# Hybrid membrane-absorption processes for acid gas removal

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Acknowledgments:

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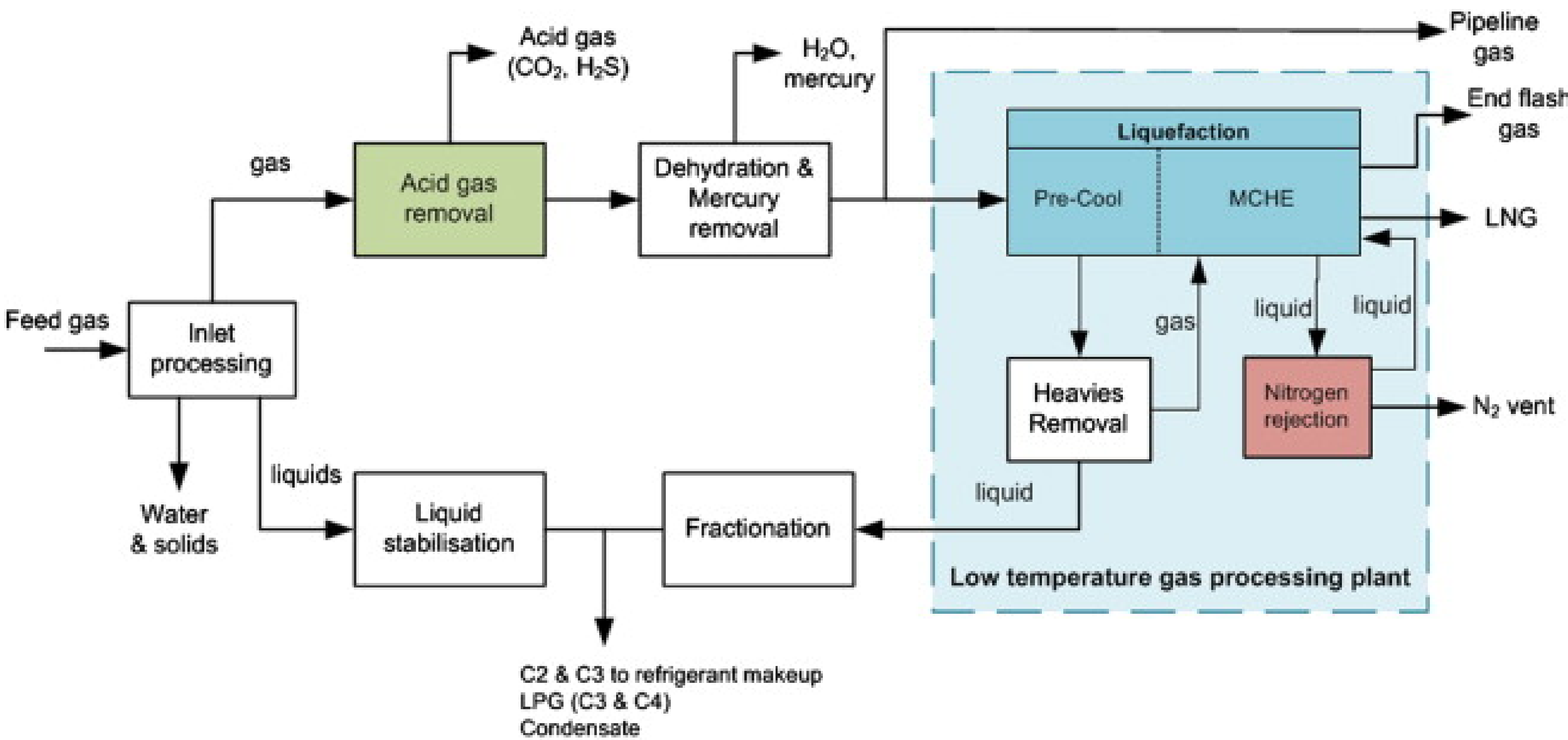
# Highlights

Comparison of (1) conventional MDEA amine absorption and (2) hybrid membrane + amine process to treat sour gas for feed to an LNG plant.

Feeds with 10%mol $CO_2$ → no apparent benefits of a hybrid system.

Very sour feed gas with 50%mol $CO_2$ the hybrid system has potential for significant reductions in equipment weight, plant volume, investment costs, and operating costs.

# Typical LNG process flow scheme




Rufford et al. (2012) J. Petroleum Sci. & Eng 95-95:p123-154

# Challenges for gas processing in remote or stranded fields

Feed to LNG plant has tight specification, e.g.:

- $CO_2 \leq 50$ppmv
- $H_2S \leq 4$ppmv

To meet these specifications amine plants require large columns, large solvent inventories, high demand for energy.

