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Process evaluation of novel CO₂ capture processes for subsea application

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Summary:

With a subsea module for sweetening of natural gas, it is possible to extract natural gas from places with a too high concentration of CO₂ is too remote or both. The separated gas containing a high amount of CO₂ needs to be reinjected into the reservoir.

In this work, it is given an overview of the different alternative of what can be implemented. Some membrane based process alternative are simulated with polymer membranes at different specification and parameters. To lower the CO₂ content down to 8 mol%, with a feed flow of 2MSm³ that contains CO₂ of 80-, 50- and 20 mol% and the rest are methane.

The membrane area required for a crossflow model were 105 000m², 188 000m² and 203 000m², and for a countercurrent model 94 000m², 176 000m² and 200 000m², respectively. The crossflow model used are from an example in Aspen Custom Modeler implemented in Aspen Plus. The countercurrent model is from literature.

For the same cases with multi components, and CO₂ remains the same and other components such as C₂, C₃, C₄ and water are added. The membrane area for a crossflow model was 93 000m², 157 000m² and 158 000m². A case with a two stage membrane system to bring the retentate flow to natural gas specification (2mol% CO₂) with feed content of 80mol% CO₂. That case required a membrane area of 106 000m² and 246 000m² and a recycle compressor at 718kW. An advantage of this is that the natural gas reaches sales specs. However, this leads to more equipment used where the focus is to minimize equipment.

For the case with 20mol% CO₂ in the feed, an estimated subsea module would cost ~62 mill. USD with operational cost annually ~1.5 mill. USD. With a potential theoretical income of ~45 mill. USD with natural gas annually, this case seems promising.

For the case with 80mol% CO₂ in the feed, an estimated subsea module would cost ~146 mill. USD with operational cost annually ~5.8 mill. USD. With a potential theoretical income of ~10 mill. USD with natural gas annually, this is not economical in the view of natural gas income. However, if there is a marked for CO₂ enhanced oil recovery in some nearby field, the CO₂ rich gas could be sold.

Preface

This Master thesis report is written in 4. semester to the course with subject code FMH606 at the University of South-eastern Norway. Programs used are Microsoft Office, Aspen Plus, and Aspen Custom modeler.

This report aims to evaluate the possibilities of cleaning CO₂ from natural gas in a subsea environment. Membrane simulations are done with equations from C.J. Geankoplis "Transport Processes and Separation Process Principles, Fourth edition" and Aspen Custom Modeler example simulations, "Gas Permeation Module Example".

Thanks to all supervisors for all the time that you took to share your knowledge and support.

Porsgrunn, 19.05.2021

Roy Sømme Ommedal

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Nomenclature

6FDA	4,4'-(hexafluoroisopropylidene) diphthalic anhydride
A_m	Membrane Area
$^{\circ}\text{C}$	Celsius
CA	Cellulose Acetate
CAPEX	Capital expenditures
CC	Installed compressor cost (USD)
DEA	diethanolamine
EOR	Enhanced oil recovery
ft^3	Cubic feet
FTM	Fixed transport membranes
GPU	Gas permeance unit
kg	Kilogram
L_f	Feed flow
L_o	Retentate flow
M	Mega (10^6)
m^2	Square meter
m^3	Cubic meter
Mcf	Mega cubic feet (Mft^3)
MDA	Methylenedianiline
MDEA	Methyl diethanolamine
MEA	Monoethanolamine
MMBtu	Metric million British thermal unit
MMscfd	Metric million standard cubic feet per day

MMM	Mixed matrix membrane
N	Normal temperature and pressure
NG	Natural gas
ODA	4,4'-Oxydianiline
OPEX	Operational expenses
P'_a/t	Permeance of component a
PC	Polycarbonates
PES	Polyethersulfone
PI	Polyimide
ppm	Parts per million
PSf	Polysulfone
P_G	Pressure of natural gas in MPa
p_h	High-pressure side of membrane
p_l	Low-pressure side of membrane
p_r	Pressure on retentate side
p_p	Pressure on permeate side
S (STP)	Standard temperature and pressure
TEG	Triethylene glycol
t_G	Temperature of natural gas
TR	Thermal rearrange
V_p	Permeate flow
$W_{cp,EOR}$	Compressor energy for reinjection
$W_{cp,Recycle}$	Compressor energy for recycle stream
w_{water}	Mass of water in natural gas per Mm^3

$x_{f,a}$	Molar fraction in the feed
$x_{o,a}$	Molar fraction in the retentate
x_{oM}	Minimum reject composition
$y_{p,a}$	Molar fraction in the permeate
Å	Ångstrøm 10^{-10} meters

Greek symbols

η_{cp}	Adiabatic efficiency of compressor
$\alpha_{a/b}$	Selectivity between component a and b
θ	Permeation cut
μ	Micro (10^{-6})
ΔP	Pressure difference

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1 Introduction

It is estimated 270trillion m^3 of develop and undeveloped natural gas (NG) resources and roughly half of that involves carbon dioxide at over 2% that will need further processing. With areas around Southeast Asia, North America, North Africa and Middle East that have reservoirs with the highest CO_2 content [1]. Many of these reservoirs are undeveloped and with limited access, that makes it hard to extract the resources. More traditional method of cleaning NG today are amine absorption, this requires more attention and maintenance after some operation time [2].

For remote location where supervision and maintenance are difficult, a membrane module becomes attractive due to the minimal of operational equipment. There are several reasons why cleaning carbon dioxide from natural gas as early as in a subsea production area is beneficial. It reduces the weight and area on the topside of the platform. It may be a key point to develop or continue production where CO_2 are deemed too high to have production operational. For sweetening of natural gas, membrane separation are more relevant when CO_2 content are above 20% [3].

The principle for a membrane is to let through some specific gas or liquid. Membranes can be categorized into seven different classes. This report will only be focusing on gas permeation in a membrane. [4]

Objectives of the report is to find and utilize membrane simulation based on public information. Evaluation for membrane materials that could be suited for a subsea facility. Study sensitivity of variations in CO_2 , pressure and membrane performance.

Structure of this report starts with chapter 2 explaining different aspects of membrane used for gas separation. Chapter 3 mention some different challenges and a list of polymer membranes. Chapter 4 contains the simulations, along with a verification on the models used. Chapter 5 gives information about some estimation of investment and operational cost. Chapter 6 have discussions about the report and chapter 7 have some conclusions made.

2 General of Membrane CO₂/CH₄ Separation

In this chapter it will be investigated mainly on membrane types and their functionality.

2.1.1 Scope

The scope of this report is to simulate the membrane process and look at a variety of different parameter for membrane that would be suitable or not for a subsea application. Could be from the membrane area to concentration on component in different streams or economical viewpoint. What kind of factors to include when choosing a membrane type. Figure 2.1 illustrates the scope with the main purpose is the membrane box, and secondary the compression, whilst not focusing on the pumping part.



Figure 2.1 illustrated the scope with a darker blue

2.2 Membrane

This subchapter will be presenting different factors to consider when choosing a membrane for subsea use.

2.2.1 Membrane classification

Membranes can be divided into several different classifications as shown in Figure 2.2. [5]

2 General of Membrane CO₂/CH₄ Separation

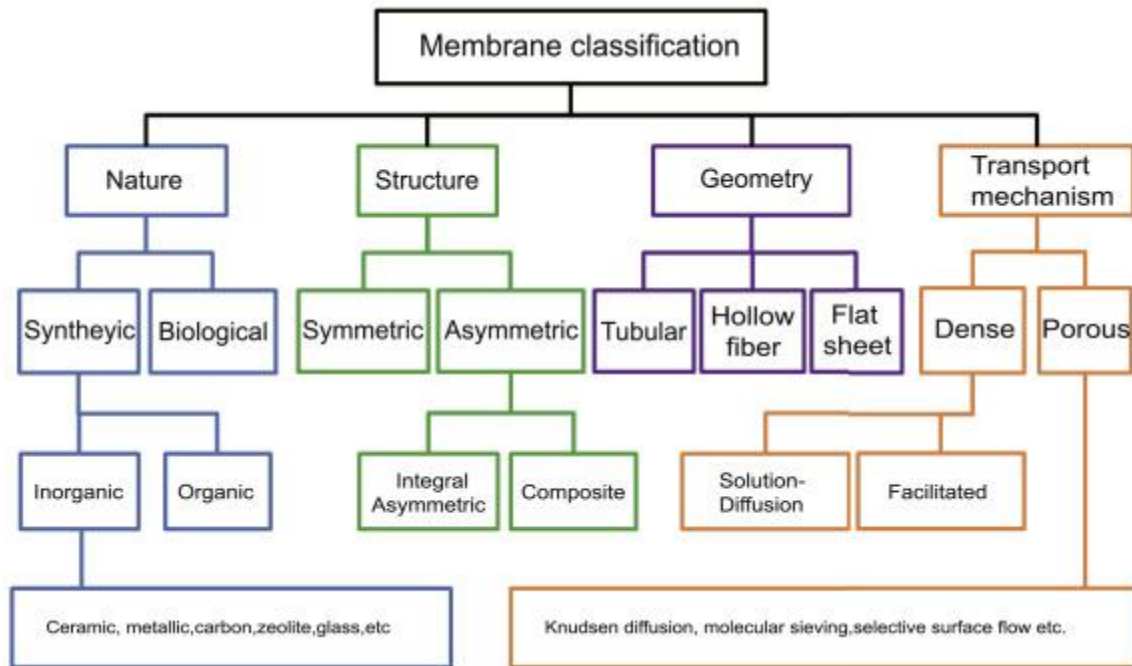


Figure 2.2 Membrane classification [5].

For membrane separation of natural gas, nature is synthetic. The structure could be both symmetric and asymmetric. Geometry should be in a hollow fiber configuration as it gives the packing density (membrane area per volume). Flat sheet configuration such as plate and frame module gives 100- to 400m²/m³ [6]. Tubular gives a packing density of 30- to 200m²/m³ compared to hollow fibers 500- to 9,000m²/m³ [7]. Both transport mechanism is to be considered.

2.2.2 Transport Mechanism in Membranes

How to measure the gas when permeating through a membrane, the common unites are Barrer for permeability and GPU for permeance. The GPU can be described as component permeate per times unit times area times pressure given in SI units it gives mole/(s·m²·pa). As for the permeability it would need the thickness of the membrane, for an asymmetric or multi-layer it would have added up with every layer.

2.2.3 Robeson upper line

Robeson upper line is set as a benchmark for gas permeation membranes, as most membranes are below this line. The first mark was set in 1991, then later raised in 2008 as membranes progress into giving better performance. Figure 2.3 shows both the prior- and present upper bound with numerous types of membranes performances. [8]

2 General of Membrane CO₂/CH₄ Separation

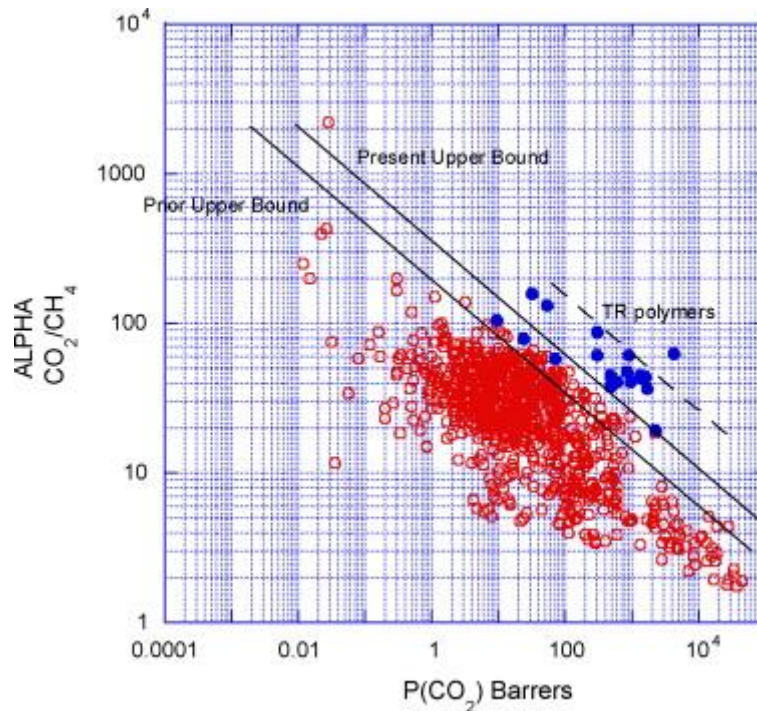


Figure 2.3 Presents both the prior- and present upper bound with numerous types of membranes performances. TR (Thermal rearrange), ALPHA (selectivity).

2.2.4 The buildup of different types of membranes

Symmetric membrane composes only one layer, while asymmetric consist of multiply layers.

2.2.4.1 Polymer membrane

For polymer membranes, there are two states to consider, glassy state and rubbery state. "Glassy membranes generally separate using difference in size; rubbery membranes separate using differences in condensability". Currently for commercial natural gas cleaning use, glassy polymer membrane is used for CO₂ separation, for heavier hydrocarbons (C₃₊) rubbery are used. Figure 2.4 gives a visual of glassy and rubbery separation specification. [3]

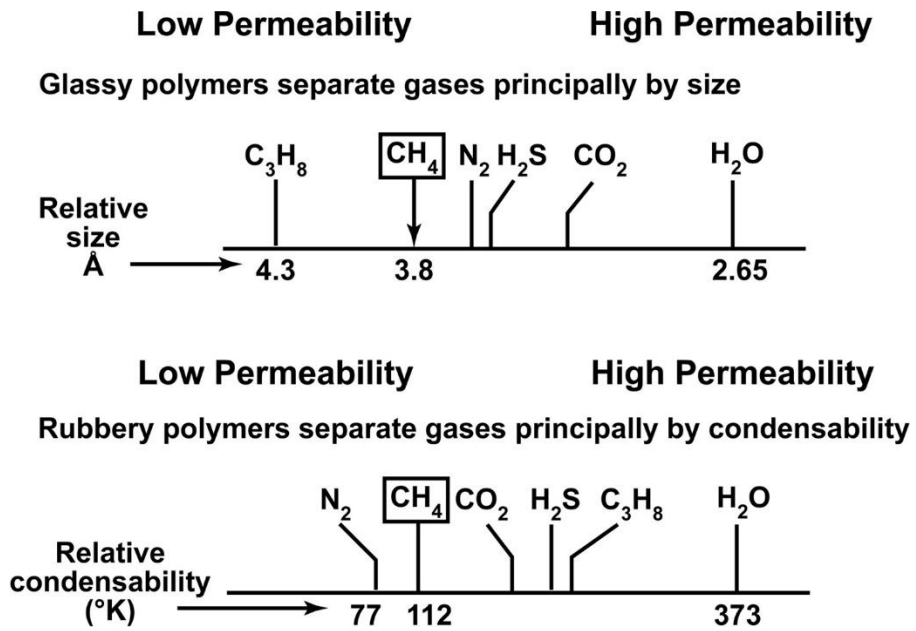


Figure 2.4 illustrates the compounds permeability next to each other, glassy polymers that relates to size and rubbery polymers relates with condensability. [3]

There are several different types of polymer membrane, some can be found in Table 2.2.

