Biogas upgrading using micro-porous hollow fiber membrane contactors

D. Hidalgo, S. Sanz-Bedate, J.M. Martín-Marroquín , J. Castro, I. Alvarellos, R. Piñero, P. Acebes, G. Antolín (*dolhid@cartif.es)

Introduction

Biogas production: some data…

- Biogas production is growing.
- In June 2018 the EU institutions agreed on a new Renewable Energy Directive including a target of 32% for renewable energy by 2030.
- The biogas sector will undoubtedly contribute in achieving this goal.
- The European biogas market is established and mature:
  - A total of 17,783 biogas plants are currently operating.
  - The electricity production is above 65,000 GWh.
- TREND: Both existing and new anaerobic digestion plants are shifting from electricity production from biogas towards upgrading the **biogas to biomethane**.

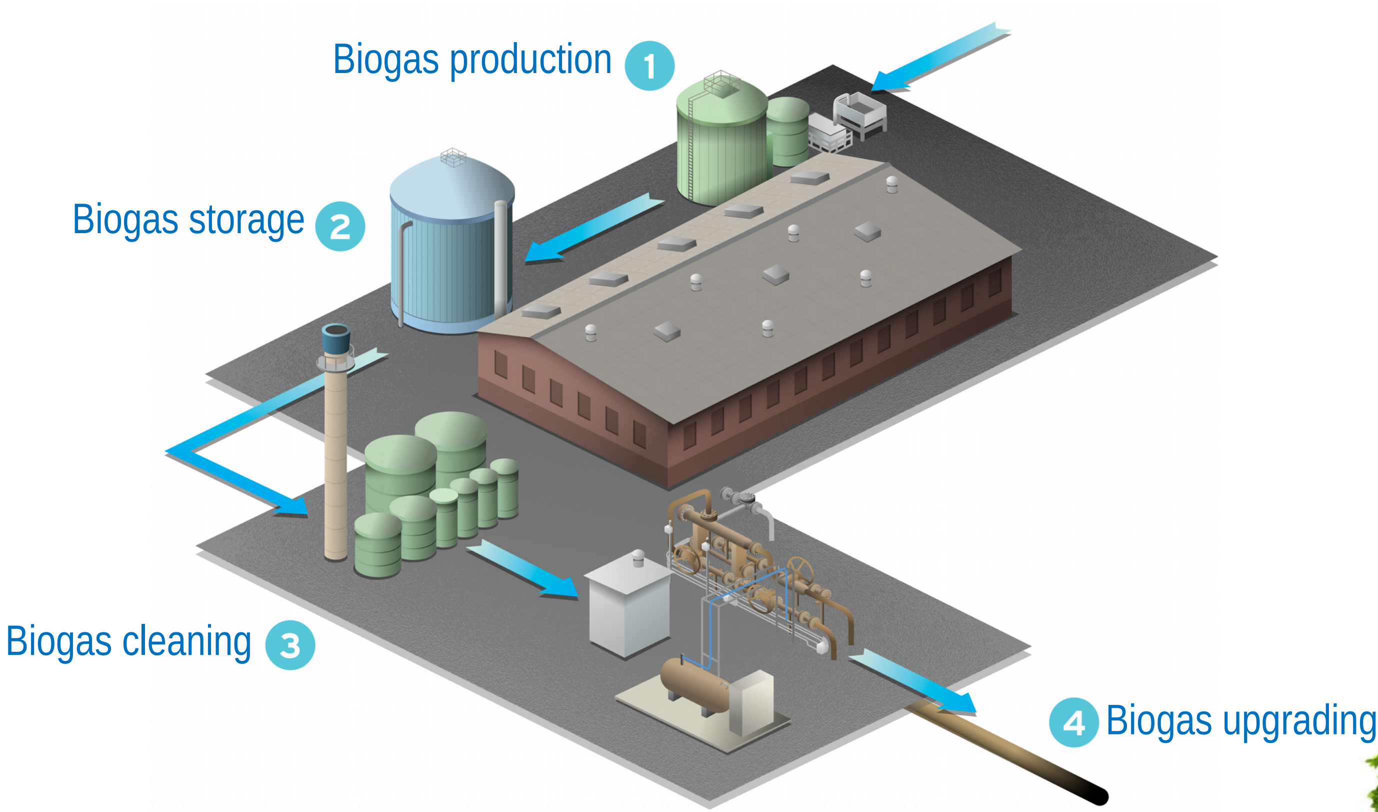
Biomethane production: some data…

- Increasing demand for methane-rich biogas (biomethane):
  - Vehicle fuel use.
  - Injection to the natural gas grid.
- The specific GHG emissions associated with the production of biomethane amount to 44.6 g CO_2eq/kWh, corresponding to an overall GHG emission reduction of 82% compared with natural gas.
- Nowadays, there are near 500 biogas upgrading plants only in Europe.
- New plants are continually being built around the world due to the increasing demand on biomethane.
- There will be soon more than 1,000 biomethane production plants operating in thirty-four countries.

These figures convert biomethane in a key option on the way to sustainable and renewable energy supplies.

From biogas to biomethane

- Biogas cleaning: to remove the trace elements.
- Biogas upgrading: to remove CO_2 and adjust the calorific value to the foreseen uses.



