Lecture (6)

Biogas Upgrading Technologies

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Prepared by

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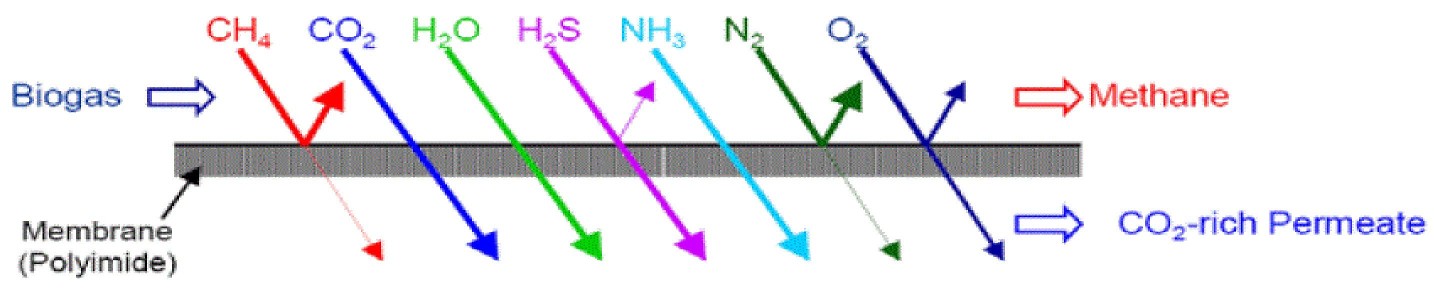
5) Membrane Technology

- In membrane separation systems CO_2 and other components as H_2O, H_2S & NH_3 are transported through a thin membrane in more or less extent while CH_4 is retaining, due to difference in particle size and/or affinity.
- The driving force behind this process is a difference in partial pressures.



Membrane separation principle

- **The properties of this separation technique are highly dependent on the type of membrane used.**
- **Many different membranes are available each with its particular specifications.**
- **Two basic systems exist:**

(1) **gas-gas separation with a gas phase at both sides of the membrane**

(2) **gas-liquid absorption separation with a liquid absorbing the diffused molecules.**

a) **Gas-gas separation, solid membrane process or dry membranes.**

- Dry membranes for biogas upgrading are made of materials that are permeable to CO_2, H_2O and NH_3. H_2S and O_2 permeate through the membrane to some extent while N_2 and CH_4 only pass to a very low extent.
- Usually membranes are in the form of hollow fibers bundler together, and very compact modules working in cross flow can be used.

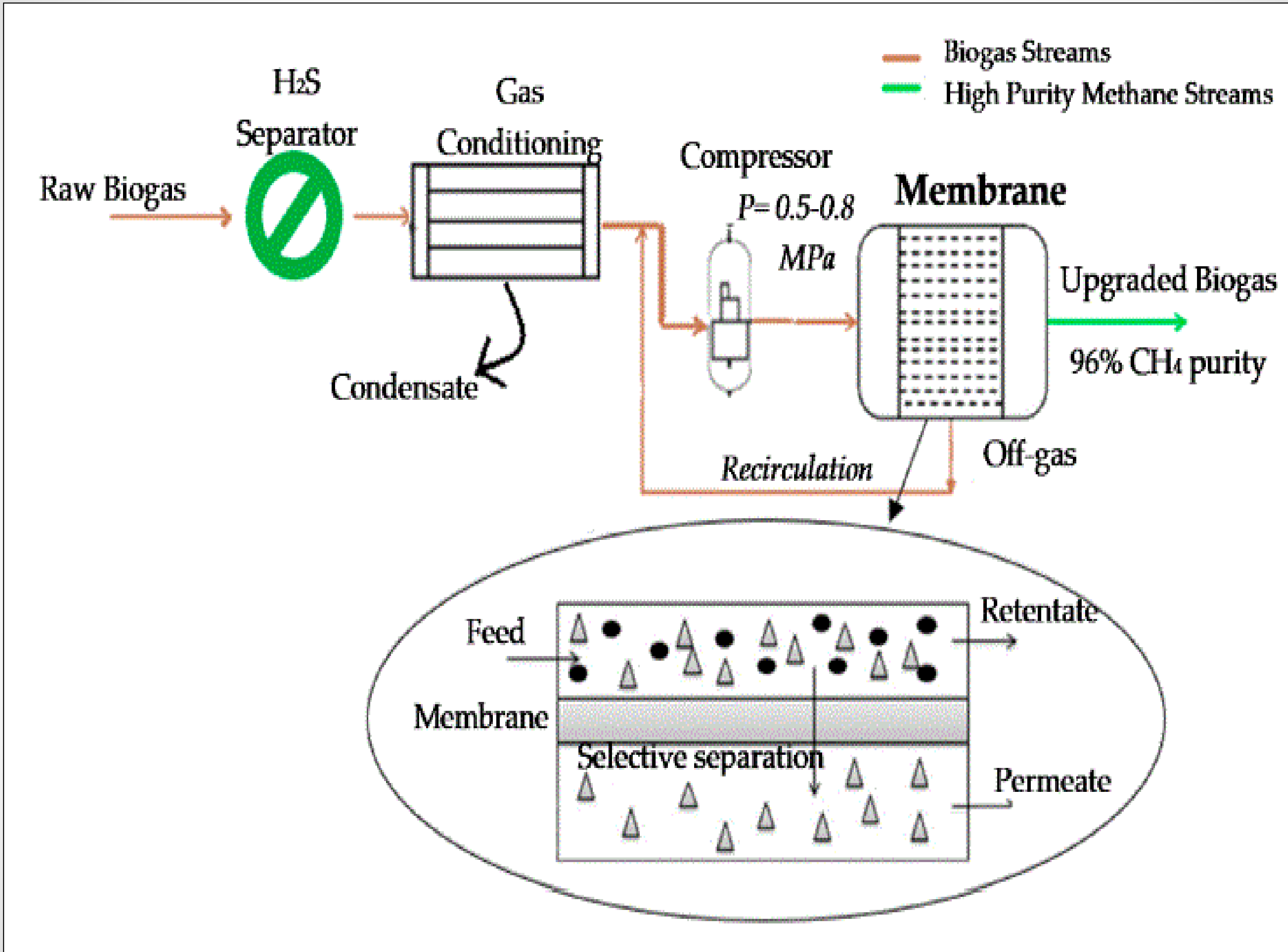
- **Before the gas enters the hollow fibers it passes through a filter that retains water, oil droplets, hydrocarbons and aerosols, which would otherwise negatively affect the membrane performance. Additionally,**
- **To increase life time of the membrane hydrogen sulfide is usually removed by cleaning with activated carbon before the membrane.**