Table 2.1 shows different types of typical Polymer membrane. [9]

Acronym	Full name
PI	Polyimide
CA	Cellulose Acetate
PSf	Polysulfone
PES	Polyethersulfone
PC	Polycarbonates

2.2.4.2 Inorganic membrane

Different types of membrane can be found in Table 2.2

Table 2.2 shows different types of typical inorganic membrane. [6]

Name	Usually contains

2 General of Membrane CO₂/CH₄ Separation

Zeolite	Si, Al, Ca ²⁺ , Na ⁺ , K ⁺ ,
Glass	SiO ₂ , B ₂ O ₃ , Na ₂ O

2.2.4.3 Mixed matrix membrane (MMM)

Mixed matrix membranes are a combination of both inorganic and dense polymer membranes as shown in Figure 2.5 [10].

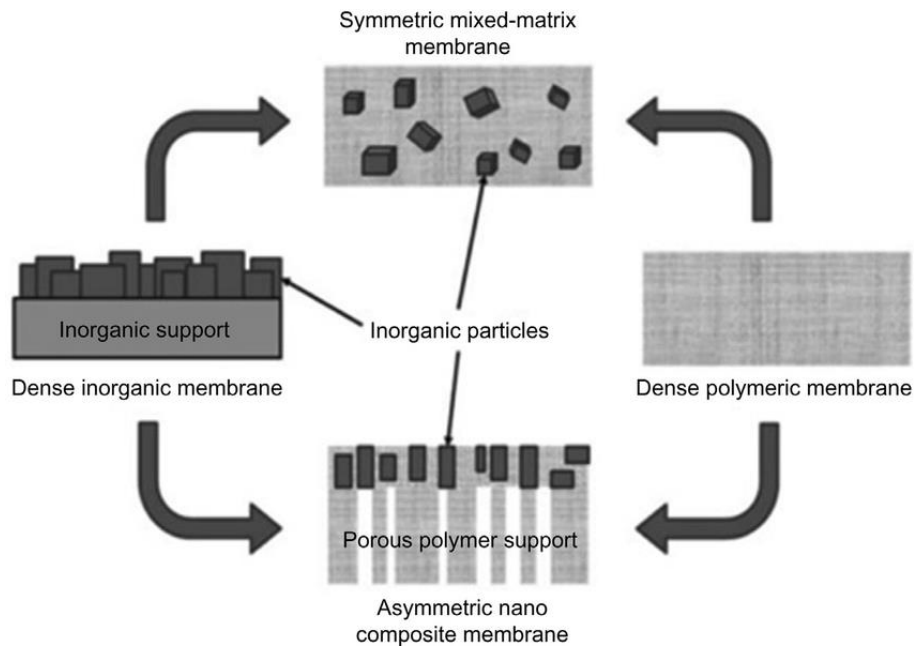


Figure 2.5 illustrate the structure of a MMM. [10]

2.2.4.4 Facilitated transport membranes (FTM).

With a facilitated transport membrane, it is possible to reach very high selectivity. Figure 2.6 illustrates that with the help of carriers fixed in the membrane to help the wanted gas over to the permeate side, while the other gas has to diffuse through a polymer layer. [11]

2 General of Membrane CO₂/CH₄ Separation

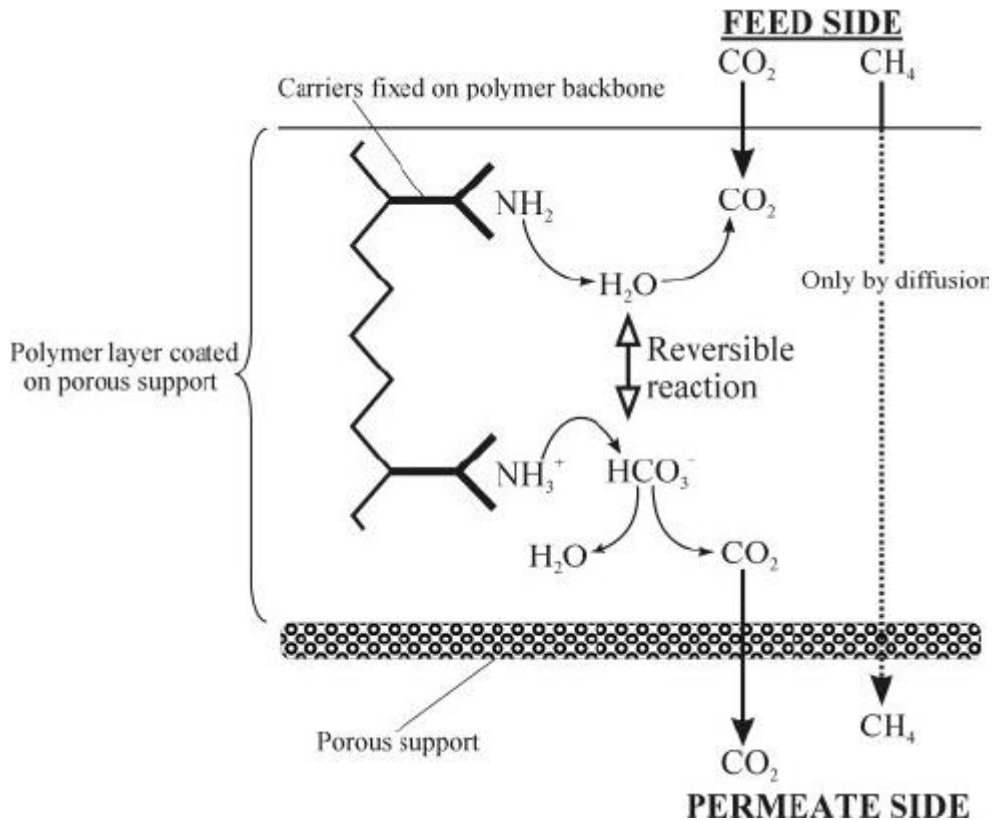


Figure 2.6 illustrates the separation mechanics for a fixed-site-carrier membrane [11].

2.2.5 Performance of different types

This subchapter it is looked at how these membrane material performs.

2.2.5.1 Polymer

Polymer membrane in most cases comes with a trade-off between higher permeability and higher selectivity described as Robeson upper bound. [9] Many are sustainable to be used with temperature as high as 500°C. [6]

A frequent problem with polymer membrane is high plasticization when CO₂, H₂S, H₂O, and heavy hydrocarbons. Aging causes a reduction in gas permeability. Aging effect differently on various types of polymer membranes. It can occur in two ways. One being the membrane thickness comprises by letting out some free volume within the membrane. The other being with a higher value of fractional free volume. A way to reduce aging is to strengthening the chain packing efficiency by adding meta or para linkages such as, 6FDA, ODA, MDA and many others. [12] Table 2.3 show some advantages and disadvantages with polymer membranes [13].

2 General of Membrane CO₂/CH₄ Separation

Table 2.3 Summary by Vinoba et al. [13]

Membranes	Advantages	Disadvantages
Polymeric membranes	Easy synthesis and fabrication	Low chemical and thermal stability
	Low production cost	Plasticization
	Good mechanical stability	Pore size not controllable
	Easy for upscaling and making variations in a module form	Follows the trade-off between permeability and selectivity
	Separation mechanism: Solution diffusion	

2.2.5.2 Inorganic membranes

Inorganic membrane can usually exceed 500°C and harsh environment. Usually, consist of multiple layers with just a thin layer for gas permeation. [6] Some inorganic membrane such as zeolite is resistance to CO₂ induced plasticization that would have led to a loss in selectivity. Usually, higher selectivity than polymer membranes. [14] When molecular sieving carbon membranes are dealing with impurities such as water, it might reduce performance or loss of function due to sorption in the micropores. [15] SAPO-34 that contains Al will strongly absorb water and possibly break the O-Al bounds that change the structure and reduces performance [16].

With Zeolite membrane permeation and selectivity drop with impurities of heavier hydrocarbons. The performance will be restored after the impurities are no longer present. [16] when fabricate large scale it not uncommon that the brittleness of the material can crack some places.

Table 2.4 show some advantages and disadvantages with inorganic membranes [13].

Table 2.4 Summary by Vinoba et al. [13]

Membranes	Advantages	Disadvantages
Inorganic Membranes	Superior chemical, mechanical and thermal stability	Brittle
	Tunable pore size	Expensive

2 General of Membrane CO₂/CH₄ Separation

Moderate the trade-off between permeability and selectivity	Difficulty in scale up
Operate at harsh conditions	
Separation mechanism: Molecular sieving (<6Å), Surface diffusion (<10-20Å), Knudsen diffusion (<0,1µm)	

2.2.5.3 Mixed matrix membranes

With MMM it is possible to surpass Robeson upper bound, Table 2.5 shows some advantages and disadvantages with polymer membranes. [13]

Table 2.5 Summary by Vinoba et al. [13]

Membranes	Advantages	Disadvantages
Mixed matrix membranes	Enhanced mechanical and thermal stability	Brittle at high fraction of fillers in polymeric matrix
	Reduced plasticization	Chemical and thermal stability depends on the polymer matrix
	Lower energy requirement	
	Compacting at high pressure	
	Surpasses the trade-off between permeability and selectivity	
	Enhanced separation performance over native polymer membranes	

2 General of Membrane CO₂/CH₄ Separation

Separation followed by the combined polymeric and inorganic membrane principle
--

2.2.5.4 Facilitated transport membranes (FTM)

FTM also have a high permeability but will be limited to low CO₂ partial pressure. The separation performance will degrade over time due to evaporation and degrading of the carrier.[9]

2.2.5.5 Gas-liquid membrane contactor

A gas-liquid membrane contactor is a combination of membranes and solvent used for absorption and desorption. A setup with that type is illustrated in Figure 2.7 [15].

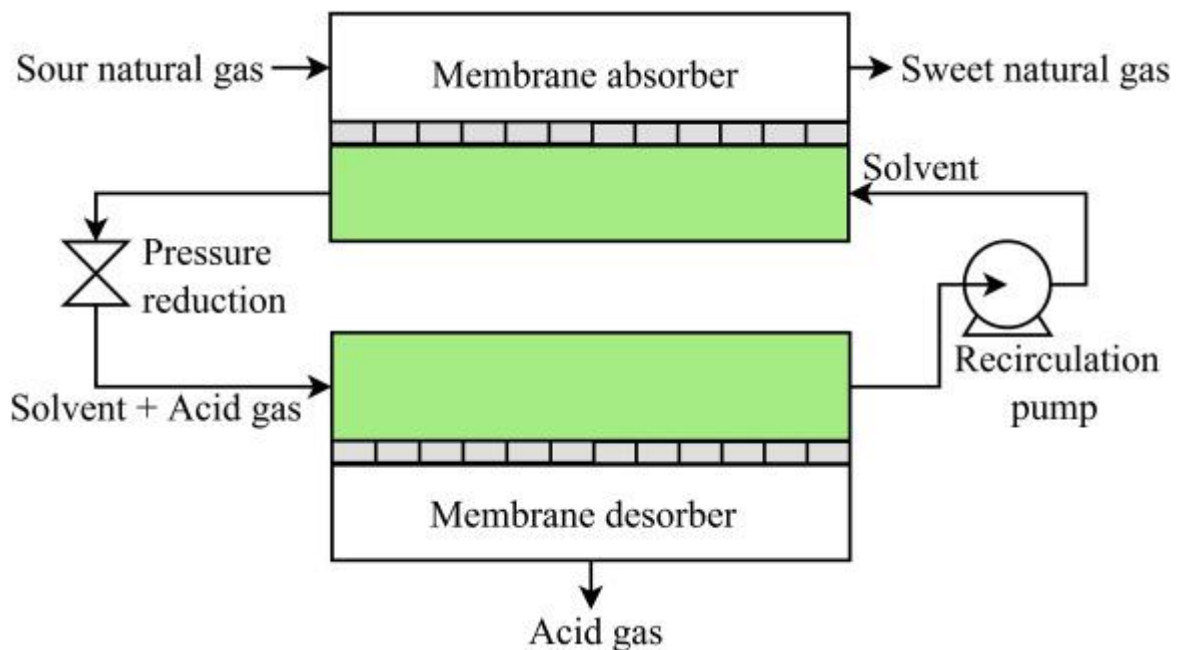


Figure 2.7 overview of membrane adsorption and -desorption that will be needed to fill a Gas-liquid membrane contactor.[15]

2.3 Other separation methods

2.3.1 Absorption

The most used technology for CO₂ removal from natural gas is absorption processes with a chemical solvent such as MEA, DEA or MDEA. [15] Absorption is predominantly done with an CO₂ carrier such as Methyl diethanolamine (MDEA) and Triethylene glycol (TEG) are usually used to dehydrate the gas. Flow rate typical under 350MMscfd (9.9MSm³/day) can have CO₂ inlet conditions up to 70% and purify it down to levels as low as 50ppmv. [2]

2.3.2 Adsorption

Pressure swing adsorption (PSA) are commercial available up to 2MMscfd (0.057MSm³/day) and does not often exceed 40mol% CO₂ in inlet stream [2]. To put the flow in to context, the Åsgard subsea compressors can handle up to 0.432MSm³/day¹ per compressor [17].

¹ Assumed to be gas volume at stander pressure and temperature.

3 Challenges

This chapter it will be tell about a few things to have in mind.

3.1 Membrane Challenges

By reviewing challenges which may arise with a membrane gas separation, it is possible to understand how certain obstacles works or can be affected.

3.1.1 Plasticization

Plasticization is the degrading of a membrane, usually due to swelling of the porous material. Glassy polymers are more affected by plasticization than rubbery polymers. The selectivity shown in the literature will usually be higher than a commercial tested, this is due to impurities in the gas that leads to plasticization [3]. Figure 3.1 shows how selectivity is affected when in contact with natural gas. [18]

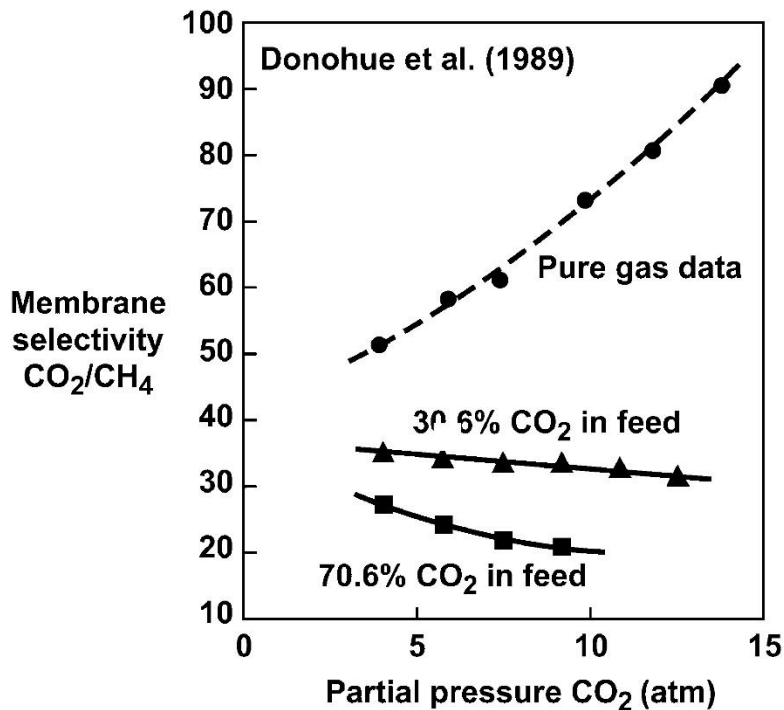


Figure 3.1 Cellulose acetate (CA) plasticization when mixed with pure gas data and natural gas. [18]

There are methods to reduce CO₂ plasticizations in polymer membranes, e.g. Thermal treatment, cross-linking and polymer blending. All these methods are based on strengthening molecular chain structure. [9]

Liu et al. studied CO₂/CH₄ separation on a TR polymer derived from an 6FDA membrane with the present of 1700ppm Toluene that CO₂ permeability reduced by 90% [19].