Upgrading process

Biogas	
CH_4 (%)	40 - 70
CO_2 (%)	30 - 60

Biogas composition after AD

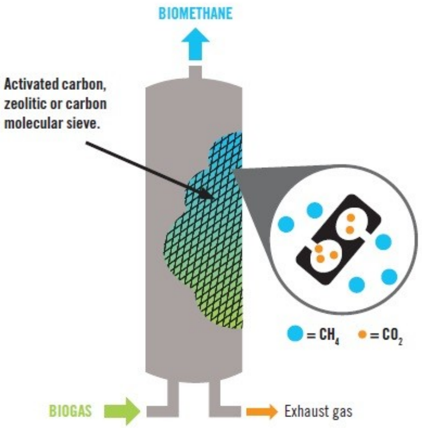
Biomethane	
CH_4 (%)	95 - 99
CO_2 (%)	1 - 5

Upgraded biogás composition

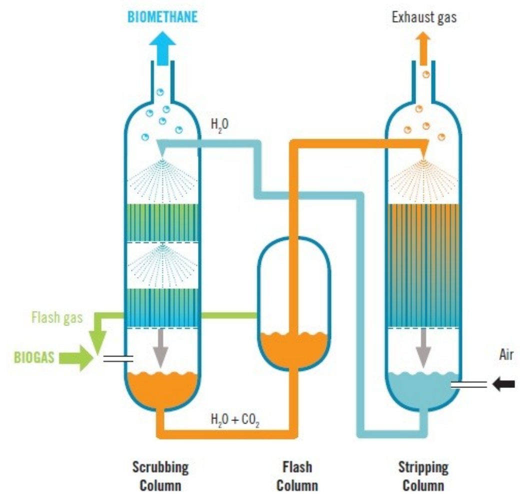
Biogas **Biomethane**

Biogas upgrading technologies

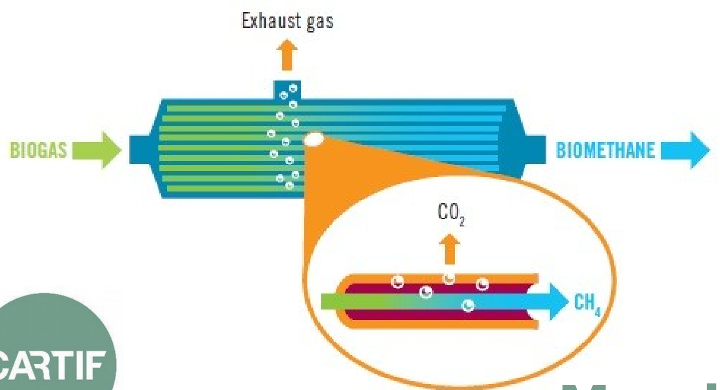
- Five technologies are mainly used in biogas upgrading plants, some of them commercially available and others at pilot or demonstration level:
  - water absorption,
  - pressure swing adsorption (PSA),
  - chemical scrubbing,
  - physical scrubbing and
  - membranes separation.