- **BioGas Upgrading (Carborex®MS Explanimation) by DMT** https://www.youtube.com/watch?v=HW24vIXZQ78

b) Gas-liquid absorption membranes

- **Gas-liquid absorption membranes for upgrading biogas have been developed only recently and are still in trial phase.**
- **A micro-porous hydrophobic membrane separates the gaseous from the liquid phase.**
- **Molecules from the gas stream, flowing in one direction, and able to diffuse through the membrane, are absorbed on the other side by liquid flowing in counter current.**
- **The liquid is prevented from flowing to the gas side due to slight pressurization of the gas.**

- These membranes. work at approximately atmospheric pressure (100 kPa), which allows low-cost construction and they have a very high selectivity.
- The removal of CO_2, carried out with an amine solution, is very efficient; biogas with 55% CH_4 can be upgraded to more than 96% CH_4 in one step.
- The amine solution can be regenerated by heating, which releases a pure CO_2-flow which can be sold for industrial applications.


Biogas Streams
High Purity Methane Streams
H2S
Separator
Gas
Conditioning
Raw Biogas
Compressor
P= 0.5-0.8
MPa
Membrane
Upgraded Biogas
96% CH4 purity
Condensate
Recirculation
Off-gas
Feed
Retentate
Membrane
Selective separation
Permeate

