h

78 % yield

90 % purity

Membrane separation (III)

Cost estimation

	Membrane separation	Total upgrading process
Investment costs (€)	233,000	749,000
Running costs (€)	81,750	126,750
Price per Nm^3 biogas (€)	0.11	**0.22**

Hybrid Membrane/Amine Processes

- It may be desirable to apply amine and membrane technologies in tandem, thereby forming a hybrid process, to capture CO_2 from flue gas.
- Micro-porous hollow fiber membranes are evolving as a new technology for CO_2 separation using amine-based chemical absorption processes.
- Micro-porous membranes are used in the gas-liquid unit where the amine solution is contacted with the CO_2 containing flue gas.
- The principle advantage of the micro-porous membrane is the reduction in the physical size and weight of the gas-liquid contacting unit.
- Unlike conventional membrane separation, the micro-porous hollow fiber membrane separation is based on reversible chemical reaction, and mass transfer occurs by diffusion of the gas through the gas/liquid interface just as in the traditional contacting columns.

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Hybrid Membrane/Amine Processes

- The hollow fiber membrane itself does not contribute to the separation but instead acts as a contacting medium between the gases the liquid.
- There are a number of advantages to using the gas-liquid membrane contactors, including:

i. High gas/liquid contact area due to the high packing density of the hollow fibers (500 to 1,500 m^2/m^3 versus 100~250 m^2/m^3 for a conventional column).

ii. Foaming is eliminated since because the gas flow does not impact the solvent and there is no connective dispersion of gas in the liquid.

iii. The membrane acts as a partition between the gas and liquid, and the gas/liquid flow rate ratio may vary in a wide range without causing flooding problems.

iv. The available gas/liquid contact area is not disturbed by variations in flow rates. This means the process can tolerate a wider range of process condition variations.

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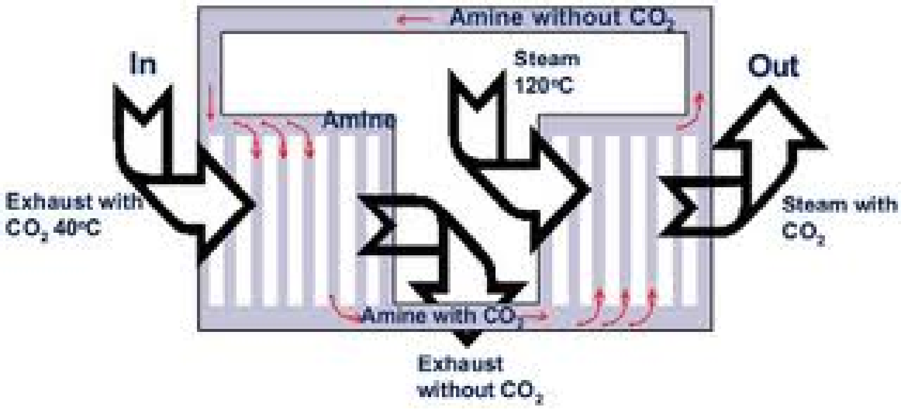
Hybrid Membrane/Amine Processes

v. Solvent degradation is minimized as oxygen (a degradation agent to amines) is prevented from intimate contact with the solvents.

vi. Unlike the absorption column that can only be operated vertically, the hollow fiber membrane contactor may be operated in any orientation to suit the overall plant layout.



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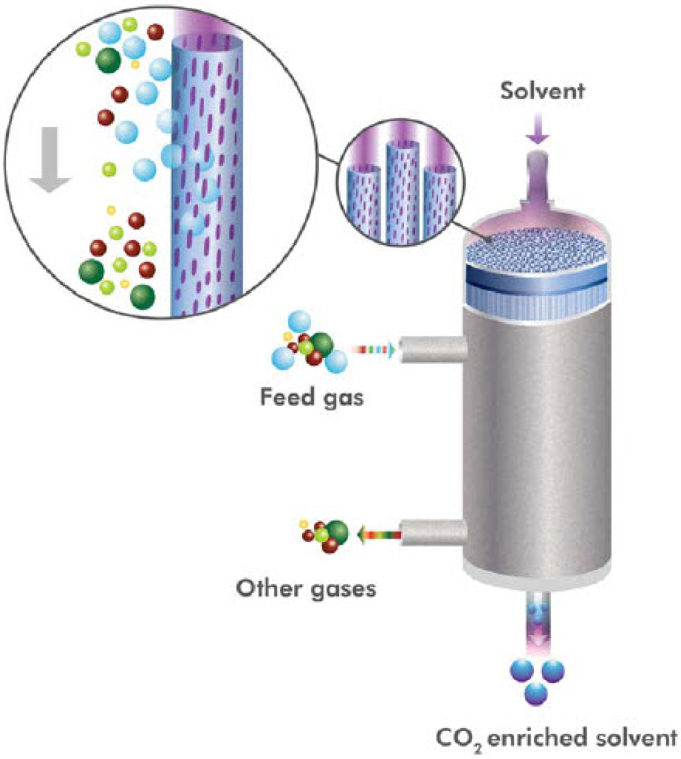
Hybrid Membrane/Amine Processes