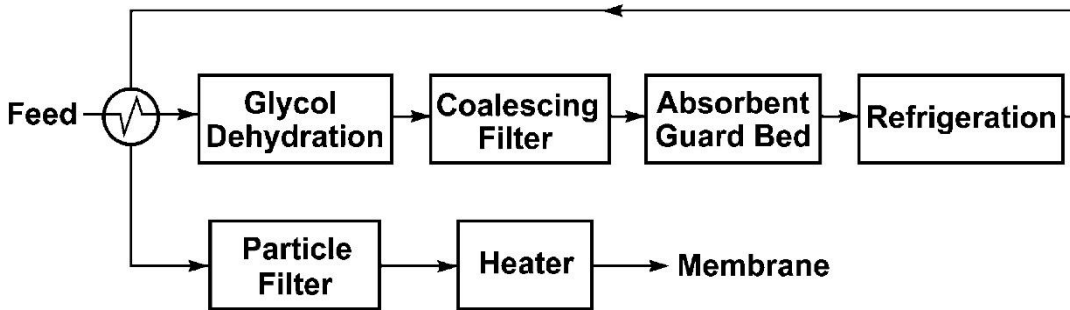
3.1.2 Membrane fouling

Membrane fouling is more common in separation processes with microfiltration, nanofiltration and reverse osmosis compared to gas separation. Fouling is when a layer is formed on the membrane that limits permeation. Some factors are gel layer formation, concentration polarization, absorption and plugging of the pores. There is virtually no fouling in dense membranes, mostly just with porous membranes. [6]

3.1.3 Membrane pretreatment

Due to particles, fouling and condensation of heavy hydrocarbons on the membrane, pretreatment as shown in Figure 3.2 are expected on natural gas [3].

Maximum Pretreatment



Minimum Pretreatment



Figure 3.2 shows a block diagram for typical NG pretreatment for membranes. [3]

3.1.4 Suppliers of gas separation membranes.

Most commercial gas separation with membrane technology is based on PI and CA [9]. Table 3.1 shows a shortlist of suppliers with one of their membrane solutions for CO₂ separation with natural gas [3].

Table 3.1 Suppliers of membrane separation used for industrial scaled for removal of CO₂ in natural gas [3]

Company	Membrane Module	Membrane material
Medal (Air Liquid)	Hollow fiber	Polyimide (PI)
Cynara (NATCO)	Hollow fiber	Cellulose acetate (CA)

ABB/MTR	Spiral-wound	Perfluoro polymer silicone rubber
---------	--------------	-----------------------------------

3.1.5 Suited Membrane materials

For a simple unit of gas membrane separations, it is desired for high permeability to reduce the size of the module and high selectivity to increase the purity of the permeated stream. Facilitated transport membranes show excellent performance but are limited to a low concentration of CO₂. Inorganic membranes have a good outcome for both but are brittle and hard to produce large scale. Mixed matrix membranes also have a high potential, but literature found for a large scale or well tested MMM over time are absent. That leaves polymer membranes that are well tested and have been in use for large scale CO₂ removal.

Zhang et al. composed the Table 3.2 that includes a list of various polymer membranes. [9]

Table 3.2 A summary of polymer membranes with the performance. [9]

Membrane material	Membrane Type	Pressure [bar]	Temp (°C)	CO ₂ Permeances (GPU) ^a	Selectivity (CO ₂ /CH ₄)	Test Type (CO ₂ vol%) ^b	Ref.
6FDA-BAPAF	Dense	30	21	24.6	22.78	S	[20]
6FDA-DAP	Dense	30	21	38.57	77.82	S	[20]
6FDA-DABA	Dense	30	21	26.3	46.96	S	[20]
6FDA-1,5-NDA	Dense	10	35	22.6* 25- 50µm (0.57)	49	S	[21]
6FDA-durene/mPDA (50:50)	Dense	10	35	84.6* 40µm (2.12)	29.9	S	[22]
6FDA-durene	Dense	10	35	458* 40µm	16.1	S	[22]

3 Challenges

				(11.45)			
Matrimid® 5218	Dense	34.5	35	10* 30- 60µm (0.25)	35.71	S	[23]
Matrimid® 5218	Dense	1.1	20-25	28.5	50	M	[24]
Matrimid® 5218 (fluorinated)	Dense	1.1	20-25	18.7	93.5	M	[24]
Poly- (dimethylsiloxane) PDMS	Dense	2-4	23	3800* Not given (95.0)	3.17	S	[25]
Polycarbonate (PC)	Dense	20	30	2* Not given (0.05)	27.2	M (40%)	[26]
Polyamides	Dense	2	35	11* 25- 50µm (0.28)	36.3	S	[27]
DMAEMA- PEGMEMMA	Dense	2	35	24.3	12.5	S	[28]
6FDA-DAT	Asym- metric	7	20	59	40	M (40%)	[29]
6FDA-DAT	Asym- metric	2	35	55	60	M (40%)	[30]
6FDA-DAT (crosslinked)	Asym- metric	2	35	32	55	M (40%)	[30]

3 Challenges

PSf	Asym-metric	5	25	80.7	40.2	S	[31]
Matrimid [®]	Asym-metric	15	20	11	67	M	[32]
Matrimid [®] /P84 blend	Asym-metric	8	35	11.5	35	M (50%)	[33]
Cellulose acetate	Asym-metric	8	35	2.5	20	M (50%)	[33]
Cross-linked PI/PES	Dual layer	6	23	28.3	101	S	[34]
PBI/Matrimid [®] blend and PSf	Dual layer	10	35	4.81	41.81	S	[35]
Matrimid [®] /PES	Dual layer	10	22	9.5	40	M (40%)	[36]
<p>^a 1 GPU = 3.35e-10 mol m⁻² s⁻¹ Pa⁻¹</p> <p>^b Test type: S = Singel gas experiment; M = Mixed gas experiment</p> <p>* 1 Barrer = 3.35e-16 mol m m⁻² s⁻¹ Pa⁻¹</p> <p>(xx) Calculated to GPU, Dense type, permeability is divided by 40μm to get permeance, that represented by the membrane thickness. Membrane thickness in dense type varies between 25-60μm. [21-23, 27]</p>							

For typical use in the industry commercial glassy polymers like PI, PSf and CA are usually chosen. PI stands out more due to the thermal strength and mechanical properties. PI shows satisfactory performance in pure gas permeability and selectivity ratio. PI based on the commercially available monomer 6FDA even better performance. [37]

3.1.6 Pressure drop

To calculate the pressure drop for a laminar flow inside a pipe the Poiseuille equation can be used.

$$\Delta P = \frac{8\pi\mu L L_p}{A_m^2} \quad (3.1)$$

ΔP being pressure drop in pascal, μ being the average dynamic viscosity and L is the length of the membrane. As an example, a one meter long membrane with the same specification as Base Case 1, that gives a pressure drop of 1.177bar and 4.709bar for 2 meter long.

However, to utilize as much of the membrane area it is best to have the permeate come to the inside of the pipes.

3.2 Specifications to reach for

Specification for transporting natural gas in the pipeline should be below 2-3% CO₂ [38]. To limit corrosion in the pipeline, CO₂ content should below 8% [3]. For CO₂-EOR the general CO₂ content ranges between 92- to 97vol% [39].

3.3 Hydrate formation and CO₂ Freezeout

Avoid by keeping a higher temperature as well and not too high of a pressure drop. CO₂ hydrates can occur with temperature at 10°C when the pressure is higher than 45bar.

3.4 Compression and Subsea

Compression is usually one of the higher costs in both CAPEX and OPEX for a membrane system. Cost of a compressor installed in onshore (CC) can be estimated by the following formula:

$$CC = USD8650 \times \frac{W_{cp}^{0.82}}{\eta_{cp}} \quad (3.2)$$

CC are the cost of an installed compressor onshore, W_{cp} is energy needed for the compressor and η_{cp} is the efficiency. [40] To assume the cost of a multiphase compressor, it is thought it might be similar cost as an installed regular compressor.

To be able to operate in subsea conditions a multiphase compressor is being used and can reduce the cost of conveying around 70% of a traditional facility [41]. This is a fairly new concept and even though Åsgard compression module operates mainly dry gas, it is the first of its kind [42]. Another limiting factor could be ratio outlet to inlet pressure, this might cause the need to have multiply compressors.

Due to limited access, it is favorable to minimize rotating machinery. Additional, in subsea a challenge is that there is usually no place to direct insignificant streams also called waste streams, this will make the pretreatment hard.

4 Membrane Simulations

Every simulation model described has some assumptions such as

- complete mixing in each cell
- isothermal conditions
- ideal gas behavior
- no pressure drop
- constant permeabilities
- Plug flow, no axial dispersion
- No flux coupling, each component permeates through the membrane with its own permeance.

4.1 Different simulations models

Simulations models for complete mix and countercurrent in this report is from example 13.4-1 and 13.8-1, respectively, from C.J. Geankoplis "Transport Processes and Separation Process Principles, Fourth Edition". These are modules with only two components in the stream. [4] The crossflow module is a numerical model from Aspen Costume Modeler that can take multiple components into account.

4.1.1 Complete mix

A complete mix module is indicated in Figure 4.1. L is the flow rate while x is mole fraction of the nonpermeated stream, while V is the flow rate while y is mole fraction of the permeated side. p_h and p_l are pressure on the high-pressure side and low-pressure side, respectively. θ being the permeate cut fraction given as follows:

$$\theta = \frac{Vp}{L_f} \quad (4.1)$$

The lowered font: f as feed, p as permeate, and o as outlet in the rejected stream. [4]

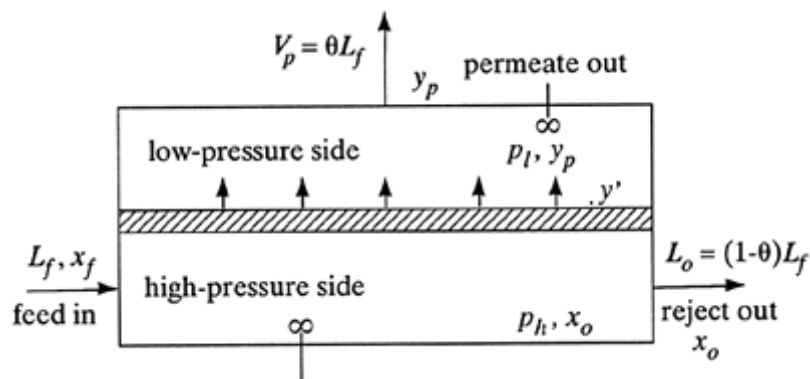


Figure 4.1 Schematic illustration of a complete mix module with symbols [4]

4 Membrane Simulations

This method is limited to the minimum reject composition x_{oM} that value is obtained as.

$$x_{oM} = \frac{x_f [1 + (\alpha - 1) \frac{p_l}{p_h} (1 - x_f)]}{\alpha * (1 - x_f) + x_f} \quad (4.2)$$

That means the molar fraction on the rejected out x_o can not be lower than the minimum reject composition x_{oM} . To get beyond this limit, it is possible to make an cascade system. [4]

Then a quadratic equation is used to find concentration of the permeate.

$$y_p = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \quad (4.3)$$

Where

$$\begin{aligned} a &= \theta + \frac{P_p}{P_f} - \frac{P_p}{P_f} * \theta - \alpha * \theta - \alpha * \frac{P_p}{P_f} + \alpha * \frac{P_p}{P_f} * \theta; & b &= 1 - \theta - x_p - \frac{P_p}{P_f} + \frac{P_p}{P_f} * \\ \theta + \alpha * \theta + \alpha * \frac{P_p}{P_f} - \alpha * \frac{P_p}{P_f} * \theta * \alpha * x_p; & \text{and} & c &= -\alpha * x_p \end{aligned} \quad (4.4)$$

Then a massbalance to give the x_o :

$$x_o = \frac{x_f - \theta y_p}{(1 - \theta)} \quad (4.5)$$

Then to add it in the final equation to get the membrane area:

$$A_m = \frac{\theta L_f y_p}{(P'_a/t) * (p_h x_o - p_l y_p)} \quad (4.6)$$

4.1.2 Crossflow

Each component transfers into next cell on the feed/retentate side by this equation:

$$L_{o,(k-1)} * x_{o,i(k-1)} = L_{o,(k)} * x_{o,i,(k)} + V_{p,(k)} * x_{p,i,(k)} \quad (4.7)$$

For the component to permeate over to the permeate side this equation is used:

$$V_p * y_{pi} = A_m * P'_a/t * (P_R * x_{o,i} - P_P * y_{P,i}) \quad (4.8)$$

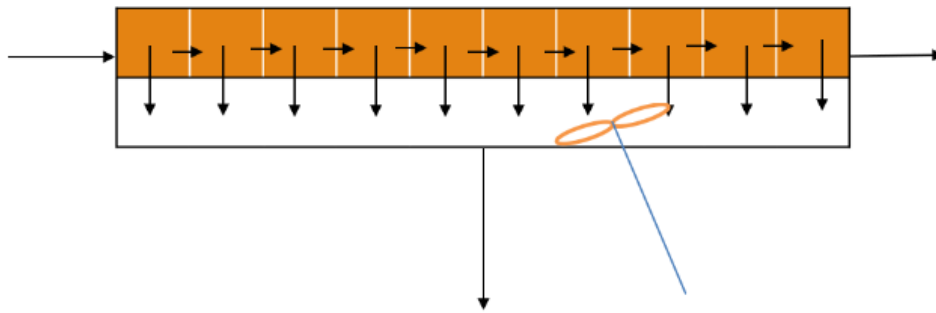


Figure 4.2 illustration on how the materials moves within the simulated membrane.

4.1.3 Countercurrent

This module uses a derivation of the finite-difference numerical method for a membrane. Figure 4.3 illustrates an asymmetric membrane, but the permeability taken as a parameter are the same for a symmetric and asymmetric calculation. [4]

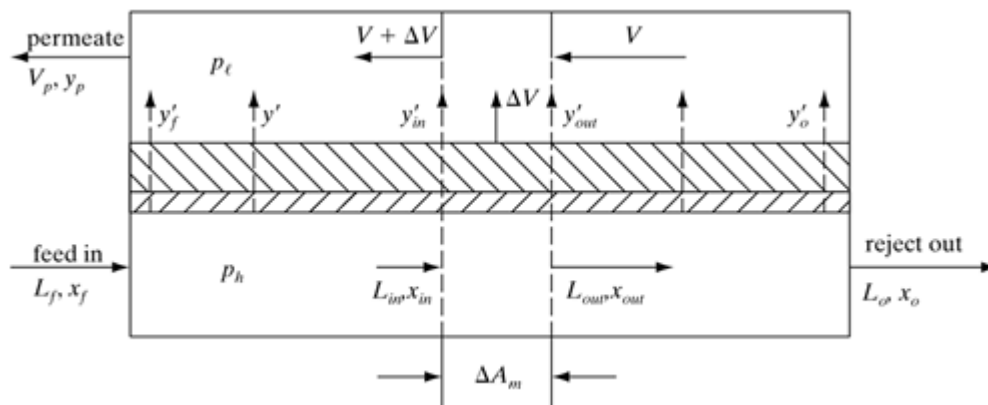


Figure 4.3 Schematic illustration of a countercurrent with asymmetric membrane module with symbols [4]

In this method each cell also uses the quadratic equation from a complete mix to get the information on what is permeated and continues calculate the retentate. This is possible due to that it is uniform pressure on both sides. Lastly the model uses the same equation from complete mix to calculate the area, except it adds up every cell.