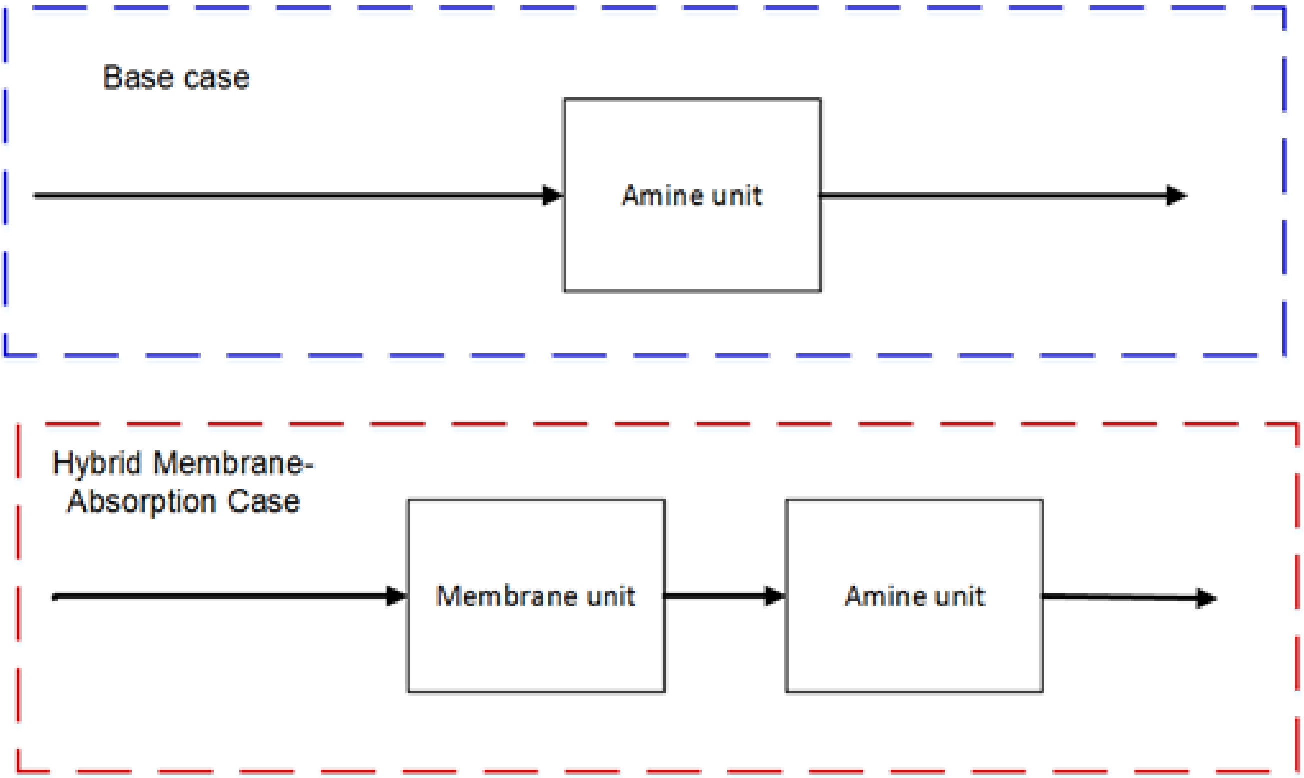
Floating LNG (FLNG) and micro-LNG plants may need significant reductions in weight, cost, and energy demand.

This project seeks to evaluate the potential of a hybrid membrane + absorption process to treat sour gas onboard FLNG plants.

# Overview of processes compared

A

B




Membrane unit alone ***could not*** achieve 50ppmv $CO_2$

# Summary of methodology

Two feed cases based on Roussanaly et al. (2014)

Simulations in *Aspen Hysys V8.6*

Process metrics considered:

- Methane slip (MS)
- Relative energy demand (RED)
- Dry equipment weight
- Dry installed weight
- Total plant volume
- Equipment cost & installed cost
- Operating cost

*Aspen Process Economic Analyzer*

| | Feed1 | Feed2 |
|---|---|---|
| | Feed compositions in mole % | |
| Methane | 83 | 41 |
| Ethane | 5 | 4.5 |
| Propane | 2 | 3.5 |
| $CO_2$ | 10 | 50 |
| $H_2S$ | 0 | 1 |
| $H_2O$ | 0 | 0 |
| $N_2$ | 0 | 0 |
| Temp., °C | 40 | 40 |
| Pressure, bar | 70 | 70 |
| Flow $Nm^3/h$ | 590,000 | 590,000 |