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Comparison

Technique	Investment cost €	Running cost €	Cost price upgraded biogas €/Nm^3 biogas	Maximum achievable yield %	Maximum achievable purity %	Advantages	Disadvantages
Chemical absorption	869,000	179,500	0.28	90	98	· Almost complete H_2S removal	· Only removal of one component in column · **Expensive catalyst**
High pressure water scrubbing	**440,000**	120,000	**0.15**	94	98	· Removes gases and particulate matter · **High purity, good yield** · Simple technique, no special chemicals or equipment required · Neutralization of corrosive gases	· Limitation of H_2S absorption due to changing pH · **H_2S damages equipment** · Requires a lot of water, even with the regenerative process
Pressure swing adsorption	805,000	187,250	0.26	91	98	· More than 97% CH_4 enrichment · Low power demand · Low level of emissions · **Adsorption of N_2 and O_2**	· Additional complex H_2S removal step needed
Cryogenic separation	908,500	**397,500**	0.40	98	91	· Can produce large quantities with high purity · Easy scaling up · No chemicals used in the process	· **A lot of equipment is required**
Membrane separation	749,000	126,750	0.22	78	89.5	· Compact and light in weight · Low maintenance · Low energy requirements · **Easy process**	· **Relatively low CH_4 yield** · H_2S removal step needed · Membranes can be expensive

Method	Option/Alternative	Advantages	Disadvantages
Absorption with water		High efficiency (>97% CH_4), Simultaneous removal of H_2S when H_2S < 300 cm3 /m³, Capacity is adjustable by changing pressure or temperature, Low CH_4 losses (<2%), tolerant to impurities	Expensive investment and operation, clogging due to bacterial growth, possible foaming, low flexibility toward variation of input gas
Absorption with polyethylene glycol		High efficiency (>97% CH_4), Simultaneous removal of organic S components, H_2S, NH_3, HCN and H_2O, Energetic more favorable than water, Regenerative, low CH_4 losses	Expensive investment and operation, difficult operation, Incomplete regeneration when stripping/vacuum (boiling required), reduced operation when dilution of glycol with water
Chemical absorption with amines		High efficiency (>99% CH_4), cheap operation, Regenerative, More CO_2 dissolved per unit of volume (compared to water), very low CH_4 losses (<0.1%)	Expensive investment, heat required for regeneration, corrosion, decomposition and poisoning of the amines by O_2 or other chemicals Precipitation of salts, possible foaming
PSA/VSA	Carbon molecular sieves Zeolites Molecular sieves Alumina silicates	Highly efficient (95-98% CH_4), H_2S is removed, low energy use: high pressure, compact technique, also for small capacities, tolerant to impurities	Expensive investment and operation, extensive process control needed, CH_4 losses when malfunctioning of valves

Membrane technology	Gas/gas Gas/liquid	H_2S and H_2O are removed, simple construction, Simple operation, high reliability, small gas flows treated without proportional increase of costs • Gas/gas: removal efficiency: <92% CH_4 (1 step) or > 96% CH_4, H_2O is removed • Gas/liquid: Removal efficiency: > 96% CH_4, cheap investment and operation, Pure CO_2 can be obtained	Low membrane selectivity: compromise between purity of CH_4 and amount of upgraded biogas, multiple steps required (modular system) to reach high purity, CH_4 losses.
Cryogenic separation		90-98% CH_4 can be reached, CO_2 and CH_4 in high purity, low extra energy cost to reach liquid biomethane (LBM)	Expensive investment and operation. CO_2 can remain in the CH_4
Biological removal		Removal of H_2S and CO_2, enrichment of CH_4, no unwanted end products	Addition of H_2, experimental - not at large scale

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Further R&D Work Required for Biogas Development

- Biogas production using easily available local waste material preferably agricultural wastes.
- Development of new and low cost improved designs of biogas plants for large sizes.
- Development of low cost technology for separation of methane, CO_2 and sulfur compounds from biogas for easy bottling of pure methane and to reduce the damages caused by S-compounds on machines using the biogas.

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Further R&D Work Required for Biogas Development

- The effect of bio-wash (liquid from digested slurry) on vegetables and crops.
- Design of kitchen waste biogas plant for restaurants
- Testing of oil seed cake based biogas plant slurry for nutrient value and its effect on crop production

Summary

- High pressure water scrubbing cheapest option
- HPWS & membrane easy to operate and no chemicals needed
- Membrane separation is promising
- Each technique has its advantages depending on the goal
- **HPWS best overall performance:**

- high yield and purity
- compact setup
- no chemicals
- only one waste stream