4.2 Verifying the simulation model

To verify simulations, it is useful to check them with existing cases. In this case example 13.4-2 from Geankoplis is used [4].

4 Membrane Simulations

Table 4.1 Case used to verify the simulations.

Feed flow:	$L_f: 1\text{Nm}^3/\text{s} = 0.0446\text{kmole}/\text{s}$
Permeance:	$P'_{O_2/t}: 0.661 \cdot 10^{-3}\text{mole}/(\text{s} \cdot \text{m}^2 \cdot \text{bar})$ $P'_{N_2/t}: 0.0661 \cdot 10^{-3}\text{mole}/(\text{s} \cdot \text{m}^2 \cdot \text{bar})$
Selectivity	$\alpha = 10$
Molar compositions in feed:	$x_{f,O_2}: 0.209$ $x_{f,N_2}: 0.791$
Pressure	Retentate: 2.53bar Permeate: 0.253bar
Permeate cut fraction:	$\theta: 0.2$ ($V_p: 0.00892\text{kmole}/\text{s}$) ($L_o: 0.03568\text{kmole}/\text{s}$)

Serval different solutions is then shown in Table 4.2.

Table 4.2 Results from example 13.4-2

Model	Solution
Complete mixing model from Geankoplis	$A_m: 32,300\text{m}^2$ $y_{p,O_2}: 0.507$ ($V_p: 0.00892\text{kmole}/\text{s}$) $x_{o,O_2}: 0.135$ ($L_o: 0.03568\text{kmole}/\text{s}$)
Crossflow model from Geankoplis	$A_m: 28,930\text{m}^2$ $y_{p,O_2}: 0.569$ ($V_p: 0.00892\text{kmole}/\text{s}$) $x_{o,O_2}: 0.119$ ($L_o: 0.03568\text{kmole}/\text{s}$)
Crossflow model from ACM done in AP	$A_m: 29,981\text{m}^2$ $y_{p,O_2}: 0.598$ ($V_p: 0.00892\text{kmole}/\text{s}$) $x_{o,O_2}: \text{Not obtained}$ ($L_o: 0.03568\text{kmole}/\text{s}$)
Countercurrent model From Geankoplis	$A_m: 28,967\text{m}^2$ $y_{p,O_2}: 0.587$ ($V_p: 0.00892\text{kmole}/\text{s}$)

	x_{o,O_2} : 0.119	(L_o : 0.03568kmole/s)
Countercurrent model	A_m : 28,967m ²	
From MemSim ²	y_{p,O_2} : 0.587	(V_p : 0.00892kmole/s)
	x_{o,O_2} : Not given	(L_o : 0.03568kmole/s)

4.3 Cases

It is chosen the membrane type 6FDA-DAP with a permeances of 38.57GPU and selectivity of 77.82 then reduce both ~20% in efficiency due to plasticization.

4.3.1 Base Case

Parameters from Base Case 1, -2 and -3 are given in Table 4.3.

Table 4.3 Parameter for Base Case 1, 2, 3.

Feed flow:	L_f : 2MSm ³ /s = 3718kmole/h = 83333m ³ _{STP} /h
Permeance:	$P'_{CO_2/t}$: 31GPU = 0.083711m ³ _{STP} /(h·m ² ·bar) $P'_{CH_4/t}$: 0.5GPU = 0.001350m ³ _{STP} /(h·m ² ·bar)
Selectivity	α_{CO_2/CH_4} = 62
Molar compositions in feed:	<p>Base Case 1</p> x_{f,CO_2} : 0.80 x_{f,CH_4} : 0.20 <p>Base Case 2</p> x_{f,CO_2} : 0.50 x_{f,CH_4} : 0.50 <p>Base Case 3</p> x_{f,CO_2} : 0.20 x_{f,CH_4} : 0.80

² Lecture notes by Lars Erik Øi in "Membrane Technology Course" 28 November 2005.

4 Membrane Simulations

Pressure Retentate: 40bar
Permeate: 8bar

Retentate: x_{o,CO_2} : 0.08

Results from Base Case 1, -2 and -3 are given in Table 4.4

Table 4.4 Results from Base Case 1, -2 and -3

Results from Base Case 1 CO₂ inlet 0.8

Crossflow model	A_m : 104,886m ²	
from ACM done in AP	y_{p,CO_2} : 0.950	(V_p : 3078kmole/h)
	x_{o,CO_2} : 0.080	(L_o : 639kmole/h)

Countercurrent model	A_m : 94,010m ²	
From Geankoplis	y_{p,CO_2} : 0.950	(V_p : 3077kmole/h)
	x_{o,CO_2} : 0.080	(L_o : 641kmole/h)

Results from Base Case 2 CO₂ inlet 0.5

Crossflow model	A_m : 187,857m ²	
from ACM done in AP	y_{p,CO_2} : 0.838	(V_p : 2061kmole/h)
	x_{o,CO_2} : 0.080	(L_o : 1657kmole/h)

Countercurrent model	A_m : 175,809m ²	
From Geankoplis	y_{p,CO_2} : 0.840	(V_p : 2055kmole/h)
	x_{o,CO_2} : 0.080	(L_o : 1663kmole/h)

Results from Base Case 3 CO₂ inlet 0.2

Crossflow model	A_m : 202,742m ²	
from ACM done in AP	y_{p,CO_2} : 0.575	(V_p : 901kmole/h)
	x_{o,CO_2} : 0.080	(L_o : 2817kmole/h)

Countercurrent model	A_m : 199,695m ²	
From Geankoplis	y_{p,CO_2} : 0.578	(V_p : 897kmole/h)
	x_{o,CO_2} : 0.080	(L_o : 2821kmole/h)

4.3.2 Cases with different Pressure Drop

Table 4.5 shows the parameters used for all three cases with a low pressure drop.

Table 4.5 Parameter from Low pressure Case 1, -2 and -3

Feed flow:	L_f : 2MSm ³ /s = 3718kmole/h = 83333m ³ _{STP} /h
Permeance:	$P'_{CO_2/t}$: 31GPU = 0.083711m ³ _{STP} /(h·m ² ·bar) $P'_{CH_4/t}$: 0.5GPU = 0.001350m ³ _{STP} /(h·m ² ·bar)
Selectivity	α_{CO_2/CH_4} = 62
Molar compositions in feed:	Case 1 Low ΔP x_{f,CO_2} : 0.80 x_{f,CH_4} : 0.20 Case 2 Low ΔP x_{f,CO_2} : 0.50 x_{f,CH_4} : 0.50 Case 3 Low ΔP x_{f,CO_2} : 0.20 x_{f,CH_4} : 0.80
Pressure	Retentate: 40bar Permeate: 15bar
Retentate:	x_{o,CO_2} : 0.08

Table 4.6 shows the results used for all three cases with a low pressure drop.

Table 4.6 Results from Low pressure Case 1, -2 and -3

Results from Case 3 CO ₂ inlet 0.8	
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4 Membrane Simulations

Crossflow model	$A_m: 292,724\text{m}^2$	
from ACM done in AP	$y_{p,CO_2}: 0.882$	($V_p: 3337\text{kmole/h}$)
	$x_{o,CO_2}: 0.080$	($L_o: 380\text{kmole/h}$)
<hr/>		
Countercurrent model	$A_m: 268,397\text{m}^2$	
From Geankoplis	$y_{p,CO_2}: 0.884$	($V_p: 3328\text{kmole/h}$)
	$x_{o,CO_2}: 0.080$	($L_o: 390\text{kmole/h}$)
<hr/>		
Results from Case 3 CO ₂ inlet 0.5		
<hr/>		
Crossflow model	$A_m: 635,554\text{m}^2$	
from ACM done in AP	$y_{p,CO_2}: 0.657$	($V_p: 2706\text{kmole/h}$)
	$x_{o,CO_2}: 0.080$	($L_o: 1011\text{kmole/h}$)
<hr/>		
Countercurrent model	$A_m: 607,814\text{m}^2$	
From Geankoplis	$y_{p,CO_2}: 0.661$	($V_p: 2688\text{kmole/h}$)
	$x_{o,CO_2}: 0.080$	($L_o: 1030\text{kmole/h}$)
<hr/>		
Results from Case 3 CO ₂ inlet 0.2		
<hr/>		
Crossflow model	$A_m: 723,467\text{m}^2$	
from ACM done in AP	$y_{p,CO_2}: 0.349$	($V_p: 1659\text{kmole/h}$)
	$x_{o,CO_2}: 0.080$	($L_o: 2059\text{kmole/h}$)
<hr/>		
Countercurrent model	$A_m: 716,134\text{m}^2$	
From Geankoplis	$y_{p,CO_2}: 0.351$	($V_p: 1649\text{kmole/h}$)
	$x_{o,CO_2}: 0.080$	($L_o: 2069\text{kmole/h}$)
<hr/>		

Table 4.7 shows the parameters used for all three cases with a high pressure drop.

4 Membrane Simulations

Table 4.7 Parameter from High pressure Case 1, -2 and -3

Feed flow:	$L_f: 2\text{MSm}^3/\text{s} = 3718\text{kmole}/\text{h} = 83333\text{m}^3_{\text{STP}}/\text{h}$
Permeance:	$P'_{\text{CO}_2}/t: 31\text{GPU} = 0.083711\text{m}^3_{\text{STP}}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$ $P'_{\text{CH}_4}/t: 0.5\text{GPU} = 0.001350\text{m}^3_{\text{STP}}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$
Selectivity	$\alpha_{\text{CO}_2/\text{CH}_4} = 62$
Molar compositions in feed:	<p>Case 1 High ΔP $x_{f,\text{CO}_2}: 0.80$ $x_{f,\text{CH}_4}: 0.20$</p> <p>Case 2 High ΔP $x_{f,\text{CO}_2}: 0.50$ $x_{f,\text{CH}_4}: 0.50$</p> <p>Case 3 High ΔP $x_{f,\text{CO}_2}: 0.20$ $x_{f,\text{CH}_4}: 0.80$</p>
Pressure	Retentate: 40bar Permeate: 2bar
Retentate:	$x_{o,\text{CO}_2}: 0.08$

Table 4.8 shows the results used for all three cases with a high pressure drop.

Table 4.8 Results from High partial pressure Case 1, -2 and -3

Results from Case 3 CO ₂ inlet 0.5		
Crossflow model	$A_m: 45,535\text{m}^2$	
from ACM done in AP	$y_{p,\text{CO}_2}: 0.981$	($V_p: 2972\text{kmole}/\text{h}$)
	$x_{o,\text{CO}_2}: 0.080$	($L_o: 746\text{kmole}/\text{h}$)
Countercurrent model	$A_m: 44,448\text{m}^2$	
From Geankoplis	$y_{p,\text{CO}_2}: 0.980$	($V_p: 2974\text{kmole}/\text{h}$)
	$x_{o,\text{CO}_2}: 0.080$	($L_o: 744\text{kmole}/\text{h}$)

Results from Case 3 CO₂ inlet 0.5

Crossflow model	$A_m: 54,835\text{m}^2$	
from ACM done in AP	$y_{p,CO_2}: 0.946$	($V_p: 1804\text{kmole/h}$)
	$x_{o,CO_2}: 0.080$	($L_o: 1914\text{kmole/h}$)

Countercurrent model	$A_m: 53,638\text{m}^2$	
From Geankoplis	$y_{p,CO_2}: 0.945$	($V_p: 1805\text{kmole/h}$)
	$x_{o,CO_2}: 0.080$	($L_o: 1914\text{kmole/h}$)

Results from Case 3 CO₂ inlet 0.2

Crossflow model	$A_m: 32,688\text{m}^2$	
from ACM done in AP	$y_{p,CO_2}: 0.863$	($V_p: 570\text{kmole/h}$)
	$x_{o,CO_2}: 0.080$	($L_o: 3147\text{kmole/h}$)

Countercurrent model	$A_m: 37,363\text{m}^2$	
From Geankoplis	$y_{p,CO_2}: 0.863$	($V_p: 570\text{kmole/h}$)
	$x_{o,CO_2}: 0.080$	($L_o: 3148\text{kmole/h}$)

4.3.3 Cases with different Retentate concentration

Table 4.9 shows the parameter used for all three cases to get a low concentration in the retentate stream, in this report this is the concentration needed to get a sales ready natural gas.

Table 4.9 parameter used for Case 1, -2 and -3 with a low CO₂ concentration in the retentate.

Feed flow:	$L_f: 2\text{MSm}^3/\text{s} = 3718\text{kmole/h} = 83333\text{m}^3_{\text{STP}}/\text{h}$
Permeance:	$P'_{CO_2}/t: 31\text{GPU} = 0.083711\text{m}^3_{\text{STP}}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$ $P'_{CH_4}/t: 0.5\text{GPU} = 0.001350\text{m}^3_{\text{STP}}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$
Selectivity	$\alpha_{CO_2/CH_4} = 62$

4 Membrane Simulations

Molar compositions in feed:

Case 1 Low cons

$$x_{f,CO_2}: 0.80$$

$$x_{f,CH_4}: 0.20$$

Case 2 Low cons

$$x_{f,CO_2}: 0.50$$

$$x_{f,CH_4}: 0.50$$

Case 3 Low cons

$$x_{f,CO_2}: 0.20$$

$$x_{f,CH_4}: 0.80$$

Pressure

Retentate: 40bar

Permeate: 8bar

Retentate:

$$x_{o,CO_2}: 0.02$$

Table 4.10 shows the results for all three cases to get a low concentration in the retentate stream.

Table 4.10 Results from low concentration of CO₂ in the retentate Case 1, -2 and -3

Results from Case 3 CO ₂ inlet 0.8		
Crossflow model from ACM done in AP	$A_m: 191,645\text{m}^2$ $y_{p,CO_2}: 0.902$ $x_{o,CO_2}: 0.020$	$(V_p: 3287\text{kmole/h})$ $(L_o: 431\text{kmole/h})$
Countercurrent model From Geankoplis	$A_m: 147,120\text{m}^2$ $y_{p,CO_2}: 0.912$ $x_{o,CO_2}: 0.020$	$(V_p: 3252\text{kmole/h})$ $(L_o: 466\text{kmole/h})$
Results from Case 3 CO ₂ inlet 0.5		
Crossflow model from ACM done in AP	$A_m: 411,410\text{m}^2$ $y_{p,CO_2}: 0.706$ $x_{o,CO_2}: 0.020$	$(V_p: 2600\text{kmole/h})$ $(L_o: 1118\text{kmole/h})$

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Countercurrent model	$A_m: 350,273\text{m}^2$	
From Geankoplis	$y_{p,\text{CO}_2}: 0.722$	$(V_p: 2542\text{kmole/h})$
	$x_{o,\text{CO}_2}: 0.020$	$(L_o: 1176\text{kmole/h})$
Results from Case 3 CO ₂ inlet 0.2		
Crossflow model	$A_m: 579,394\text{m}^2$	
from ACM done in AP	$y_{p,\text{CO}_2}: 0.390$	$(V_p: 1811\text{kmole/h})$
	$x_{o,\text{CO}_2}: 0.020$	$(L_o: 1907\text{kmole/h})$
Countercurrent model	$A_m: 554,077\text{m}^2$	
From Geankoplis	$y_{p,\text{CO}_2}: 0.396$	$(V_p: 1778\text{kmole/h})$
	$x_{o,\text{CO}_2}: 0.020$	$(L_o: 1940\text{kmole/h})$

Table 4.11 shows the parameter used for all three cases to get a high concentration of CO₂ in the retentate stream.