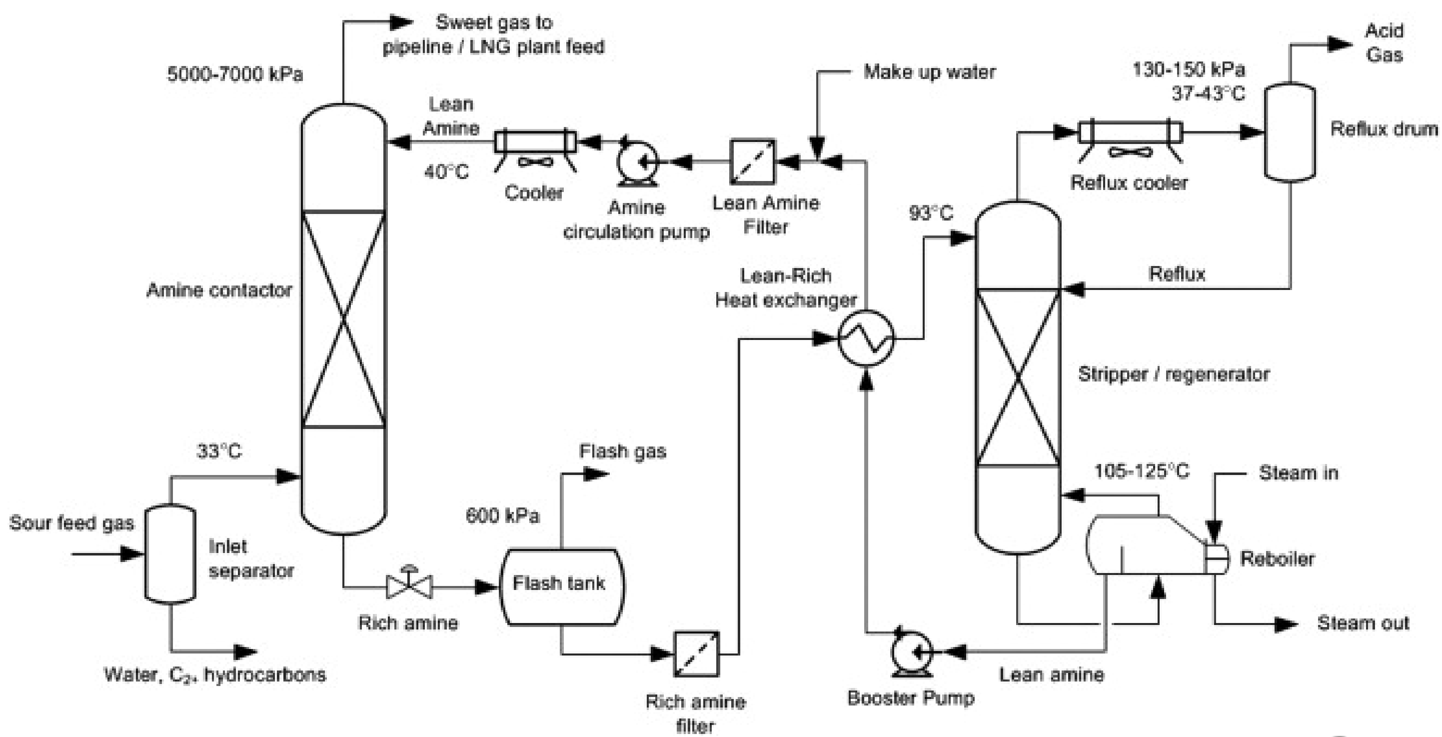
# Base Case: 50% MDEA absorption

50% methyl-di-ethanolamine (MDEA) solvent + piperazine (PZ)