Adsorption

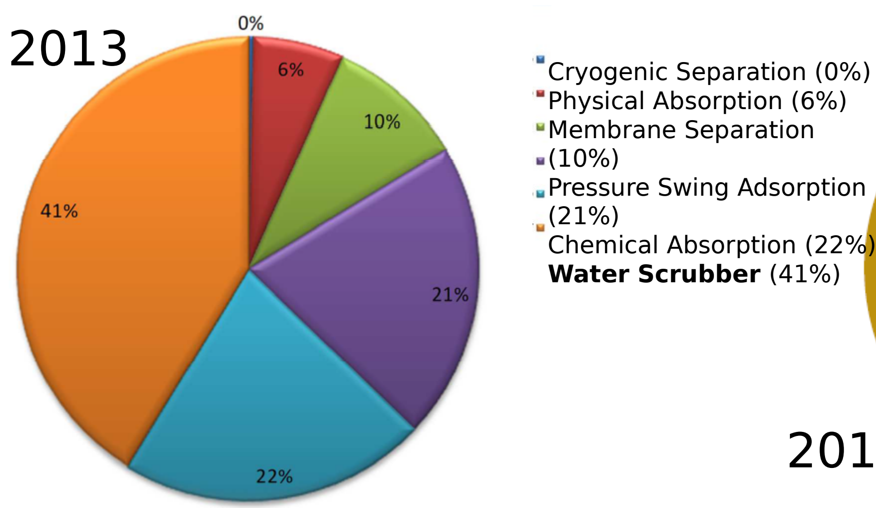


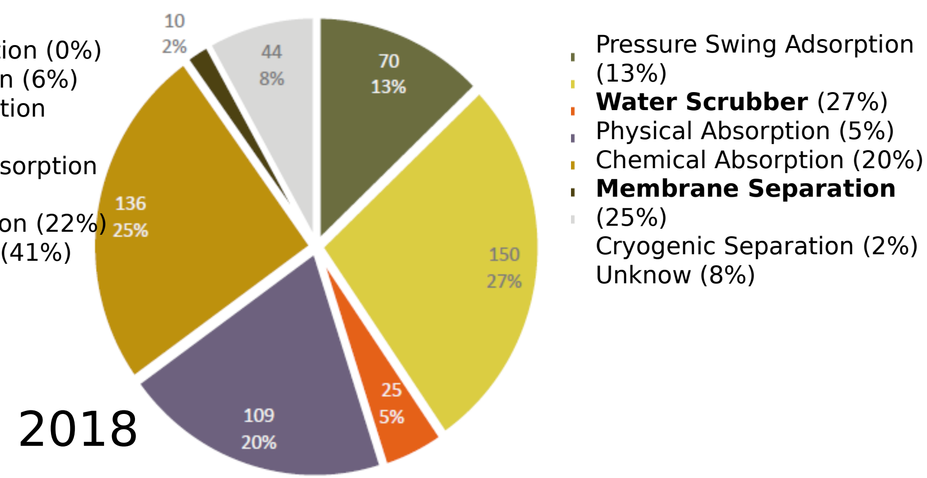
Absorption / Scrubbing



Membran

Biogas upgrading technologies: evolution





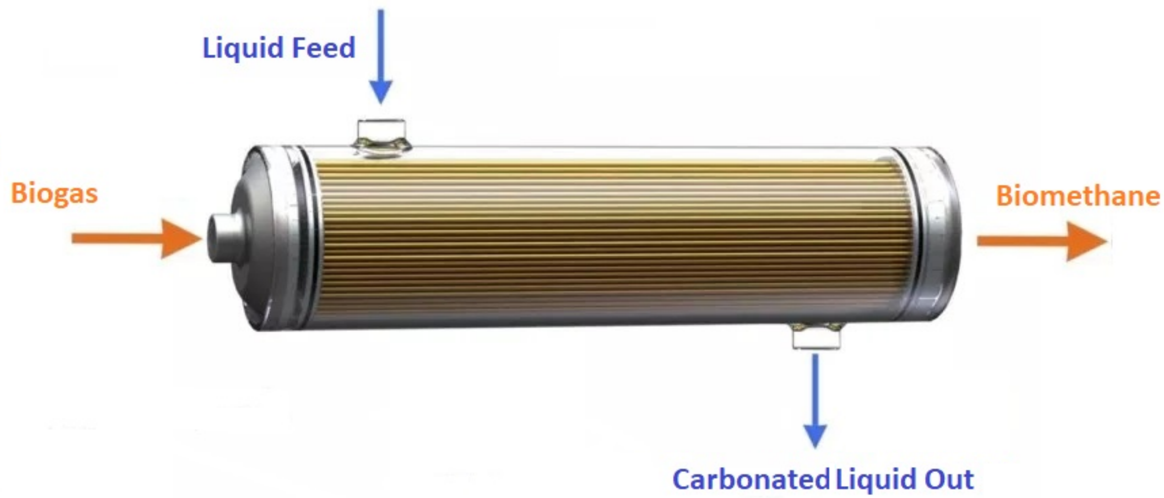
- Water absorption has been traditionally the most popular upgrading technology with 40% share years ago, followed by PSA and chemical scrubbing with 20% share each.
- Nowadays, membrane separation competes for the first place with water scrubbing.
- Use of membranes has increased to make this one of the market leading technologies in biogas upgrading since 2014/2015.

Biogas upgrading with membranes

- The main advantages of membrane-based technologies are:
  - moderate energy requirement,
  - low cost,
  - flexible operation,
  - modularity,
  - smaller footprint and lower weight compared to absorption processes.
  - Interesting when biogas production units do no reach a scale large enough to support conventional technologies capital expenditures.
- Two options:
  - Gas-gas membrane-based separation systems.
  - Gas-liquid membrane-based separation system (membrane contactors).

Biogas upgrading with membranes

Gas-liquid system:



Gas-gas system:

Biogas upgrading with membranes

- Gas-gas membrane-based separation systems:
  - Most of the biogas upgrading plants operating today with membrane technology are gas-gas modality.
  - Operates at high pressures.
- Gas-liquid membrane-based separation (membrane contactors):
  - Have been traditionally used in the food industry for liquid gasification or degasification processes.
  - Combines membrane with conventional phase contacting operation such as absorption.
  - Operates at low pressures (meaning lower operational costs).
  - A liquid solvent acting like absorber is needed.

Membrane contactors: operational issues

- The solvent must be selected carefully in order to achieve a high separation performance minimizing operational complexity.
- The solvent:
  - Should have a high absorption capacity for CO_2 and high selectivity.
  - Should be compatible with the type of membrane used.
  - Easy regeneration.
- Temperature, pressure, and flow rates, both gas and solvent streams, should be carefully controlled to avoid gas losses and increase gas absorption.

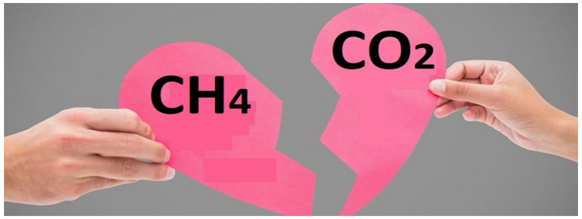
Proposed technological concept

Start point

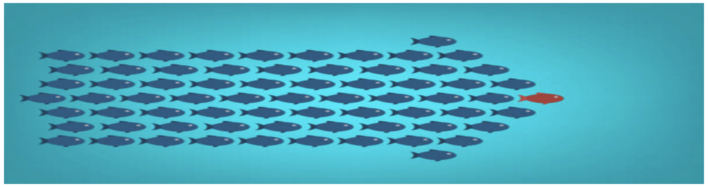
- Although gas-gas membrane systems have been already commercialized and applied on a large scale, **gas-liquid membrane systems for biogas upgrading are just now emerging** and only some pilot and demo plants are running.
- Since **operating conditions** can significantly affect the performance of membrane contactors, this should be **a matter of deep study** before a broad implementation of the technology.

Aim of the work

- This study seeks to **find optimal operational conditions** to maximize the separation of the two principal biogas components, methane and carbon dioxide, using membrane contactors.