Table 4.11 parameter used for Case 1, -2 and -3 with a high CO₂ concentration in the retentate.

Feed flow:	$L_f: 2\text{MSm}^3/\text{s} = 3718\text{kmole/h} = 83333\text{m}^3_{\text{STP}}/\text{h}$
Permeance:	$P'_{\text{CO}_2}/t: 31\text{GPU} = 0.083711\text{m}^3_{\text{STP}}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$ $P'_{\text{CH}_4}/t: 0.5\text{GPU} = 0.001350\text{m}^3_{\text{STP}}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$
Selectivity	$\alpha_{\text{CO}_2/\text{CH}_4} = 62$
Molar compositions in feed:	<p>Case 1 High cons</p> $x_{f,\text{CO}_2}: 0.80$ $x_{f,\text{CH}_4}: 0.20$ <p>Case 2 High cons</p> $x_{f,\text{CO}_2}: 0.50$ $x_{f,\text{CH}_4}: 0.50$ <p>Case 3 High cons</p> $x_{f,\text{CO}_2}: 0.20$ $x_{f,\text{CH}_4}: 0.80$

4 Membrane Simulations

Pressure Retentate: 40bar
Permeate: 8bar

Retentate: x_{o,CO_2} : 0.15

Table 4.12 shows the results for all three cases to get a high concentration of CO₂ in the retentate stream.

Table 4.12 Results from high concentration of CO₂ in the retentate Case 1, -2 and -3

Results from Case 3 CO ₂ inlet 0.8		
Crossflow model from ACM done in AP	A_m : 69,601m ² y_{p,CO_2} : 0.970 x_{o,CO_2} : 0.150	(V_p : 2947kmole/h) (L_o : 771kmole/h)
Countercurrent model From Geankoplis	A_m : 66,582m ² y_{p,CO_2} : 0.970 x_{o,CO_2} : 0.150	(V_p : 2948kmole/h) (L_o : 770kmole/h)
Results from Case 3 CO ₂ inlet 0.5		
Crossflow model from ACM done in AP	A_m : 97,292m ² y_{p,CO_2} : 0.906 x_{o,CO_2} : 0.150	(V_p : 1722kmole/h) (L_o : 1996kmole/h)
Countercurrent model From Geankoplis	A_m : 94,376m ² y_{p,CO_2} : 0.906 x_{o,CO_2} : 0.150	(V_p : 1722kmole/h) (L_o : 1996kmole/h)
Results from Case 3 CO ₂ inlet 0.2		
Crossflow model from ACM done in AP	A_m : 51,021m ² y_{p,CO_2} : 0.713	(V_p : 330kmole/h)

	$x_{o,CO_2}: 0.150$	$(L_o: 3389\text{kmole/h})$
Countercurrent model	$A_m: 50,793\text{m}^2$	
From Geankoplis	$y_{p,CO_2}: 0.714$	$(V_p: 330\text{kmole/h})$
	$x_{o,CO_2}: 0.150$	$(L_o: 3389\text{kmole/h})$

4.3.4 Lower Permeance and selectivity

In many cases to get a well proven and tested membrane it usually has lower permeability and selectivity. In this case it will be investigated the asymmetric cellulose acetate membrane parameter used is given in Table 4.13.

Table 4.13 Parameters from Case 1, -2 and -3 with an asymmetric CA

Feed flow:	$L_f: 2\text{MSm}^3/\text{s} = 3718\text{kmole/h} = 83333\text{m}^3_{\text{STP}}/\text{h}$
Permeance:	$P'_{CO_2}/t: 2.5\text{GPU} = 0.006751\text{m}^3_{\text{STP}}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$ $P'_{CH_4}/t: 0.125\text{GPU} = 0.0003375\text{m}^3_{\text{STP}}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$
Selectivity	$\alpha_{CO_2/CH_4} = 20$
Molar compositions in feed:	Case 1 $x_{f,CO_2}: 0.80$ $x_{f,CH_4}: 0.20$ Case 2 $x_{f,CO_2}: 0.50$ $x_{f,CH_4}: 0.50$ Case 3 $x_{f,CO_2}: 0.20$ $x_{f,CH_4}: 0.80$
Pressure	Retentate: 40bar Permeate: 8bar
Retentate:	$x_{o,CO_2}: 0.08$

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Table 4.14 shows the results from an asymmetric CA membrane.

Table 4.14 Results from Case 1, -2 and -3 with an asymmetric CA

Results from Case 1 CO ₂ inlet 0.8		
Crossflow model from ACM done in AP	$A_m: 891,982\text{m}^2$ $y_{p,\text{CO}_2}: 0.912$ $x_{o,\text{CO}_2}: 0.080$	$(V_p: 3217\text{kmole/h})$ $(L_o: 501\text{kmole/h})$
Countercurrent model From Geankoplis	$A_m: 855,369\text{m}^2$ $y_{p,\text{CO}_2}: 0.913$ $x_{o,\text{CO}_2}: 0.080$	$(V_p: 3215\text{kmole/h})$ $(L_o: 503\text{kmole/h})$
Results from Case 2 CO ₂ inlet 0.5		
Crossflow model from ACM done in AP	$A_m: 1,348,00\text{m}^2$ $y_{p,\text{CO}_2}: 0.753$ $x_{o,\text{CO}_2}: 0.080$	$(V_p: 2319\text{kmole/h})$ $(L_o: 1399\text{kmole/h})$
Countercurrent model From Geankoplis	$A_m: 1,325,126\text{m}^2$ $y_{p,\text{CO}_2}: 0.755$ $x_{o,\text{CO}_2}: 0.080$	$(V_p: 2312\text{kmole/h})$ $(L_o: 1406\text{kmole/h})$
Results from Case 3 CO ₂ inlet 0.2		
Crossflow model from ACM done in AP	$A_m: 1,220,000\text{m}^2$ $y_{p,\text{CO}_2}: 0.487$ $x_{o,\text{CO}_2}: 0.080$	$(V_p: 1094\text{kmole/h})$ $(L_o: 2624\text{kmole/h})$
Countercurrent model From Geankoplis	$A_m: 1,210,793\text{m}^2$ $y_{p,\text{CO}_2}: 0.489$ $x_{o,\text{CO}_2}: 0.080$	$(V_p: 1092\text{kmole/h})$ $(L_o: 2626\text{kmole/h})$

4.3.5 Multi components

Saturated water content in natural gas depends on temperature and pressure, the mass in kg of water w_{Water} per Mm^3 of natural gas, can be described as followed. [43]

$$w_{water} = 593.335 \cdot \exp(0.05486 \cdot t_G) \cdot P_G^{-0.81462} \quad (4.9)$$

t_G are the temperature of the gas in Celsius and P_G are in MPa. This gives 248kg/h with a gas flow rate at $2Nm^3$ pressure of 4MPa and a temperature of 50°C.

This can also be done in Aspen HYSYS as shown in Figure 4.4, with CO2 content of 80mol% this gives 332kg/h. With CO2 content of 20mol% that gives 257kg/h and with CO2 content of 0mol% that gives 236kg/h.

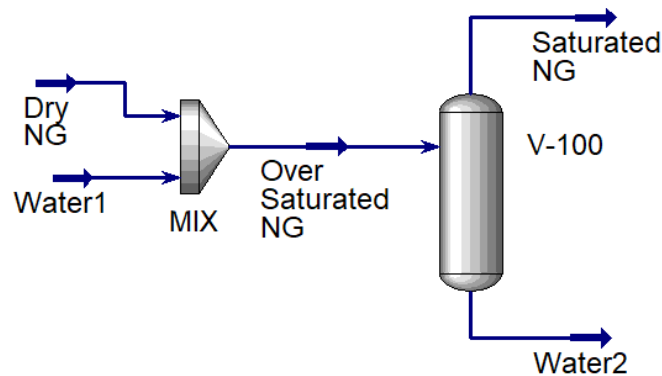


Figure 4.4 Screenshot from Aspen HYSYS

Table 4.15 shows a possibly composition of what a natural gas may contain.

Table 4.15 A possible dry Natural gas compositions

Component	Composition (mol%)		
	Case 1	Case 2	Case 3
CO2	80.0	50.0	20.0
Methane	12.8	32.0	51.2
Ethane	3.2	8.0	12.8
Propane	3.2	8.0	12.8
C4+	0.8	2.0	3.2
Sum	100.0	100.0	100.0

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Table 4.16 shows the composition when it is saturated with water.

Table 4.16 A possible saturated with water in Natural gas compositions

Component	Composition (mol%)		
	Case 1	Case 2	Case 3
CO ₂	79.6	49.8	19.9
Methane	12.7	31.8	51.0
Ethane	3.2	8.0	12.75
Propane	3.2	8.0	12.75
C ₄₊	0.8	2.0	3.2
Water	0.5	0.4	0.4
Sum	100.0	100.0	100.0

Table 4.17 gives the parameter for all three cases.

Table 4.17 Multi component cases with its parameters

Feed flow:	$L_f: 2\text{MSm}^3/\text{s} = 3718\text{kmole}/\text{h} = 83333\text{m}^3_{\text{STP}}/\text{h}$
Permeance:	$P'_{\text{CO}_2/t}: 31\text{GPU} = 0.083711\text{m}^3_{\text{STP}}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$ $P'_{\text{CH}_4/t}: 0.5\text{GPU} = 0.001350\text{m}^3_{\text{STP}}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$ $P'_{\text{C}_2\text{H}_6/t}: 0.89\text{GPU} = 0.002392\text{m}^3_{\text{STP}}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$ $P'_{\text{C}_3\text{H}_8/t}: 1.24\text{GPU} = 0.003348\text{m}^3_{\text{STP}}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$ $P'_{\text{C}_4+/t}: 1.55\text{GPU} = 0.004186\text{m}^3_{\text{STP}}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$ $P'_{\text{H}_2\text{O}/t}: 200\text{GPU} = 0.540007\text{m}^3_{\text{STP}}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$
Selectivity	$\alpha_{\text{CO}_2/\text{CH}_4} = 62$ $\alpha_{\text{CO}_2/\text{C}_2\text{H}_6} = 35$ $\alpha_{\text{CO}_2/\text{C}_3\text{H}_8} = 25$

$$\alpha_{\text{CO}_2/\text{C}_4^+} = 20$$

$$\alpha_{\text{H}_2\text{O}/\text{CH}_4} = 400^3$$

Molar compositions in feed:

Base Case 1 Multiply Components

$$x_{f,\text{CO}_2}: 0.796$$

$$x_{f,\text{CH}_4}: 0.127$$

$$x_{f,\text{C}_2\text{H}_6}: 0.032$$

$$x_{f,\text{C}_3\text{H}_8}: 0.032$$

$$x_{f,\text{C}_4^+}: 0.008$$

$$x_{f,\text{H}_2\text{O}}: 0.005$$

Base Case 2 Multiply Components

$$x_{f,\text{CO}_2}: 0.498$$

$$x_{f,\text{CH}_4}: 0.319$$

$$x_{f,\text{C}_2\text{H}_6}: 0.08$$

$$x_{f,\text{C}_3\text{H}_8}: 0.08$$

$$x_{f,\text{C}_4^+}: 0.02$$

$$x_{f,\text{H}_2\text{O}}: 0.004$$

Base Case 3 Multiply Components

$$x_{f,\text{CO}_2}: 0.199$$

$$x_{f,\text{CH}_4}: 0.51$$

$$x_{f,\text{C}_2\text{H}_6}: 0.128$$

$$x_{f,\text{C}_3\text{H}_8}: 0.128$$

$$x_{f,\text{C}_4^+}: 0.032$$

$$x_{f,\text{H}_2\text{O}}: 0.004$$

Pressure

Retentate: 40bar

Permeate: 8bar

Retentate:

$$x_{o,\text{CO}_2}: 0.08$$

³ All Selectivity from C₂H₆ to H₂O are guessed, the assumption is that this membrane will have similar ratio as given in the literature.[44] Y. Cui, H. Kita, and K.-i. Okamoto, "Preparation and gas separation performance of zeolite T membrane," *Journal of Materials Chemistry*, vol. 14, no. 5, pp. 924-932, 2004. [45] A. Kargari and H. Sanaeepur, "Application of membrane gas separation processes in petroleum industry," *Advances in petroleum engineering*, vol. 1, pp. 592-622, 2015. [46] J. Liu, G. Zhang, K. Clark, and H. Lin, "Maximizing ether oxygen content in polymers for membrane CO₂ removal from natural gas," *ACS applied materials & interfaces*, vol. 11, no. 11, pp. 10933-10940, 2019.

Table 4.18 gives the results from all multi component cases.

Table 4.18 Multi component case 1, -2 and -3

Crossflow model			
from ACM done in AP			
	<i>Case 1</i>	<i>Case 2</i>	<i>Case 3</i>
Area	$A_m: 92,407\text{m}^2$	$A_m: 157,412\text{m}^2$	$A_m: 157,672\text{m}^2$
Retentate Flow	$L_o: 606\text{kmole/h}$	$L_o: 1596\text{kmole/h}$	$L_o: 2776\text{kmole/h}$
CO ₂	$x_{o,\text{CO}_2}: 0.08$	$x_{o,\text{CO}_2}: 0.08$	$x_{o,\text{CO}_2}: 0.08$
CH ₄	$x_{o,\text{CH}_4}: 0.633$	$x_{o,\text{CH}_4}: 0.624$	$x_{o,\text{CH}_4}: 0.611$
C ₂ H ₆	$x_{o,\text{C}_2\text{H}_6}: 0.138$	$x_{o,\text{C}_2\text{H}_6}: 0.140$	$x_{o,\text{C}_2\text{H}_6}: 0.142$
C ₃ H ₈	$x_{o,\text{C}_3\text{H}_8}: 0.122$	$x_{o,\text{C}_3\text{H}_8}: 0.126$	$x_{o,\text{C}_3\text{H}_8}: 0.134$
C ₄₊	$x_{o,\text{C}_4+}: 0.0275$	$x_{o,\text{C}_4+}: 0.0292$	$x_{o,\text{C}_4+}: 0.0319$
H ₂ O	$x_{o,\text{H}_2\text{O}}: 0.000024$	$x_{o,\text{H}_2\text{O}}: 0.00022$	$x_{o,\text{H}_2\text{O}}: 0.0013$
Permeate Flow	$V_p: 3112\text{kmole/h}$	$V_p: 2122\text{kmole/h}$	$V_p: 942\text{kmole/h}$
CO ₂	$y_{p,\text{CO}_2}: 0.935$	$y_{p,\text{CO}_2}: 0.812$	$y_{p,\text{CO}_2}: 0.550$
CH ₄	$y_{p,\text{CH}_4}: 0.0285$	$y_{p,\text{CH}_4}: 0.0878$	$y_{p,\text{CH}_4}: 0.211$
C ₂ H ₆	$y_{p,\text{C}_2\text{H}_6}: 0.0114$	$y_{p,\text{C}_2\text{H}_6}: 0.0352$	$y_{p,\text{C}_2\text{H}_6}: 0.0850$
C ₃ H ₈	$y_{p,\text{C}_3\text{H}_8}: 0.0145$	$y_{p,\text{C}_3\text{H}_8}: 0.0451$	$y_{p,\text{C}_3\text{H}_8}: 0.1097$
C ₄₊	$y_{p,\text{C}_4+}: 0.0042$	$y_{p,\text{C}_4+}: 0.0131$	$y_{p,\text{C}_4+}: 0.0322$
H ₂ O	$y_{p,\text{H}_2\text{O}}: 0.0060$	$y_{p,\text{H}_2\text{O}}: 0.0068$	$y_{p,\text{H}_2\text{O}}: 0.0120$

4.3.6 Two Stage Compression membrane system

There are two possible configurations to have, first configuration A has a compressor for the first permeate that goes into a second membrane as shown in Figure 4.5. This is recommended when having a lower concentration of CO₂ in the feed (>30mol%) [47]. Another purpose for

4 Membrane Simulations

this is to use the recompression at a lower pressure drop in the second membrane and then not to exceed four times the compression ratio on the compressor.