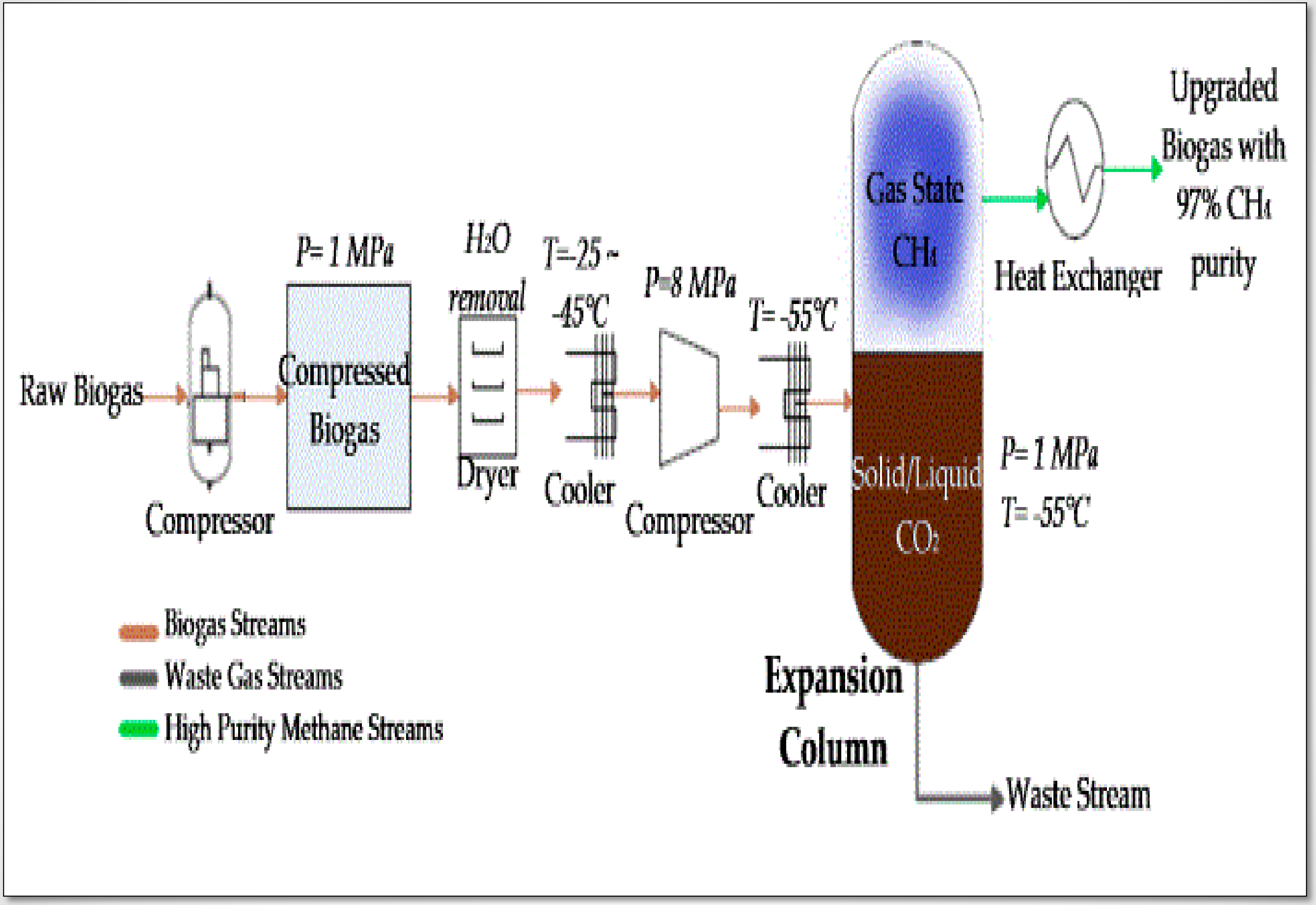
6) Cryogenic separation process

- This technology is conducted through a gradual decrease of biogas temperature separating the liquefied CH_4 from both CO_2 and rest components in order to obtain a product in accordance with the quality standards for Liquefied Natural Gas (LNG).
- The separation is carried out by initially drying and compressing the raw biogas up to 80 bars followed by a stepwise temperature drop up to $-110\ ^{\circ}C$.

- Thus, the low contained impurities (i.e. H_2O, H_2S, siloxanes, halogens etc.) and subsequently, CO_2 which is the second most dominant component of biogas are gradually removed in order to recover almost pure biomethane (> 97%).
- Despite the promising results, the cryogenic separation process is still under development and only few facilities are operating in commercial scale.

Limitation of the wider establishment of Cryogenic technique

1) The high investment and operation costs,
2) Losses of CH_4
3) Practical problems (e.g. clogging) derived from either the increased concentration of solid CO_2 or Presence of rest impurities.



Raw Biogas
Compressor
P= 1 MPa
Compressed Biogas
H2O removal
Dryer
T=-25 ~ -45℃
Cooler
P=8 MPa
Compressor
T= -55℃
Cooler
Gas State CH4
Solid/Liquid CO2
P= 1 MPa
T= -55℃
Expansion Column
Heat Exchanger
Upgraded Biogas with 97% CH4 purity
Waste Stream
Biogas Streams
Waste Gas Streams
High Purity Methane Streams

7) Chemical hydrogenation process

- The reduction of CO_2 with H_2 can be conducted chemically based on Sabatier reaction (Methanation reaction).
- The Sabatier reaction was discovered by the French chemist Paul Sabatier and Jean-Baptiste Senderens in 1897.
- It involves the reaction of hydrogen with carbon dioxide at elevated temperatures (optimally 300–400 °C) and pressures in the presence of a nickel catalyst to produce methane and water.

- It is described by the following exothermic reaction.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H = -165\ kJ/mol$$

- Optionally, ruthenium on alumina (aluminium oxide) makes a more efficient catalyst.
- Due to high selectivity, complete conversion of CO_2 and H_2 can be practically achieved.

- **Nevertheless, despite the high process efficiency, specific drawbacks still remain.**
- **For instance, the sustainability is affected by the presence of trace gasses in the biogas, which degenerate the catalysts leading to increased need for periodical replacement.**
- **Additional technical challenges of the process are the scarcity of elements to synthesize efficient catalysts, the need for pure gasses and the high energy cost to maintain the operational conditions.**

References

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