Contactor: P=70bar; Mellapak 250Y structured packing

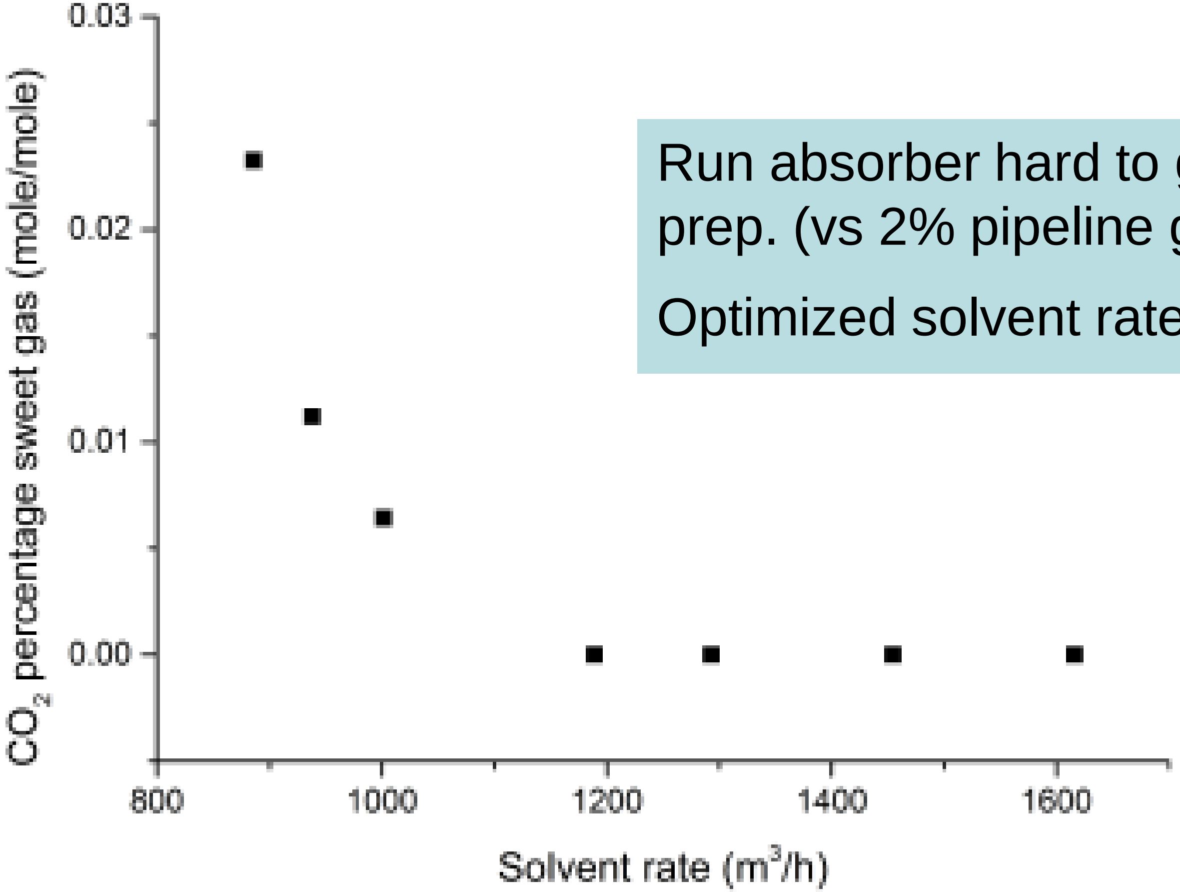
Stage efficiencies: 0.15 $CO_2$; 0.8 $H_2S$