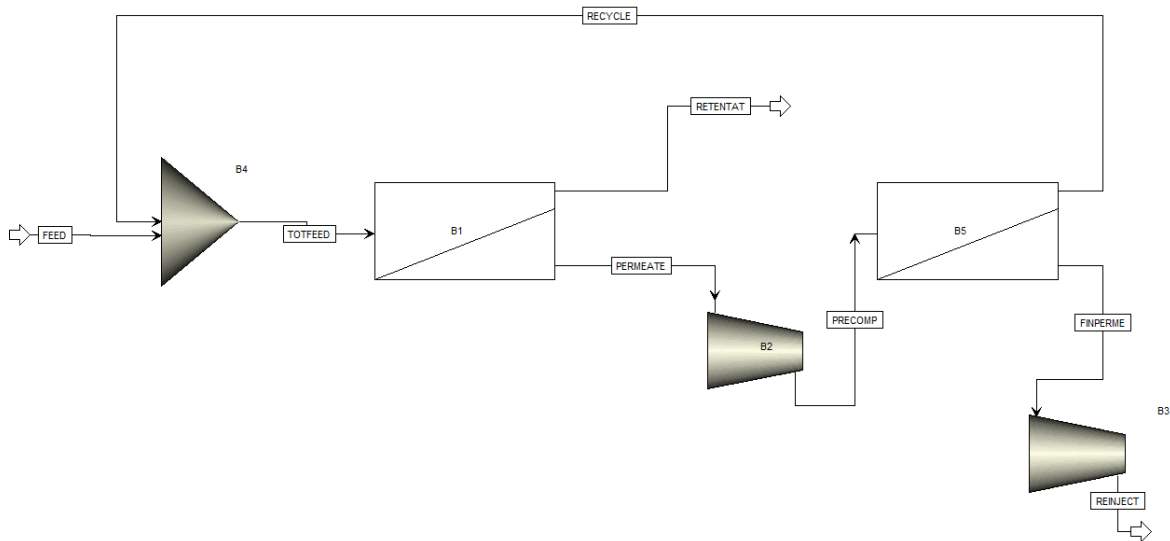


Figure 4.5 Screenshot from Aspen plus of configuration A

Table 4.19 shows Parameter and results for Two stage Case 3 with configuration A.

Table 4.19 Parameter and results for Two stage Case 3 with configuration A.

Feed flow:	$L_f: 2\text{MSm}^3/\text{s} = 3718\text{kmole}/\text{h} = 83333\text{m}^3_{\text{STP}}/\text{h}$
Permeance:	$P'_{\text{CO}_2}/t: 31\text{GPU} = 0.083711\text{m}^3_{\text{STP}}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$ $P'_{\text{CH}_4}/t: 0.5\text{GPU} = 0.001350\text{m}^3_{\text{STP}}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$
Selectivity	$\alpha_{\text{CO}_2/\text{CH}_4} = 62$
Molar compositions in feed:	Base Case 3 $x_{f,\text{CO}_2}: 0.20$ $x_{f,\text{CH}_4}: 0.80$
Pressure	
1. Membrane	Retentate: 40bar Permeate: 10bar
2. Membrane	Retentate: 40bar Permeate: 25bar
System retentate:	$x_{o,\text{CO}_2}: 0.08$

Results from Crossflow Model

Area	$A_{m,1}$: 528,880m ² $A_{m,2}$: 50,000m ²
System molar fraction and flow	y_{p,CO_2} : 0.929 (V _p : 526kmole/h) x_{o,CO_2} : 0.080 (L _o : 3192kmole/h)
Compressor energy [kW] (η_{cp} =100%)	$W_{cp,EOR}$: 1,020kW $W_{cp,Recycle}$: 4,231kW

second configuration B permeate exits the system from the first membrane, in the second membrane permeate is recycled back to the feed as shown in Figure 4.6. The compressor used for CO₂ injection exceeds the four times ratio limit and will need a secondary compressor for that task.

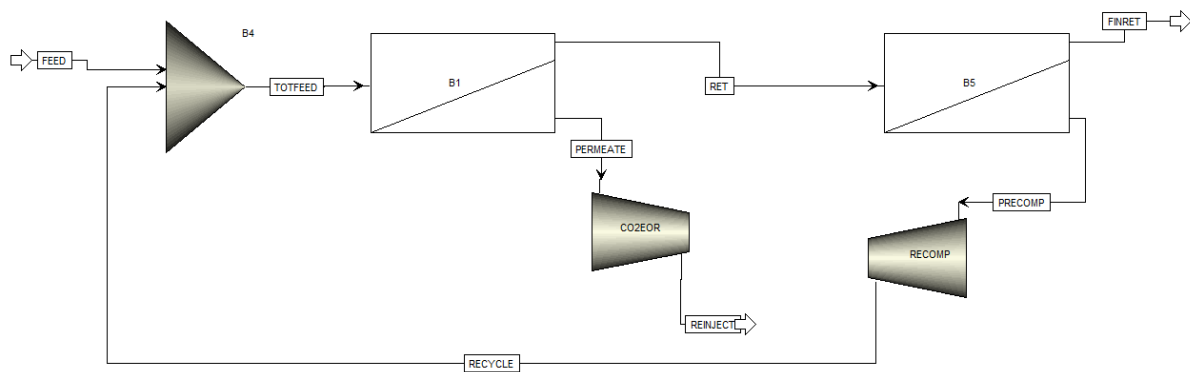


Figure 4.6 Screenshot from Aspen Plus of configuration B

Table 4.20 shows parameter and results for Two stage Case 2 with configuration B.

Table 4.20 Parameter and results for Two stage Case 2 with configuration B.

Feed flow:	L_f : 2MSm ³ /s = 3718kmole/h = 83333m ³ _{STP} /h
Permeance:	$P'_{CO_2/t}$: 31GPU = 0.083711m ³ _{STP} /(h·m ² ·bar) $P'_{CH_4/t}$: 0.5GPU = 0.001350m ³ _{STP} /(h·m ² ·bar)
Selectivity	α_{CO_2/CH_4} = 62

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Molar compositions in feed: **Base Case 2**
 x_{f,CO_2} : 0.50
 x_{f,CH_4} : 0.50

Pressure

1. Membrane	Retentate: 40bar Permeate: 8bar
2. Membrane	Retentate: 40bar Permeate: 10bar

System retentate: x_{o,CO_2} : 0.08

Results from Crossflow Model

Area	$A_{m,1}$: 60,829m ² $A_{m,2}$: 275,115m ²
System Molar fraction and flow	y_{p,CO_2} : 0.950 (V_p : 1795kmole/h) x_{o,CO_2} : 0.080 (L_o : 1923kmole/h)
Compressor energy [kW] (η_{cp} =100%)	$W_{cp,EOR}$: 4,803kW $W_{cp,Recycle}$: 1,467kW

With the parameters from Table 4.21 it is the only case that deliver up to NG specification that do not need more treatment.

Table 4.21 Parameter and results for Two stage Case 1 with configuration B.

Feed flow:	L_f : 2MSm ³ /s = 3718kmole/h = 83333m ³ _{STP} /h
Permeance:	$P'_{CO_2/t}$: 31GPU = 0.083711m ³ _{STP} /(h·m ² ·bar) $P'_{CH_4/t}$: 0.5GPU = 0.001350m ³ _{STP} /(h·m ² ·bar)
Selectivity	α_{CO_2/CH_4} = 62
Molar compositions in feed:	Base Case 1 x_{f,CO_2} : 0.80 x_{f,CH_4} : 0.20

Pressure

4 Membrane Simulations

- | | |
|-------------|-------------------------------------|
| 1. Membrane | Retentate: 40bar
Permeate: 8bar |
| 2. Membrane | Retentate: 40bar
Permeate: 10bar |

System retentate: x_{o,CO_2} : 0.02

Results from Crossflow Model

Area	$A_{m,1}$: 105,682m ² $A_{m,2}$: 245,519m ²
System Molar fraction and flow	y_{p,CO_2} : 0.950 (V_p : 3118kmole/h) x_{o,CO_2} : 0.020 (L_o : 600kmole/h)
Compressor energy [kW] (η_{cp} =100%)	$W_{cp,EOR}$: 7,853kW $W_{cp,Recycle}$: 718kW

4.3.7 Summarize of the cases

Table 4.22 summarize the results from case 1 with a CO₂, inlet concentration of 80mol%.

Table 4.22 Summary of case 1 with CO₂ inlet of 80mol%

	Base Case 1	Low ΔP	High ΔP	x_{o,CO_2} =0.02	x_{o,CO_2} =0.15	CA mem	Multi comp	2 stage mem
Area 1000m ²	105	293	46	192	70	892	92	352
Retentate (L_o) (kmole/h)	641	380	746	431	771	501	606	600
x_{o,CH_4}	0.92	0.92	0.92	0.98	0.85	0.92	0.92	0.98
Permeate (V_p) (kmole/h)	3077	3337	2972	3287	2947	3217	3112	3118
y_{p,co_2}	0.95	0.884	0.981	0.902	0.97	0.912	0.935	0.95

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Table 4.23 summarize the results from case 1 with a CO₂, inlet concentration of 50mol%.

Table 4.23 Summary of case 2 with CO₂ inlet of 50mol%

	Base Case 2	Low ΔP	High ΔP	x_{o,CO_2} =0.02	x_{o,CO_2} =0.15	CA mem	Multi comp	2 stage mem
Area 1000m ²	188	634	55	411	97	1348	157	336
Retentate (L_o) (kmole/h)	1657	1011	1914	1118	1996	1399	1596	1923
x_{o,CH_4}	0.92	0.92	0.92	0.98	0.85	0.92	0.92	0.92
Permeate (V_p) (kmole/h)	2061	2706	1804	2600	1722	2319	2122	1795
y_{p,co_2}	0.838	0.657	0.946	0.722	0.906	0.753	0.812	0.95

Table 4.24 summarize the results from case 1 with a CO₂, inlet concentration of 20mol%.

Table 4.24 Summary of case 3 with CO₂ inlet of 20mol%

	Base Case 3	Low ΔP	High ΔP	x_{o,CO_2} =0.02	x_{o,CO_2} =0.15	CA mem	Multi comp	2 stage mem
Area 1000m ²	203	723	33	579	51	1220	158	579
Retentate (L_o) (kmole/h)	2817	2059	3147	1907	3389	2624	2776	3192
x_{o,CH_4}	0.92	0.92	0.92	0.98	0.85	0.92	0.92	0.92
Permeate (V_p) (kmole/h)	901	1659	570	1811	330	1094	942	526
y_{p,co_2}	0.575	0.349	0.863	0.39	0.713	0.487	0.55	0.929

5 Cost and Size

The schematic plot shown in Figure 5.1 gives an overview of what choice of CO₂ removal technology is generally recommended, with the given gas flow rate and CO₂ concentration. [3] In these cases, when it is 2Msm³/day that equal 70.79 MMscfd, this puts the recommendations in a combination.

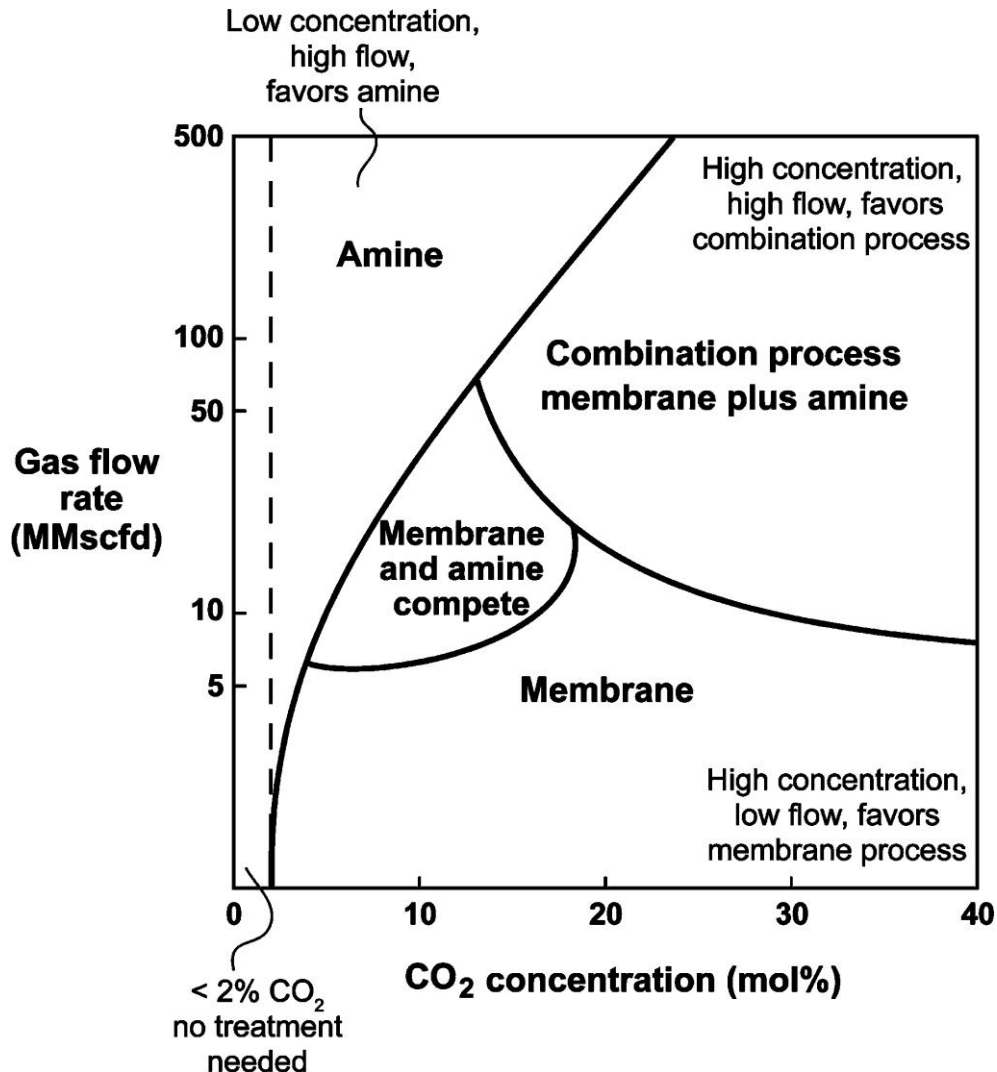


Figure 5.1 a schematic plot of recommended choice for CO₂ removal. [3]

To oversimplify the CAPEX of equipment in a subsea module, e.g. the cost of the equipment is 22% of the total cost of a subsea module [48].