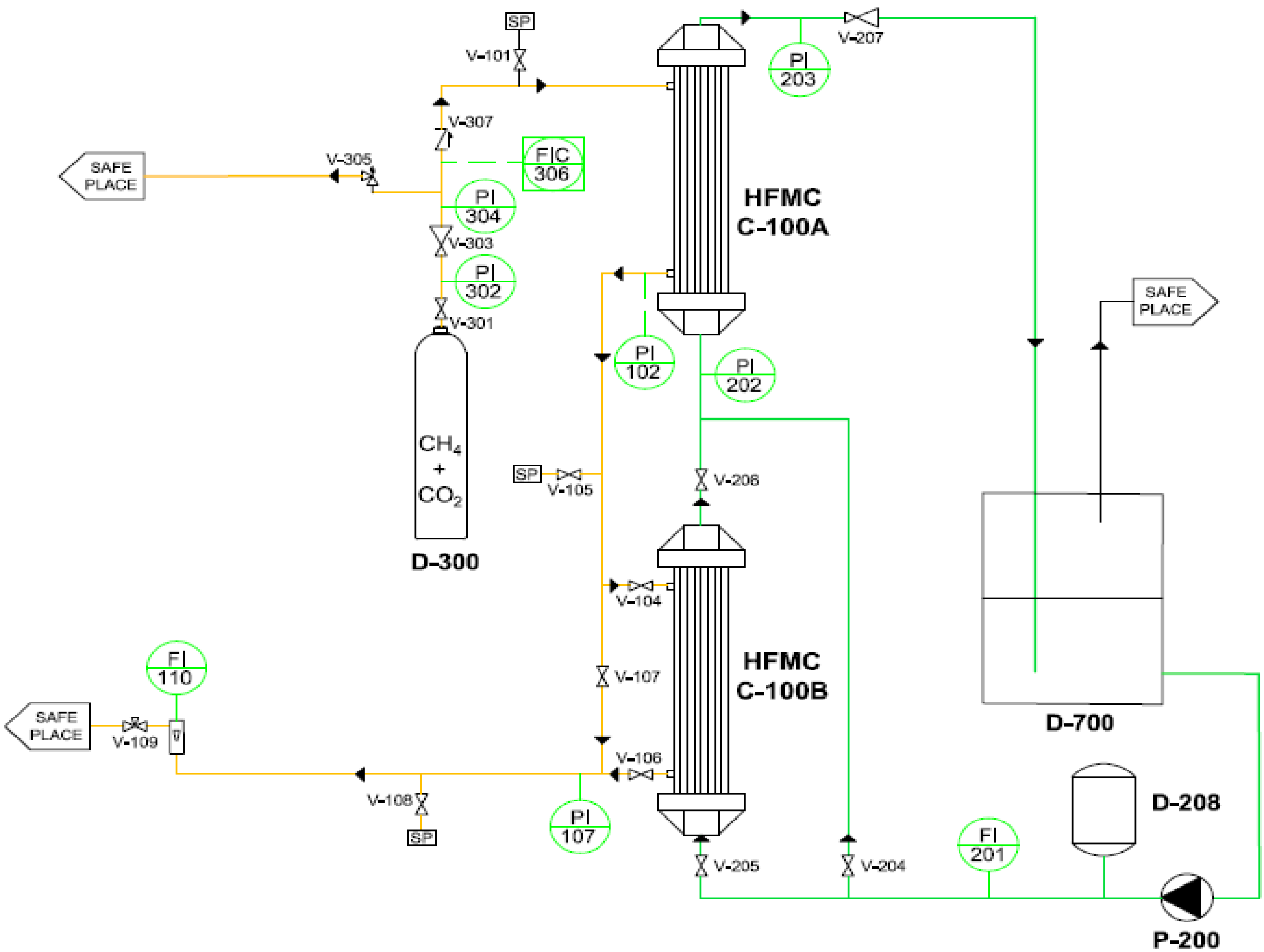


- The **influence of operational parameters** such as mass exchange surface, operational pressure and liquid/gas ratio will be studied.



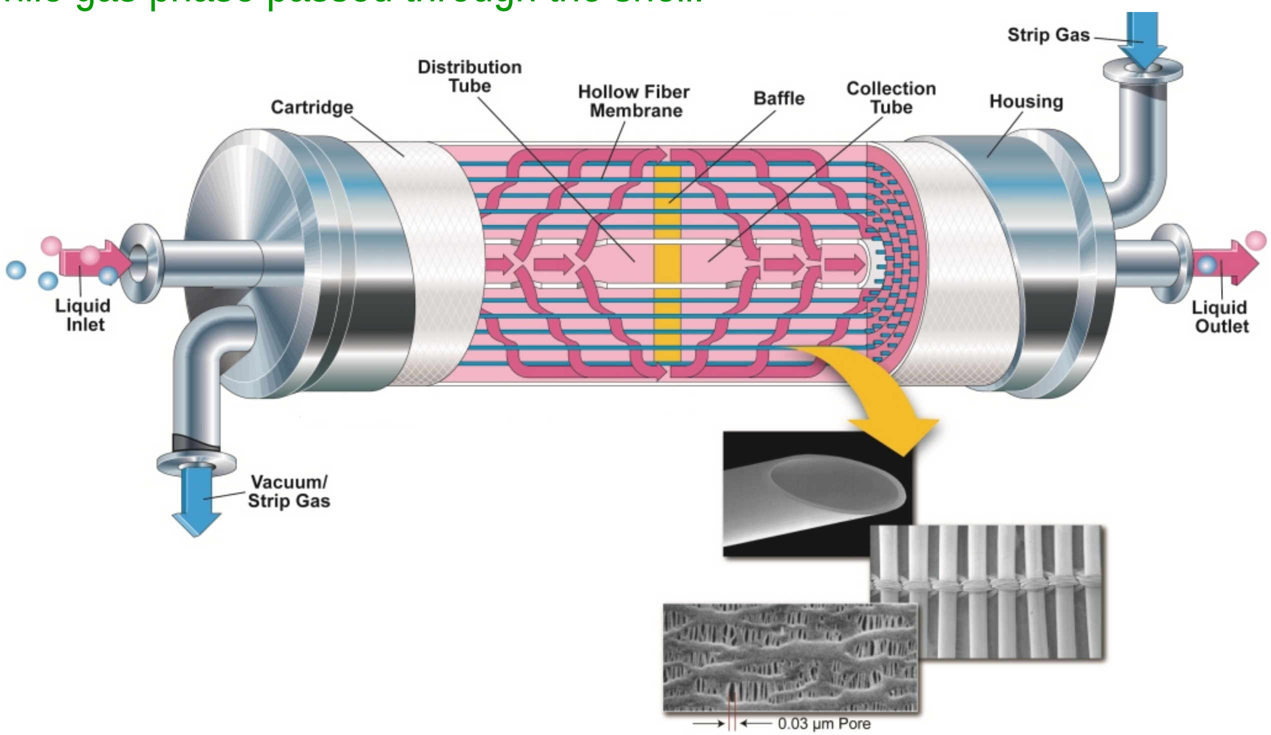
- This work also evaluates **the impact of different solvents** (deionized water, sodium hydroxide and sodium chloride) on methane recovery and the effect multiple solvent cycles compared to single-pass operation.