Stripper: 1.9 bar, 50ºC



# Solvent rate required to achieve 50 ppmv $CO_2$ specification

Feed 1, 10% $CO_2$



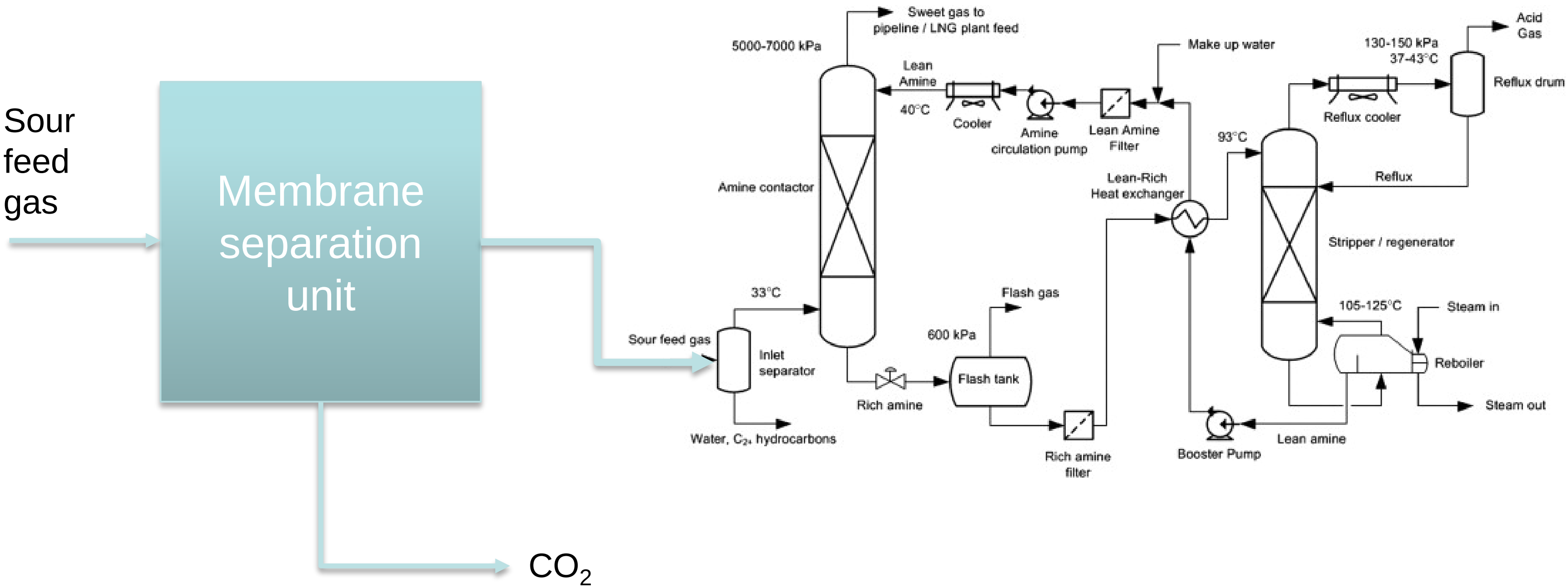

Run absorber hard to get 50 ppmv $CO_2$ for LNG prep. (vs 2% pipeline gas)

Optimized solvent rate = 1258$m^3$/h

# Summary amine unit requirements for Feed 1 and Feed 2

| | Feed1 | Feed2 |
|---|---|---|
| $CO_2$, %mol | 10 | 50 |
| $H_2S$, %mol | 0 | 1 |
| Solvent rate $m^3/hr$ | 1258 | 4105 |
| Absorber stages | 20 | 20 |
| Absorber diameter, m | 10 | 15 |
| Stripper stages | 7 | 7 |
| Reboiler duty, Btu/gal lean solvent | 880 | 880 |

# Hybrid membrane-amine process



# Membrane separation unit model

Material: cellulose acetate (CA) membrane

Selectivity P_$CO_2$/P_$CH_4$ = 15 (Niu and Rangaiah, 2014)
Selectivity P_$H_2S$/P_$CH_4$ = 19

Permeate pressure = 1.38 bar

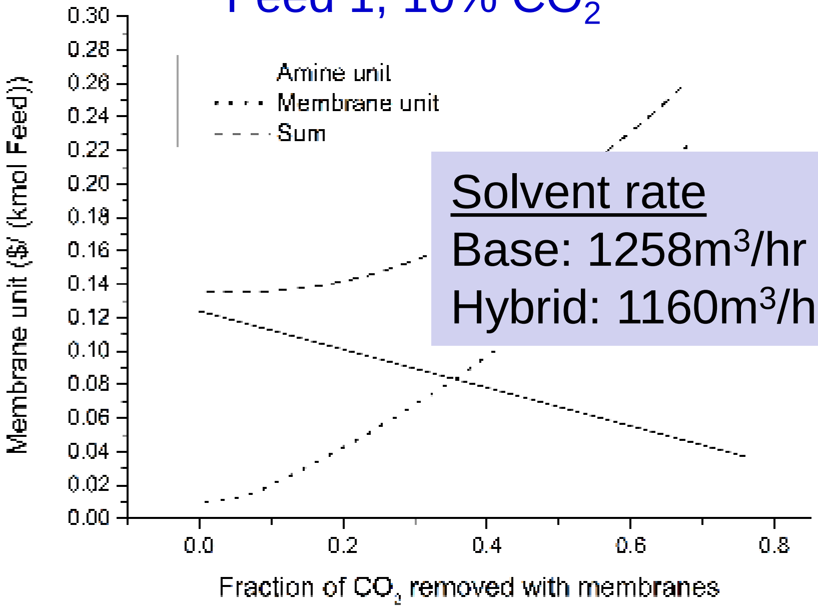
Membrane thickness = 100 nm (i.e. CA thickness on a substrate)