5.1 Compression for CO₂-EOR

In all examples it is required to inject the permeated stream into a reservoir, this requires heavy compression. For a this report it will be compressed up to 100bar. Table 5.1 shows the result

5 Cost and Size

for Base Case 1 to -3, with a compressor efficiency of 100% from Aspen Plus. Table 5.2 shows then cost for two compressors, Utility cost will be similar for both cases.

Table 5.1 Compression cost for Base Case 1 to -3 with a singular compressor

	Base Case 1	Base Case 2	Base Case 3
Amount to compress [kmol/h]	3078kmol/h	2061kmol/h	901kmol/h
Energy W_{cp} [hp] / [kW] ($\eta_{cp}=100\%$)	14,572hp/7868kW	9,182hp/4958kW	3,848hp/2078kW
Efficiency η_{cp}	0.8	0.8	0.8
Compressor cost [USD]	USD 26,950,000	USD 18,454,000	USD 9,045,000
Utility cost	USD0.065/kWh	USD0.065/kWh	USD0.065/kWh
Energy cost per year [USD/year]	5,833,000 USD/year	3,676,000 USD/year	1,540,000 USD/year

Table 5.2 Compression cost for Base Case 1 to -3 with two compressors with a ratio outlet to inlet pressure of 4

	Base Case 1	Base Case 2	Base Case 3
Amount to compress [kmol/h]	3078kmol/h	2061kmol/h	901kmol/h
Energy W_{cp} [hp] / [kW]	1. 7,058hp/ 3811kW 2. 7,514hp/ 4057kW	1. 4,447hp/ 2401kW 2. 4,736hp/ 2557kW	1. 1,863hp/ 1006kW 2. 1,985hp/ 1072kW
Efficiency η_{cp}	0.8	0.8	0.8
Installed cost CC [USD]	USD 30,529,000	USD 20,905,000	USD 10,245,000

As presented in Table 5.1 and Table 5.2, it is favorable to inject the least.

5.2 Potential Income

Natural gas varies in price, from the last five years it ranges from 1.48- to 4.55USD/MMBtu, but averages around 2.5- to 3.0USD/MMBtu in the US [49]. As of April 2021 the European Union import price of natural gas was 7.147USD/MMBtu [50]. Table 5.3 shows a theoretical income from the different base cases.

Table 5.3 potential income from Base Case 1, to -3

	Base Case 1	Base Case 2	Base Case 3
Flow of NG at CO ₂ 0.08mol%	14,370m ³ _{STP} /h	37,265m ³ _{STP} /h	63,237m ³ _{STP} /h
Theoretical NG at CO ₂ 0.02mol%	13,508m ³ _{STP} /h	35,029m ³ _{STP} /h	59,443m ³ _{STP} /h
Price of NG	2.5USD/MMBtu	2.5USD/MMBtu	2.5USD/MMBtu
1. Income/hour	1,163USD/h	3,118USD/h	5,120USD/h
2. Income/day	27,920USD/d	74,833USD/d	122,869USD/d
3. Income/year (run time 100%)	10,191,000USD/y	27,314,000USD/y	44,847,000USD/y
Price of NG	7.147USD/MMBtu	7.147USD/MMBtu	7.147USD/MMBtu
1. Income/hour	3,326USD/h	8,914USD/h	14,636USD/h
2. Income/day	79,817USD/d	213,933USD/d	351,259USD/d
3. Income/year (run time 100%)	29,133,000USD/y	78,086,000USD/y	125,210,000USD/y
1m ³ = 35.31ft ³ 1MMBtu = 1MMBtu · 1.025 = Mcf =Mft ³			

5.3 Membrane

Hao et al. estimated polymer membranes cost with the module costed 5USD/ft² (~18USD/m²) back in 2002, with a lifetime of four years [40]. The cost will vary upon the membrane, some of the more advanced membrane is likely to be higher and basic membrane could be lower. Table 5.4 uses the membrane area from the crossflow model and a two stage compression for CO₂ reinjection.

5 Cost and Size

Table 5.4 CAPEX of Base Case 1 to -3 in subsea module

	Base Case 1	Base Case 2	Base Case 3
Area [m²]	104,886m ²	187,857m ²	202,742m ²
Membrane Cost [USD]	USD 1,852,000	USD 3,317,000	USD 3,580,000
Compressor Two-Stage [USD]	USD 30,529,000	USD 20,905,000	USD 10,245,000
Installed subsea factor [-]	4.5	4.5	4.5
Total Module cost	USD 145,715,000	USD 108,999,000	USD 62,213,000

Table 5.5 CAPEX of Case 1 to -3 with a two stage membrane in subsea module

	Case 1 ($y_{p,CO_2}=0.8$)	Case 2 ($y_{p,CO_2}=0.5$)	Case 3 ($y_{p,CO_2}=0.2$)
Area [m²]	352,000m ²	336,000m ²	579,394m ²
Membrane Cost [USD]	6,215,000USD	5,933,000USD	10,224,000USD
Recycle Compressor [USD]	3,784,000USD	6,799,000USD	16,204,335USD
Compressor EOR [USD]	29,907,000USD	17,980,000USD	5,047,000USD
Installed subsea factor [-]	4.5	4.5	4.5
Total Module cost	166,083,000USD	138,201,000USD	141,636,000USD

5.3.1 Size of subsea module.

Given the hollow fiber configuration of a membrane that can pack 500- to 9,000m²/m³ per module, then assume 5,000m²/m³ are going to be used. Then assume that the membrane module is going to take up 20% of that volume when installed. This will give the final volume of the subsea structure of 1,000m²/m³, Table 5.6 gives the volume for the different cases.

Table 5.6 The Volume size needed to be put in a subsea structure.

	Base Case 1	Base Case 2	Base Case 3
Area [m²]	104,886m ²	187,857m ²	202,742m ²
Volume per area of membrane [m²/m³]	1,000m ² /m ³	1,000m ² /m ³	1,000m ² /m ³
Volume needs in subsea structure. [m³]	105m ³	188m ³	203m ³

5.4 Membrane Contactors

Membrane contactors is similar to an absorption system, experiments conducted by Kværner concluded that weight and size could be reduced by 65- to 75% compared to traditional towers. It was reported that a run of 5000 hours was done and it showed no indication of reduction in performance. [51]

5.5 Comparisons

Gutierrez et al. studied three different sweetening processes, two different Amine absorption and two stage membrane, with a flow of 250Mm³/d with an CO₂ content of 4mol%. [52]

Table 5.7 Shows operation cost and utilities cost for three cases by Gutierrez et al. [52]

	Unit	Basic Amine (MDEA)	Two Stage Membrane
Total utilities cost	USD/year	408,766	330,726
Total Operation Cost	USD/year	1,750,790	2,040,820

6 Discussion

There are many different programs to simulate a gas membrane model. First to come across is Almeesoft, a commercial software integrated with HYSYS or Unisim [53]. Another standalone software with no technical support called MemCal was produced by Hoorfar et al. [54]. Then a software in CAPE-OPEN that did not get further develop called MEMSIC 2.0 [55]. All these either had to be bought or was not fully develop, and Aspen Plus had a feature to implement models from Aspen Custom Modeler.

To start with, it was thought to use the simulation models described by Rodrigues et al. [56]. In that report, three models were used, one complete mixing, one countercurrent and one discretized model using nodes. Considerable effort was put into these with little success in running a working case.

Then the models made for an example in Aspen Custom Modeler was put in use. This Crossflow model was similar to Rodrigues' countercurrent model, the difference being in Rodrigues model, a logarithmic approached was used the same way to calculate a crossflow model in a heat exchanger and there are cells on the permeate side. This model implemented in Aspen Plus works well to change any parameters as well as configuration.

The countercurrent from Geankoplis is good, this model only contains ten cells compared to the model in ACM that contains 100 cells. Drawback here is that membrane area must be calculated and cannot be constant.

These models used all have relatively high uncertainty. As to the membrane material chosen, it will most definitely have different permeance and selectivity if it was measured with a raw natural gas and at different temperature and pressure.

With every simulated case it is possible to reduce the CO₂ content in the stream to an acceptable level, whether it being to satisfactory pipeline specification or to sales. Differences in permeability, pressure and configuration plays a vital part. It all comes to different compromises on what is sought after, whether it being sales ready natural gas, high enough concentration of CO₂ in the permeate, economically limited or just a preliminary treatment for transport.

From every case, if the result is that the membrane area increases, that will lead to a higher amount in the permeate stream with a lower concentration of CO₂.

A drawback of the cases with high methane in the feed is that the reinject gas has a high content of methane (y_{p,CH_4} : 0.42). This could be solved by adding a two stage membrane system, however, this also increases the membrane area and needs a separate compressor.

as far as the potential income gets, natural gas have a history of fluctuation and gas prices will vary depending on region.

For the correction factor used for the cost of a subsea module, is example of traditional equipment used for subsea e.g. valve head on the well (xmas tree) and manifolds. The cost of multiphase flow compressor is simply assumed cost of a regular installed compressor, this might be wildly inaccurate, but gets a value based on the size of the compressor.

All these results can not reveal anything about the effect of impurities in the stream. How the membrane will respond to not having any pretreatment and lifetime in any regards. Additionally, a pressure drop will have to be calculated and added manually to get a clearer energy balance over the system.

6.1 Best suited membrane

Select a membrane material for a subsea application is a complex task, some thoughts are given below.

- Should exceed the regular lifetime of a membrane.
- Favorable to operate at high pressure and temperature.
- The material should be easy to fabricate in a hollow fiber structure.
- High permeability and selectivity.
- Should be resistance to plasticization.
- Should tolerate impurities of higher hydrocarbons.
- Low maintenance
- It should be appropriately tested under realistic and worst case scenarios.
- Fairly low cost

A material that overcomes many of these challenges are the MMM, however, it is hard to find large scale or even some commercially available of these in the literature.

6.1.1 Recommendation for CO₂/CH₄ Separation

Jeon and Lee concluded that when looking at the polymer membrane for CO₂/CH₄ separation for biogas, the economic focus should be with PI, PSf and Thermal rearrange (TR) polymer membrane [57]. Baker and Lokhandwala states in 2008 that most industrial membrane CO₂/CH₄ separation is done with CA [3].

Dalane et al. suggest, based on the porous membrane contactors at National Carbon Capture Center in USA that "membrane absorption is of interest for subsea separation" [15].

The combined effect of MMM is highly desirable for gas separation. The focus on MMM should be on material combined and the fabrication process of the membrane. [58]

For CO₂ separation in syngas, high permeability and selectivity is wanted. As for flue gas, high CO₂ permeability is more critical than high selectivity. [13]

6.2 Future steps

Permeability when induced to raw natural gas, and over time. Interesting with to look further in MMM. furthermore, it would be interesting to look at the possibility with membrane contactors in a subsea setting as Dalane et al. did in the report "Potential applications of membrane separation for subsea natural gas processing: A review". [15]

7 Conclusion

The three main goals for this report, firstly to find and utilize membrane simulation based on available resources and public information. Second to evaluate processes suited to a subsea system and material, thirdly to run different simulations on multiple parameters variations.

The simulations were solved by implementing an example from Aspen Custom Modeler in Aspen Plus. Moreover, the crossflow model used is described in Geankoplis book worked to its purpose.

The material selected was a polymer membrane of polyimides with strengthening chain stiffness by the monomer 6FDA. However, the MMM looks attractive because it is fairly simple to fabricate and have benefit from both organic and inorganic materials.

It showed some clear direction of what is wanted by running several simulations, higher pressure difference had a significant impact. If a high concentration of natural gas is desired in the retentate, this will lead to a considerable amount of natural gas loss in the reinjected stream. An increased membrane area can not always solve concentrations in different streams, but a two stage membrane system will be more efficient.

For the case with 20mol% CO₂ in the feed, an estimated subsea module would cost ~62 mill. USD with operational cost annually ~1.5 mill. USD. With a potential theoretical income of ~45 mill. USD with natural gas annually, this case seems promising.

For the case with 80mol% CO₂ in the feed, an estimated subsea module would cost ~146 mill. USD with operational cost annually ~5.8 mill. USD. With a potential theoretical income of ~10 mill. USD with natural gas annually. This is not economical in the view of natural gas income. However, if there is a marked for CO₂ enhanced oil recovery in some nearby field, the CO₂ rich gas could be sold.

References

- [1] W. Burgers, P. Northrop, H. Kheshgi, and J. Valencia, "Worldwide development potential for sour gas," *Energy Procedia*, vol. 4, pp. 2178-2184, 2011.
- [2] T. E. Rufford *et al.*, "The removal of CO₂ and N₂ from natural gas: A review of conventional and emerging process technologies," *Journal of Petroleum Science and Engineering*, vol. 94, pp. 123-154, 2012.
- [3] R. W. Baker and K. Lokhandwala, "Natural gas processing with membranes: an overview," *Industrial & Engineering Chemistry Research*, vol. 47, no. 7, pp. 2109-2121, 2008.
- [4] C. J. Geankoplis, *Transport processes and separation process principles:(includes unit operations)*. Prentice Hall Professional Technical Reference, 2003.
- [5] Z. Dai, L. Ansaloni, and L. Deng, "Recent advances in multi-layer composite polymeric membranes for CO₂ separation: A review," *Green Energy & Environment*, vol. 1, no. 2, pp. 102-128, 2016.
- [6] M. Mulder and J. Mulder, *Basic principles of membrane technology*. Springer Science & Business Media, 1996.
- [7] S. Sridhar, B. Smitha, and T. Aminabhavi, "Separation of carbon dioxide from natural gas mixtures through polymeric membranes—a review," *Separation & Purification Reviews*, vol. 36, no. 2, pp. 113-174, 2007.
- [8] L. M. Robeson, "The upper bound revisited," *Journal of membrane science*, vol. 320, no. 1-2, pp. 390-400, 2008.
- [9] Y. Zhang, J. Sunarso, S. Liu, and R. Wang, "Current status and development of membranes for CO₂/CH₄ separation: A review," *International Journal of Greenhouse Gas Control*, vol. 12, pp. 84-107, 2013.
- [10] G. Dong, H. Li, and V. Chen, "Challenges and opportunities for mixed-matrix membranes for gas separation," *Journal of Materials Chemistry A*, vol. 1, no. 15, pp. 4610-4630, 2013.
- [11] T.-J. Kim, M. W. Uddin, M. Sandru, and M.-B. Hägg, "The effect of contaminants on the composite membranes for CO₂ separation and challenges in up-scaling of the membranes," *Energy Procedia*, vol. 4, pp. 737-744, 2011.
- [12] Y. Xiao, B. T. Low, S. S. Hosseini, T. S. Chung, and D. R. Paul, "The strategies of molecular architecture and modification of polyimide-based membranes for CO₂ removal from natural gas—A review," *Progress in Polymer Science*, vol. 34, no. 6, pp. 561-580, 2009.
- [13] M. Vinoba, M. Bhagiyalakshmi, Y. Alqaheem, A. A. Alomair, A. Pérez, and M. S. Rana, "Recent progress of fillers in mixed matrix membranes for CO₂ separation: A review," *Separation and Purification Technology*, vol. 188, pp. 431-450, 2017.
- [14] A. Bos, I. Pünt, M. Wessling, and H. Strathmann, "CO₂-induced plasticization phenomena in glassy polymers," *Journal of membrane science*, vol. 155, no. 1, pp. 67-78, 1999.