Experimental set-up



Experimental set-up

- Commercial bottle of synthetic biogas (40% CO_2, 60% CH_4).
- Deionized water (DI), sodium chloride (NaCl) and sodium hydroxide (NaOH) 1M solutions were subsequently used as comparative absorption solvents.
- HFMC, Liqui-Cel® 1.7 x 5.5 MiniModule®: liquid phase circulated inside the fibers while gas phase passed through the shell.



Experimental set-up

First results

System performance with deionized water as solvent

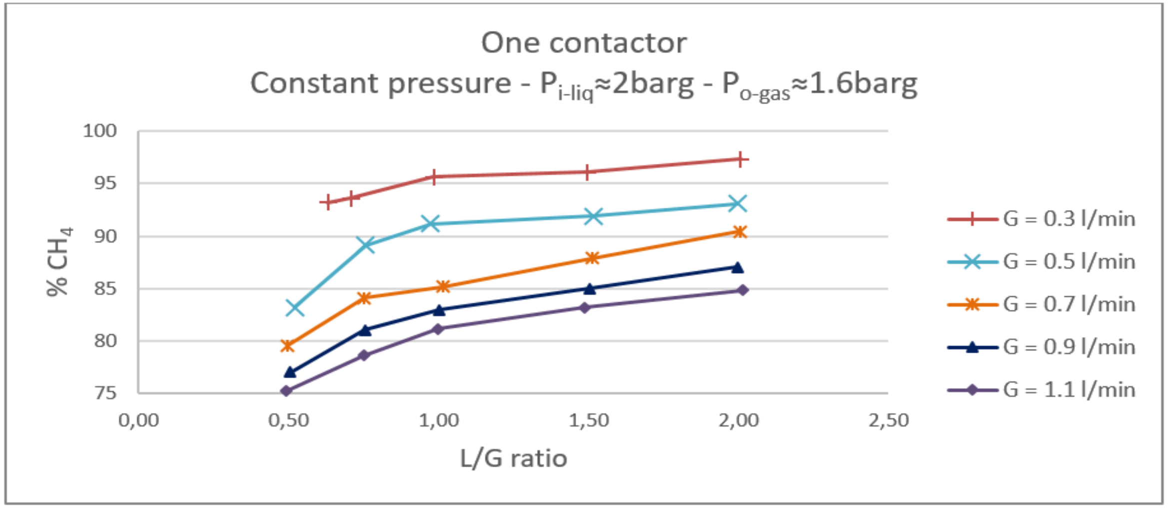
- A set of experiments was carried out using deionized water as solvent, first, with one membrane module operating alone and, later, with two membrane modules operating in series, in all the cases with a single-pass solvent use at ambient temperature (19-21ºC).

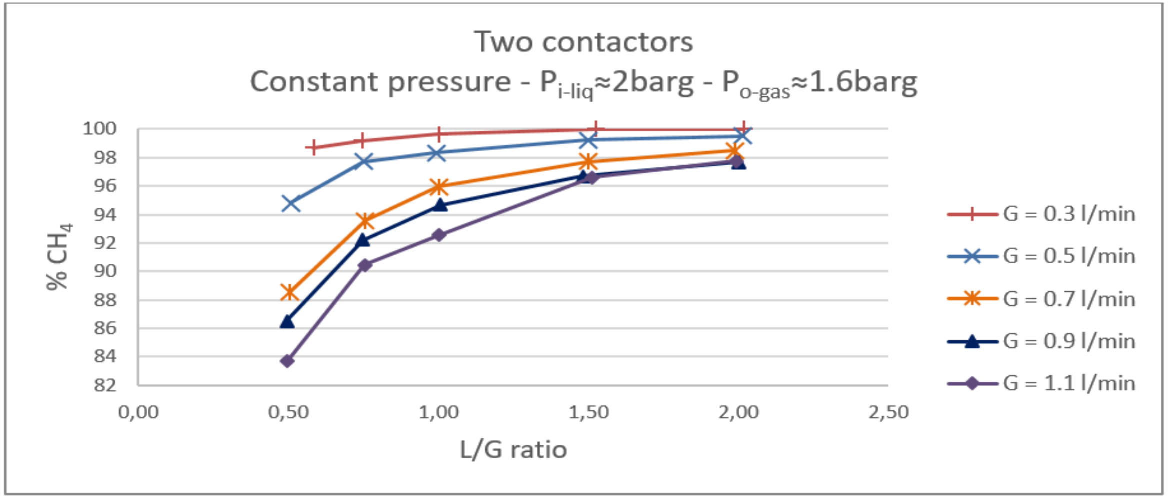
- The **first experiment** consisted in keeping constant the gas pressure (Po-gas) and the liquid pressure (Pi-liq) and gradually increasing the liquid/gas flows ratio (L/G).
- Selected pressure for the liquid phase was around 2 barg and for the gas phase was approx. 1.6 barg.
- The L/G ratio varied in the range 0.5 - 2 for different biogas flows (0.3 – 1.1 l/min).
- For each experience, gas flow was fixed with the controller and liquid flow was increased from 0.5G to 2G.