Modeled membrane unit in a user defined subflowsheet

# How much $CO_2$ to remove in the membrane unit?

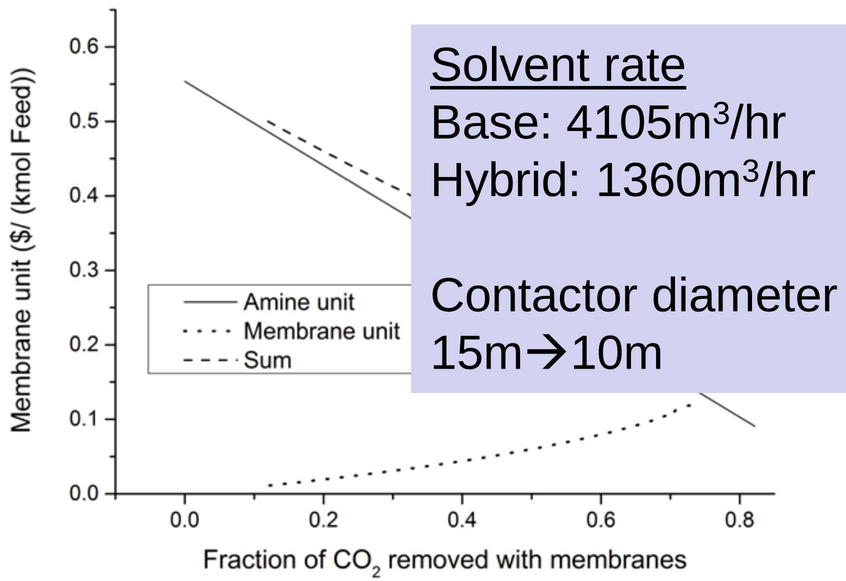
Each mole of $CO_2$ removed in membrane unit reduces solvent rate & reboiler duty required in the amine section. *Control = membrane area*.
→ Reducing hydraulic load also effects equipment sizing

Feed 1, 10% $CO_2$




<u>Solvent rate</u>
Base: 1258m³/hr
Hybrid: 1160m³/hr

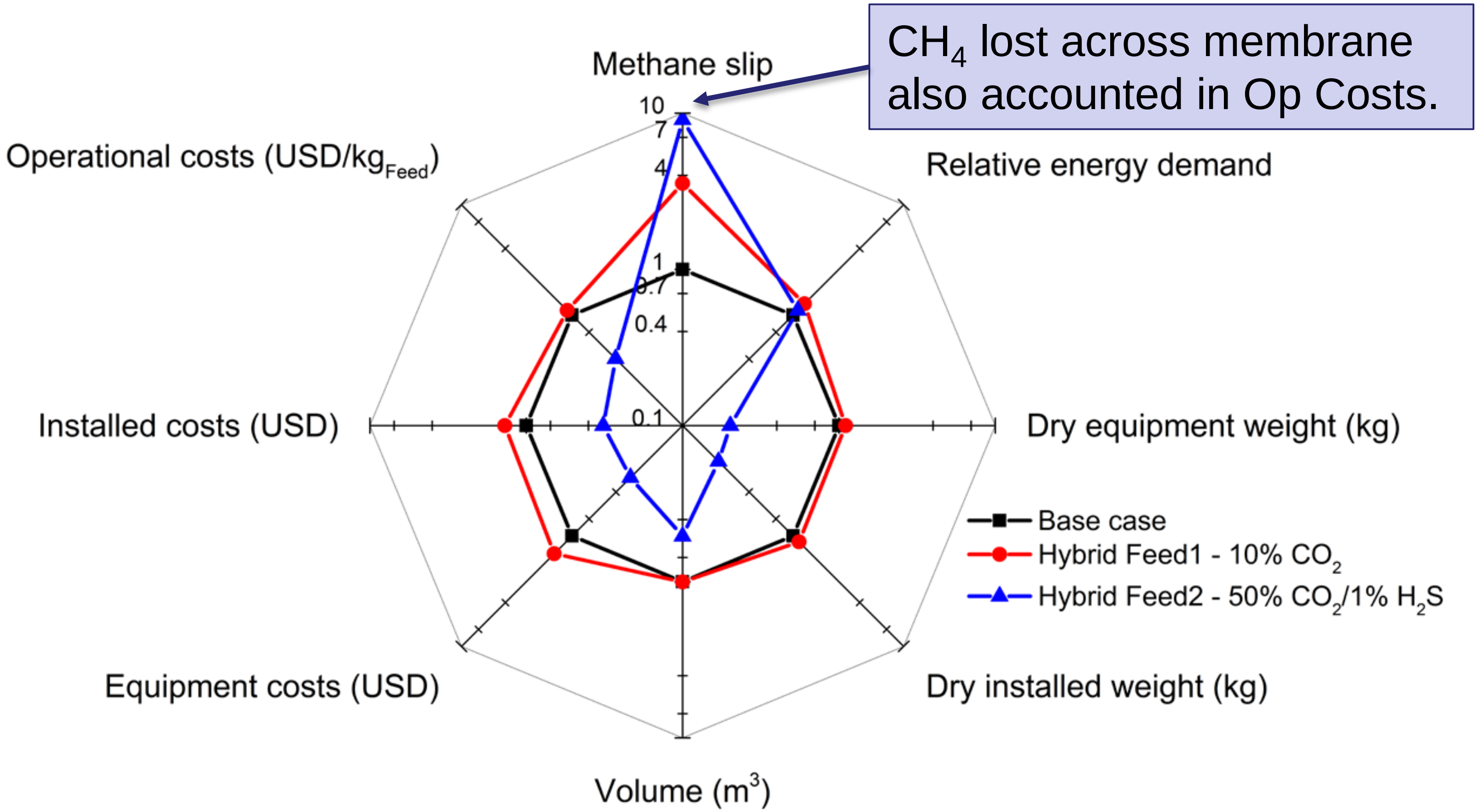
Feed 2, 50% $CO_2$ + 1% $H_2S$




<u>Solvent rate</u>
Base: 4105m³/hr
Hybrid: 1360m³/hr

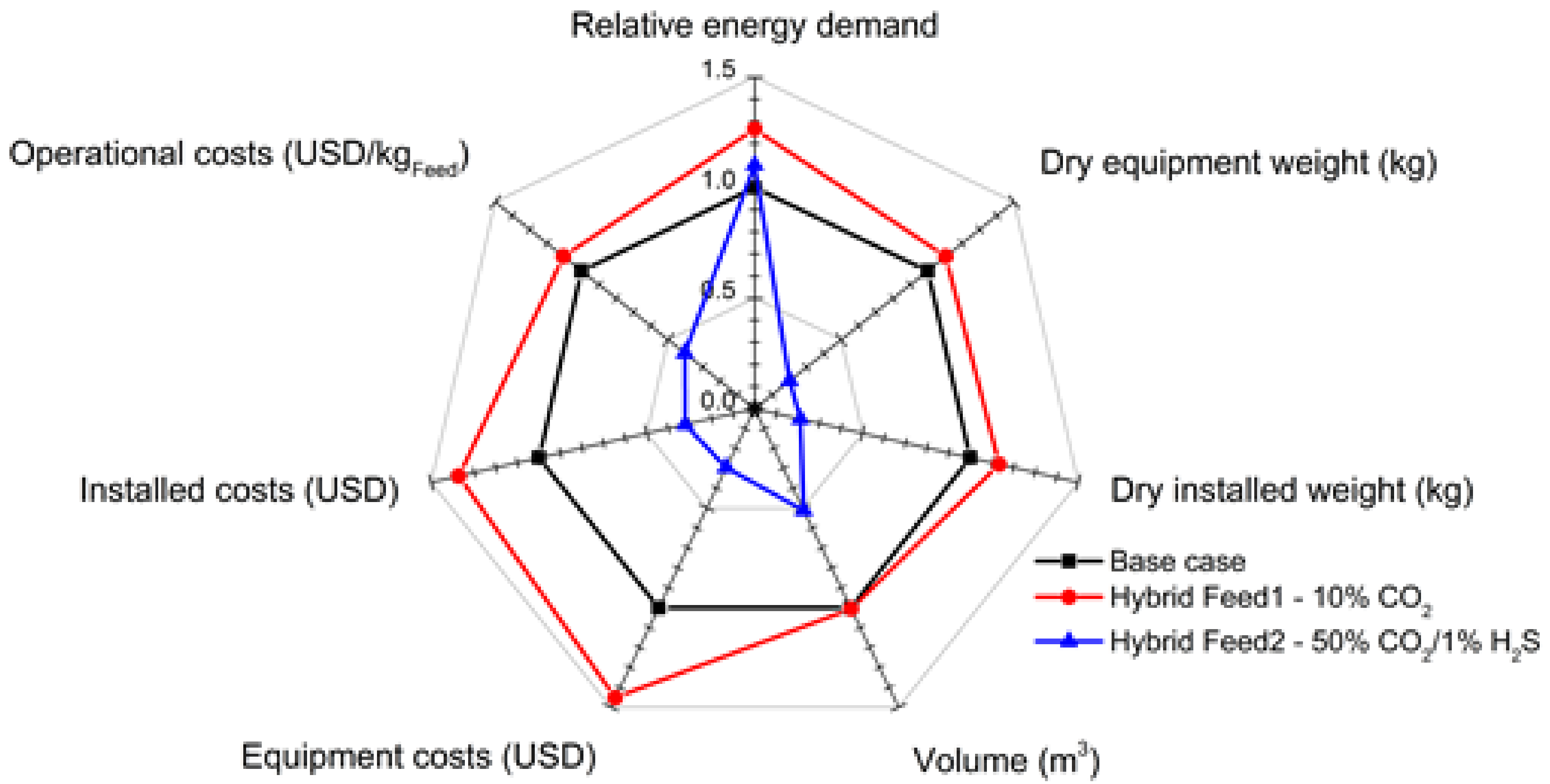
Contactor diameter
15m→10m

# Process metrics spider plot (log scale)




THE UNIVERSITY OF QUEENSLAND
AUSTRALIA
Create change

# Process metrics Spider plots (linear)



# Feed 1 10% $CO_2$ summary

No clear advantage of hybrid system for this feed scenario and membrane properties.