www.houseful.eu

www.cyted.org/es/biometrans

System performance with deionized water as solvent





System performance with deionized water as solvent

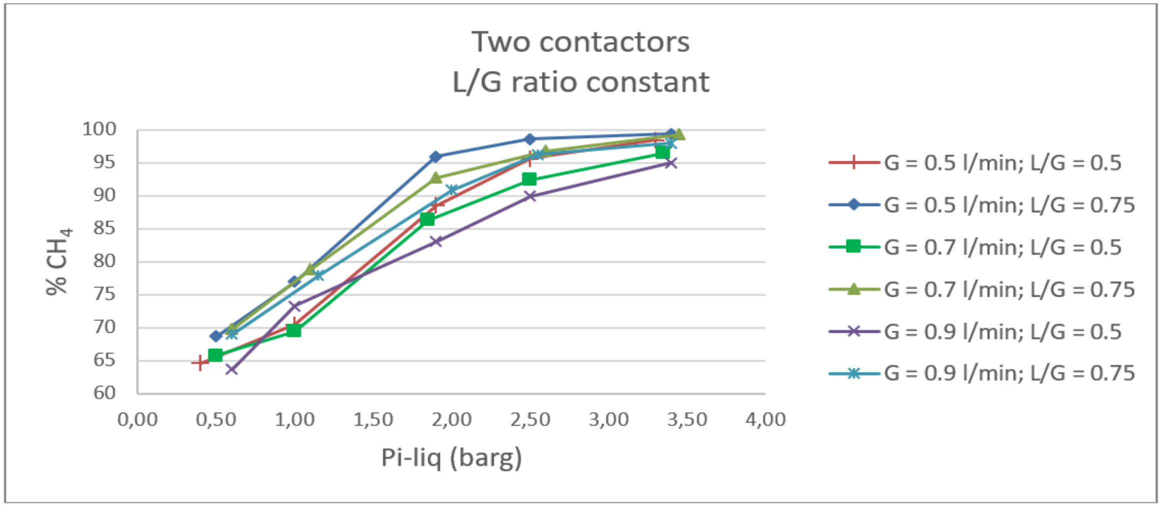
First experiment conclusions:

- For all the conditions assayed, the **better performance of the system was achieved at the lower gas flow** (0.3 l/min) and at the higher liquid/gas ratio (L/G=2).
- Under these operational conditions, biomethane purity was 97.34% (v/v) when operating with one contactor and 99.98% (v/v) when operating with two contactors in series.
- These maximum yields were obtained when the gas and solvent flow rates were 0.3 l/min and 0.6 l/min, respectively.
- It is also **clear the influence of the available mass exchange surface** in the system performance, related in this case with the number of membrane modules connected.
- pH of the liquid phase dropped in all experiments around two units due to the CO_2 absorption.

System performance with deionized water as solvent

- A **second experiment** consisted in keeping constant the L/G ratio while Pi-liq was increased in order to determine de influence of operational pressure in biogas upgrading.
- 0.5, 0.7 and 0.9 l/min of gas were consecutively fed in the pilot plant operated with two contactors in series.
- Liquid phase flow was adjusted accordingly and each assay was performed at L/G = 0.5 and then repeated at L/G = 0.75.
- Liquid pressure was progressively increased from 0.5 barg up to 3.5 barg.

System performance with deionized water as solvent



Second experiment conclusions:

- **Low pressures are not suitable for high biogas upgrading performance**.
- Higher methane concentration in the outlet gas stream, 99.44%, was achieved at the higher Pi-liq assayed, 3.4 barg (G = 0.5 l/min and L/G = 0.75).
- At high pressures biomethane upgrading is less dependent on flow and flow ratios.

System performance with NaCl and NaOH as solvents

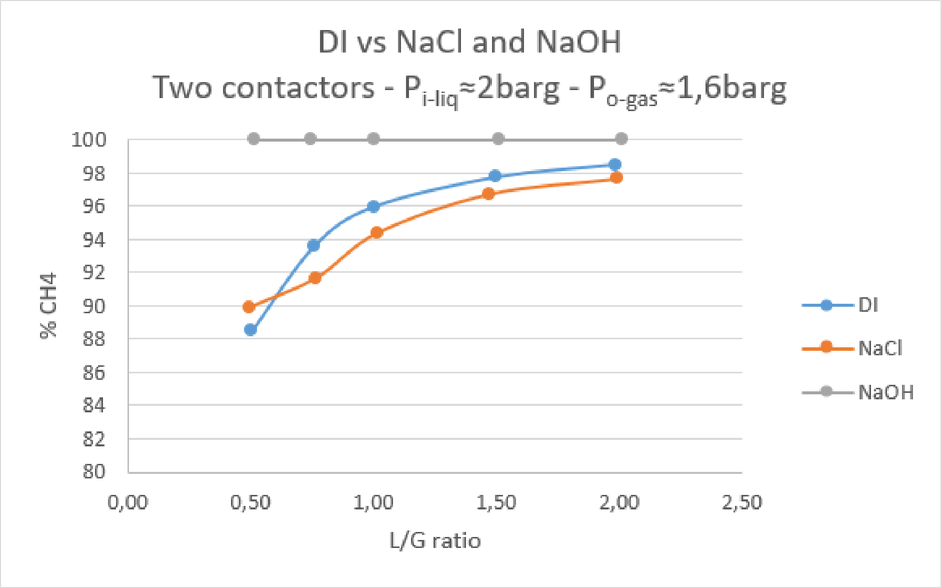
- An experimental set was designed to compare the behavior of the system when it worked with DI, NaCl 1M and NaOH 1M as solvents in a single-pass solvent use way.