- 7.8% lower solvent rate in hybrid process, doesn't impact column size
- 30% drop in energy for reboiler, pumps in amine unit

Those benefits offset by:

- methane slip in membrane unit
- Small increase in equipment weight (MSU + base case amine unit)
- Hybrid process costs all increase

# Feed 2 50% $CO_2$ + 1% $H_2S$ Summary

For very sour gas feed there is potential to use bulk separation properties of the membrane unit.

- 67% reduced solvent rate in hybrid process
- 80% reduced equipment weight, 50% reduced plant volume

Methane slips increases → ~10% $CH_4$ in feed lost across membrane

- Still energy savings allow 40% reduction in operating costs
- Methane slip has implications on any $CO_2$ processing/storage plans

# Key limitations of study

Assumption gas to membrane unit is essentially dry.

Captures estimate of membrane replacement as an annualised cost, but doesn't capture any effect of fouling on separation performance

We only looked at 10% and 50% $CO_2$ scenarios, didn't search for feed concentration at which hybrid process becomes preferred option.

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# Unconventional gas research at UQ

## Gas separations

Helium recovery

Membranes (da Costa, Smart)

Adsorption (Rufford, Birkett, Zhu)

GTL/GTX (Rudolph)

Modelling (Do, Bhatia, Birkett)

Electrochemical $CO_2$ reduction

## Coal seam gas

Solids production issues

Relative permeability

Stress-strain-perm models

Two phase flow in the well bore

Well abandonment

UQ-CCSG

https://ccsg.centre.uq.edu.au/

# Cited references

Niu, Mark Wendou, G. P. Rangaiah. 2014. Retrofitting amine absorption process for natural gas sweetening via hybridization with membrane separation (in *International Journal of Greenhouse Gas Control* **29**: 221-230

Roussanaly, S., R. Anantharaman, K. Lindqvist. 2014. Multi-criteria analyses of two solvent and one low-temperature concepts for acid gas removal from natural gas (in *Journal of Natural Gas Science and Engineering* **20**: 38-49.

Rufford, Thomas E., Simon Smart, Guillaume C.Y. Watson et al. 2012. The removal of $CO_2$ and $N_2$ from natural gas: A review of conventional and emerging process technologies (in *Journal of Petroleum Science and Engineering* **94-95**: 123-154.

**Methane slip (MS)** The methane slip depicts the percentage of methane lost during the purification process. It is defined in Equation 5.1.

$$MS = 1 - \frac{CH_4 \ in \ the \ product \ gas}{CH_4 \ in \ the \ raw \ natural \ gas} \tag{5.1}$$

**Relative energy demand (RED)** This indicator is the ratio of lost and required energy based on the combustion heat of the product gas $\dot{Q}_{Prod}$, depicted in Equation 5.2. The absolute energy demand can be calculated by summing up the differences in the combustion heats of the raw gas $\dot{Q}_{Raw}$ along with the product gas $\dot{Q}_{Prod}$, electrical energy $P_{el}$ and the required heat of the reboiler $\dot{Q}_{Reb}$. The electrical energy $P_{el}$ in the gas facilities is provided by gas turbines. For calculating $P_{el}$ a turbine efficiency of $\eta = 0.4$ is assumed.

$$RED = \frac{\dot{Q}_{Raw} - \dot{Q}_{Prod} + P_{el}/\eta + \dot{Q}_{Reb}}{\dot{Q}_{Prod}} \tag{5.2}$$

**Operational costs** Table 5.2 provides the information needed for calculating the operational costs. Maintaining costs are neglected in this paper.

**Table 5.2:** Values for calculating the operational costs of base and hybrid case

| | Value | Unit | Source |
|---|---|---|---|
| Cost for reboiler steam | 0.0145 | \$/kg | [20] |
| Cost for electricity | 0.07 | \$/kWh | [20] |
| Cost for cooling water | 0.01 | \$/t | [20] |
| Cost for process water | 0.0005 | \$/kg | [20] |
| $CH_4$ Loss | 4 | \$/MMBtu | [20],[39] |
| Lower heating value methane | 10 | kWh/m$^3$ | [40] |
| Cost for MDEA | 5.5 | \$/kg | [41] |
| Cost for PZ | 7.7 | \$/kg | [41] |
| Solvent Degradation | 0.25 | kg/$t_{CO_2}$ | [20] |
| Temperature saturated steam | 140 | °C | |
| Efficiency of reboiler heating | 0.9 | | |