- **In a first run**, the pilot plant was operated with two membrane contactors at Pi-liq ≈ 2 barg and Po-gas ≈ 1.6 barg.
- L/G ratio was progressively raised from 0.5 to 2 by increasing L from 0.35 l/min to a maximum of 1.4 l/min at a fixed G = 0.7 l/min.
- The three solvents were tested consecutively with cleaning periods in between of the assays.

www.houseful.eu

www.cyted.org/es/biometrans

System performance with NaCl and NaOH as solvents



First run conclusions:

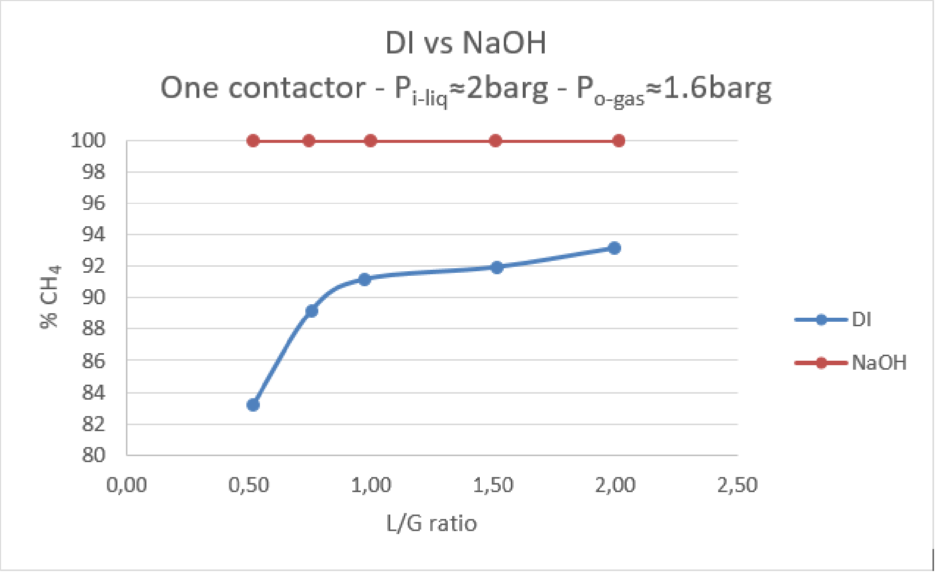
- CO_2 removal from the liquid phase reached >99% even for low L/G values when NaOH was used a solvent.
- NaCl was the solvent yielding the worst results. At L/G = 2, for example, NaCl achieved 97.9% of CH4 purity versus 98.5% achieved when using DI and 99,9% when using NaOH.

CARTIF

System performance with NaCl and NaOH as solvents

- In a **second run**, the pilot plant was operated with one membrane contactor, thus reducing by half the available surface area for molecules diffusion.
- The operational conditions set, in this case, were G = 0.5 l/min, Pi-liq ≈ 2 barg and Po-gas ≈ 1.6 barg.
- Liquid flow, L, was progressively increased from 0.25 l/min to 1 l/min, thus increasing L/G ratio progressively from 0.5 to 2.

System performance with NaCl and NaOH as solvents



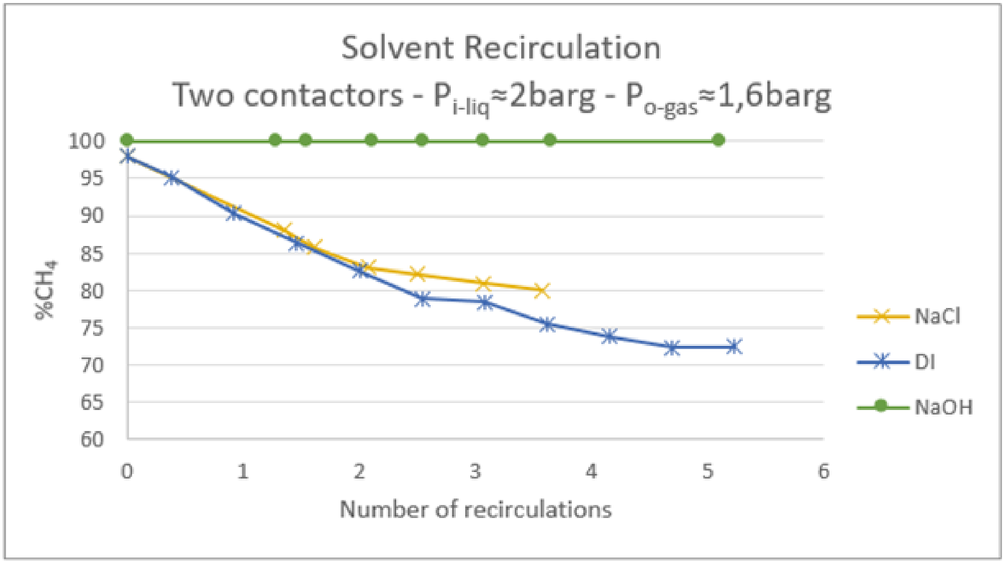
Second run conclusions:

- CO_2 removal from the liquid phase reached again 100% when NaOH 1M was used a solvent.
- The absorbent reactivity had the greatest effect on the efficiency of CO_2 removal.

Solvent recirculation

- Taking into the account the **sustainability of the process**, from the financial and environmental point of view, solvent recirculation should be considered.
- A new set of experiments was designed to **compare single-pass solvent use to recirculating the solvent** in multi-pass operation to enable a greater utilization of the available liquid phase.
- DI, NaCl 1M and NaOH 1M were used again as solvents.
- Inlet liquid pressure and gas out pressure were kept constant at Pi-liq ≈ 2 barg and Po-gas ≈ 1.6 barg during the whole experimentation.
- Liquid flow and gas flow were also fixed at L = 1 l/min and G = 0.5 l/min.
- Percentage of CH_4 in the outlet gas was compared following subsequent solvents uses without regeneration.
- The three solvents were recirculated in consecutive experiments from 0 to 5 times.

Solvent recirculation

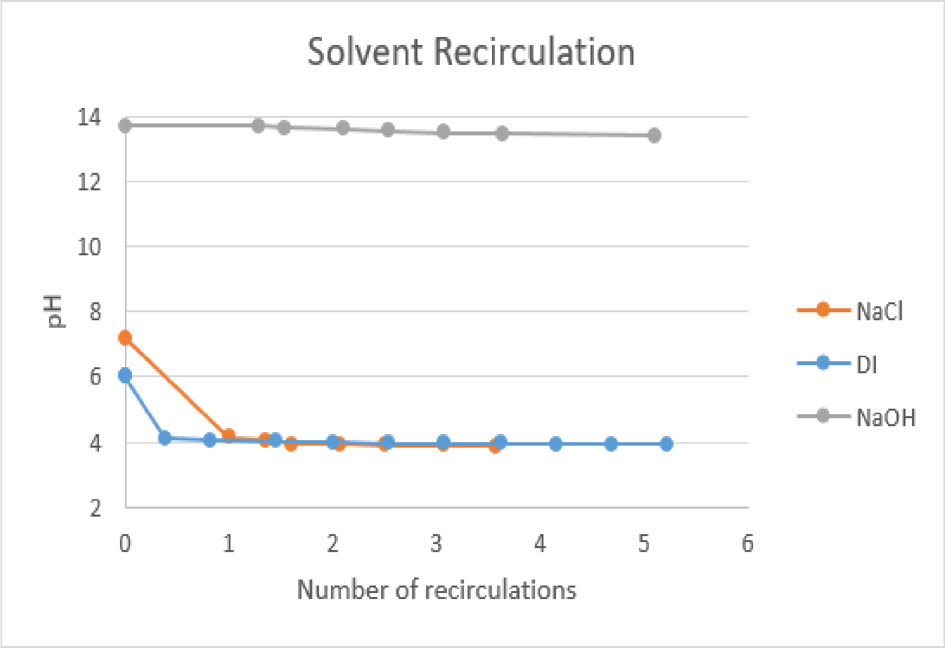


Conclusions:

- For DI and NaCl solvents, outlet gas content in methane rapidly diminished and the trend is increasingly pronounced as the number of solvent recirculations increases.
- In comparison, the CO_2 removal and outlet gas quality recorded for NaOH solution following five recirculations was analogous to single pass, demonstrating a sustained excess of highly reactive hydroxide ions.

Solvent recirculation

- The monitoring of the pH of the liquid phase shows a drastic drop at the beginning of the experimentation when DI and NaCl are used as solvents. This indicate that the solvent saturation with CO_2 occurs very quickly.
- The opposite situation is found when NaOH is used. In this case, the pH decreases very slowly and, as a consequence, the solvent maintains its activity along time.



Conclusions and future prospects

Conclusions (1)

- **Pressure is a crucial parameter**.

For the pilot system under study, pressures under 1.5 barg are not suitable for biogas upgrading. For intermediate pressures 1.5 - 3 barg biogas purification is highly dependent on biogas flow and L/G ratio. At relative high pressures, above 3 barg, greatest results of biomethane quality were obtained under different operation conditions. Gas and liquid flow and L/G ratio seems to play, in this case, a less relevant role.

- **Biogas upgrading showed better performance at higher L/G ratio**, but this entails an increase on operation costs.

To reduce L/G ratio some action can be implemented such as introducing more mass exchange surface (extra membranes), elevate pressure operation or treat lower raw biogas flows.

- **Solvent plays an important role.**

Minimize solvent usage while keeping the quality of outlet gas supposes an investment cost reduction. NaOH solutions showed better upgrading yields than DI water and HCl solution, even using only one membrane contactor.

Conclusions (2)

- **Solvent recirculation without regeneration is not feasible with DI water or NaCl solution.**

In these cases, solvent is progressively saturated. NaOH allowed several recirculation cycles without showing solvent degradation.

- **For physical solvents as DI or NaCl, an enhancement in gas-side methane purity is manifested when liquid phase flow was increased.**
- **For chemically reactive** solvents as NaOH, **the process is gas phase controlled**, which is illustrated by the negligible gradient recorded for CO_2 separation following an increase in the liquid phase flow.

www.houseful.eu

www.cyted.org/es/biometrans

Future prospects

- Hollow fiber membrane contactors for biogas upgrading have a large improvement path until become a stable industrial process.
- For further development of CO_2 absorption membrane, the challenge is how to improve **membrane durability** in operation in the presence of contaminants such as SO_2.
- Another aspect to be investigated is membrane **fouling**. In industrial applications where the gas stream contains contaminants such as suspended particles, the membrane fouling becomes a bigger concern.
- Also **wetting** phenomenon should be addressed, avoiding the penetration of the absorbent liquid into membrane pores so that a low mass transfer resistance can be achieved.
- Finally, during biogas upgrading, **methane losses** occurs. Further research on methane slip and measures for its reduction will contribute to the feasibility of the process.

Further information:

dolhid@cartif.es
Fundación CARTIF, Boecillo, Valladolid (SP)
Tel. +34 983 546504

Thank you for your attention