- [15] K. Dalane, Z. Dai, G. Mogseth, M. Hillestad, and L. Deng, "Potential applications of membrane separation for subsea natural gas processing: A review," *Journal of Natural Gas Science and Engineering*, vol. 39, pp. 101-117, 2017.
- [16] S. Li, G. Alvarado, R. D. Noble, and J. L. Falconer, "Effects of impurities on CO₂/CH₄ separations through SAPO-34 membranes," *Journal of Membrane Science*, vol. 251, no. 1-2, pp. 59-66, 2005.
- [17] E. Haun, "A piece of the puzzle," *OE Offshore Engineer*, 2019. [Online]. Available: <https://www.oedigital.com/news/470215-a-piece-of-the-puzzle>.
- [18] M. Donohue, B. Minhas, and S. Lee, "Permeation behavior of carbon dioxide-methane mixtures in cellulose acetate membranes," *Journal of membrane science*, vol. 42, no. 3, pp. 197-214, 1989.
- [19] Q. Liu, M. Galizia, K. L. Gleason, C. A. Scholes, D. R. Paul, and B. D. Freeman, "Influence of toluene on CO₂ and CH₄ gas transport properties in thermally rearranged (TR) polymers based on 3, 3'-dihydroxy-4, 4'-diamino-biphenyl (HAB) and 2, 2'-bis-(3, 4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA)," *Journal of Membrane Science*, vol. 514, pp. 282-293, 2016.
- [20] K.-J. Kim, S.-H. Park, W.-W. So, D.-J. Ahn, and S.-J. Moon, "CO₂ separation performances of composite membranes of 6FDA-based polyimides with a polar group," *Journal of membrane science*, vol. 211, no. 1, pp. 41-49, 2003.
- [21] R. Wang, C. Cao, and T.-S. Chung, "A critical review on diffusivity and the characterization of diffusivity of 6FDA-6FpDA polyimide membranes for gas separation," *Journal of Membrane Science*, vol. 198, no. 2, pp. 259-271, 2002.
- [22] Y. Liu, M. L. Chng, T.-S. Chung, and R. Wang, "Effects of amidation on gas permeation properties of polyimide membranes," *Journal of membrane science*, vol. 214, no. 1, pp. 83-92, 2003.
- [23] D. Q. Vu, W. J. Koros, and S. J. Miller, "Effect of condensable impurities in CO₂/CH₄ gas feeds on carbon molecular sieve hollow-fiber membranes," *Industrial & engineering chemistry research*, vol. 42, no. 5, pp. 1064-1075, 2003.
- [24] D. Syrtsova, A. Kharitonov, V. Teplyakov, and G.-H. Koops, "Improving gas separation properties of polymeric membranes based on glassy polymers by gas phase fluorination," *Desalination*, vol. 163, no. 1-3, pp. 273-279, 2004.
- [25] N. José, L. d. A. Prado, and I. Yoshida, "Synthesis, characterization, and permeability evaluation of hybrid organic-inorganic films," *Journal of Polymer Science Part B: Polymer Physics*, vol. 42, no. 23, pp. 4281-4292, 2004.
- [26] S. Sridhar, B. Smitha, S. Mayor, B. Prathab, and T. Aminabhavi, "Gas permeation properties of polyamide membrane prepared by interfacial polymerization," *Journal of materials science*, vol. 42, no. 22, pp. 9392-9401, 2007.
- [27] K. Ghosal *et al.*, "Gas separation properties of aromatic polyamides with sulfone groups," *Polymer*, vol. 36, no. 4, pp. 793-800, 1995.
- [28] J. Pengfei, C. Yiming, J. Xingming, and Y. Quan, "Preparation of Hollow Fiber Composite Membrane for CO₂ Separation and Its Gas Permeation Properties," *Petrochemical Technology*, p. 09, 2010.

- [29] C. Cao, R. Wang, T. S. Chung, and Y. Liu, "Formation of high-performance 6FDA-2, 6-DAT asymmetric composite hollow fiber membranes for CO₂/CH₄ separation," *Journal of Membrane Science*, vol. 209, no. 1, pp. 309-319, 2002.
- [30] C. Cao, T.-S. Chung, Y. Liu, R. Wang, and K. Pramoda, "Chemical cross-linking modification of 6FDA-2, 6-DAT hollow fiber membranes for natural gas separation," *Journal of membrane science*, vol. 216, no. 1-2, pp. 257-268, 2003.
- [31] A. Ismail, S. Shilton, I. Dunkin, and S. Gallivan, "Direct measurement of rheologically induced molecular orientation in gas separation hollow fibre membranes and effects on selectivity," *Journal of Membrane Science*, vol. 126, no. 1, pp. 133-137, 1997.
- [32] G. Dong, H. Li, and V. Chen, "Factors affect defect-free Matrimid® hollow fiber gas separation performance in natural gas purification," *Journal of Membrane Science*, vol. 353, no. 1-2, pp. 17-27, 2010.
- [33] T. Visser, N. Masetto, and M. Wessling, "Materials dependence of mixed gas plasticization behavior in asymmetric membranes," *Journal of Membrane Science*, vol. 306, no. 1-2, pp. 16-28, 2007.
- [34] Y. Liu, T.-S. Chung, R. Wang, D. F. Li, and M. L. Chng, "Chemical cross-linking modification of polyimide/poly (ether sulfone) dual-layer hollow-fiber membranes for gas separation," *Industrial & engineering chemistry research*, vol. 42, no. 6, pp. 1190-1195, 2003.
- [35] S. S. Hosseini, N. Peng, and T. S. Chung, "Gas separation membranes developed through integration of polymer blending and dual-layer hollow fiber spinning process for hydrogen and natural gas enrichments," *Journal of Membrane Science*, vol. 349, no. 1-2, pp. 156-166, 2010.
- [36] L. Jiang, T.-S. Chung, D. F. Li, C. Cao, and S. Kulprathipanja, "Fabrication of Matrimid/polyethersulfone dual-layer hollow fiber membranes for gas separation," *Journal of membrane science*, vol. 240, no. 1-2, pp. 91-103, 2004.
- [37] G. Genduso, B. S. Ghanem, and I. Pinnau, "Experimental Mixed-Gas Permeability, Sorption and Diffusion Polyimide of Membrane: CO₂-CH₄ Mixtures Unveiling in the 6FDA-mPDA Effect of Competitive Sorption on Permeability Selectivity," *Gas Transport in Glassy Polymers*, vol. 9, no. 10, p. 37, 2021.
- [38] E. Sanders, "BCFD-scale membrane separation systems for CO₂ removal application in oil and gas production," in *83rd GPA Annual Convention. New Orleans, LA*, 2004.
- [39] J. P. Meyer, "Summary of carbon dioxide enhanced oil recovery (CO₂EOR) injection well technology," *American Petroleum Institute, Washington, DC*, 2007.
- [40] J. Hao, P. Rice, and S. Stern, "Upgrading low-quality natural gas with H₂S- and CO₂-selective polymer membranes: Part I. Process design and economics of membrane stages without recycle streams," *Journal of Membrane Science*, vol. 209, no. 1, pp. 177-206, 2002.
- [41] F. Cao, T. Gao, S. Li, Z. Xing, and P. Shu, "Experimental analysis of pressure distribution in a twin screw compressor for multiphase duties," *Experimental Thermal and Fluid Science*, vol. 35, no. 1, pp. 219-225, 2011.

- [42] Equinor. "Åsgard subsea gas compression." Equinor. <https://www.equinor.com/en/where-we-are/norway/asgard-subsea-gas-compression.html> (accessed 10/05, 2021).
- [43] P. Gandhidasan, A. A. Al-Farayedhi, and A. A. Al-Mubarak, "Dehydration of natural gas using solid desiccants," *Energy*, vol. 26, no. 9, pp. 855-868, 2001.
- [44] Y. Cui, H. Kita, and K.-i. Okamoto, "Preparation and gas separation performance of zeolite T membrane," *Journal of Materials Chemistry*, vol. 14, no. 5, pp. 924-932, 2004.
- [45] A. Kargari and H. Sanaeepur, "Application of membrane gas separation processes in petroleum industry," *Advances in petroleum engineering*, vol. 1, pp. 592-622, 2015.
- [46] J. Liu, G. Zhang, K. Clark, and H. Lin, "Maximizing ether oxygen content in polymers for membrane CO₂ removal from natural gas," *ACS applied materials & interfaces*, vol. 11, no. 11, pp. 10933-10940, 2019.
- [47] A. K. Datta and P. K. Sen, "Optimization of membrane unit for removing carbon dioxide from natural gas," *Journal of Membrane Science*, vol. 283, no. 1-2, pp. 291-300, 2006.
- [48] B. YONG, *Subsea engineering handbook*. Elsevier Science, 2010.
- [49] Nasdaq. "Market activity, Natural Gas." <https://www.nasdaq.com/market-activity/commodities/ng%3Anmx> (accessed 12.05, 2021).
- [50] Ycharts. "European Union Natural Gas Import Price." https://ycharts.com/indicators/europe_natural_gas_price (accessed 17.05, 2021).
- [51] O. Falk-Pedersen, M. S. Grønvold, P. Nøkleby, F. Bjerve, and H. F. Svendsen, "CO₂ capture with membrane contactors," *International journal of green energy*, vol. 2, no. 2, pp. 157-165, 2005.
- [52] J. P. Gutierrez, E. L. A. Ruiz, and E. Erdmann, "Energy requirements, GHG emissions and investment costs in natural gas sweetening processes," *Journal of Natural Gas Science and Engineering*, vol. 38, pp. 187-194, 2017.
- [53] Almeesoft. "Software for Calculations of Membrane Gas Separation Join the Leading Gas Membranes Separation Companies." http://almeesoft.com/gas-membrane_calculations.html (accessed 16.05, 2021).
- [54] M. Hoorfar, Y. Alcheikhhamdon, and B. Chen, "A novel tool for the modeling, simulation and costing of membrane based gas separation processes using Aspen HYSYS: Optimization of the CO₂/CH₄ separation process," *Computers & Chemical Engineering*, vol. 117, pp. 11-24, 2018.
- [55] J. v. Baten, "MEMSIC 2.0: Membrane Gas Separation Simulator," 2017. [Online]. Available: https://www.colan.org/wp-content/uploads/2017/10/Y17_COEU_MEMSIC.pdf.
- [56] D. Rodrigues, D. Foglia, W. Wukovits, and A. Friedl, "Model Development of a Membrane Gas Permeation Unit for the Separation of Hydrogen and Carbon Dioxide," *Chemical Engineering Transactions*, vol. 21, pp. 1303-1308, 2010.
- [57] Y.-W. Jeon and D.-H. Lee, "Gas membranes for CO₂/CH₄ (biogas) separation: a review," *Environmental Engineering Science*, vol. 32, no. 2, pp. 71-85, 2015.

- [58] D. F. Mohshim, H. b. Mukhtar, Z. Man, and R. Nasir, "Latest development on membrane fabrication for natural gas purification: a review," *Journal of Engineering*, vol. 2013, 2013.

Appendices

Appendix A – Project description

Appendix B – Complete mixing model of O₂ and N₂

Appendix C – Crossflow model codes from ACM

Appendix D – Counter current model in Excel

Appendix E – Pressure drop by Hagen-Poiseuille equation

Appendix A – Project description



FMH606 Master's Thesis

Title: Process evaluation of novel CO₂ capture processes for subsea application.

USN supervisor: Lars Erik Øi

External partners: Aker Carbon Capture, Pål Helge Nøkleby (Aker Carbon Capture, Zabia Marie Furre Elamin; Aker Solutions, Jostein Kolbu)

Task background: There are several areas within CO₂ handling (transportation, injection conditions, separation, compression, etc) that are important to stakeholders within offshore CO₂ EOR. Better knowledge and system solutions within these areas to what is known today will improve technical and economic prerequisites to sanction commercial use of offshore CO₂ EOR. One of the main challenges related to offshore CO₂ EOR is how to separate and reinject back produced CO₂ from the CO₂ flooded oil reservoir. Modification of existing topside processing trains have shown to become very costly as the separation trains are not constructed to handle the huge gas volumes and corrosive CO₂. Below topic are hence related to new concepts for subsea CO₂ separation to minimize the exposure of topside facilities by CO₂.

Master Thesis involving process simulation, assessment of various separation concepts and theoretical understanding.

Task description:

The general aim is to evaluate different CO₂ capture processes for subsea applications.

1. Literature search on CO₂ capture processes.
2. Calculations of material and energy balances for alternatives process from well head to CO₂ injection wellhead.
 - May include membrane models based on public information.
3. Comparisons of different process alternatives.
 - Including different cases.
 - May include rough cost estimations for relevant cases.
4. Evaluation of the suggested alternatives.
 - Compared to more traditional alternatives.
 - What is most suited for a subsea implementation.

Student category: PT

Practical arrangements: The work will be carried out mainly at USN or from home. The task is in collaboration with Aker Carbon Capture

Signatures:

Supervisors (date and signature):

22/11-21 Lars Erik Øi

Student: Roy Sømme Ommedal (date and signature): Roy S Ommedal
27/07/21

Appendix B – Complete mixing model of O₂ and N₂

	A	B	C	D	E	F	G	H	I	J	K
1	Example: 13.4-2										
2											
3	Comp A:	O2	Given:	y,a,f; α; θ; Pf; Pp							
4	Comb B:	N2	Find:	y,a,p; y,a,r; A							
5	Assumptions: Mix flow										
6	Area	A	32233	m2	calc						
7	Permeance / Kp,a		6,61E-04	[mole/(s*m2	con	$n, f = n, r * n, p$					
8	Permeance / Kp,b		6,61E-05	[mole/(s*m2	con						
9	Flux of A	N"a		[mole/(s*m2	calc	$n, f * y, a, f = n, r * y, a, r + n, p * y, a, p$					
10	Flux of B	N"b		[mole/(s*m2	calc						
11	Selectivity	α a/b	10	[-]	con						
12	Perm. frac.c	θ	0,2	[-]	con	$A = \frac{F.p*y.a.p}{Kp.a*(y.a.r*Pf-y.a.p*Pp)}$ (Geankoplis)					
13	Flow Feed	n,f	44,6	[mol/s]	con						
14	Frac A Feed	y,a,f	0,209	[-](mole)	con						
15	Frac B Feed	y,b,f	0,791	[-](mole)	con						
16	Pressure Fee	Pf	2,53	[bar]	con	$\theta = \frac{Vp}{Lf}$					
17	Flow Ret	n,r	35,68	[mol/s]	calc						
18	Frac A Ret	y,a,r	0,135	[-](mole)	calc	$y,a,p = \frac{-b + \sqrt{b^2 - 4ac}}{2a}$					
19	Frac B Ret	y,b,r	0,865	[-](mole)	calc	$a = \theta + \frac{Pp}{Pf} - \frac{Pp}{Pf} * \theta - \alpha * \theta - \alpha * \frac{Pp}{Pf} + \alpha * \frac{Pp}{Pf} * \theta$					
20	Pressure Ret	Pr	2,53	[bar]	calc						
21	Flow Perm	n,p	8,92	[mol/s]	con	$b = 1 - \theta - y, a, f - \frac{Pp}{Pf} + \frac{Pp}{Pf} * \theta + \alpha * \theta + \alpha * \frac{Pp}{Pf} - \alpha * \frac{Pp}{Pf} * \theta + \alpha * y, a, f$					
22	Frac A Perm	y,a,p	0,507	[-](mole)	calc						
23	Frac B Perm	y,b,p	0,493	[-](mole)	calc	$c = -\alpha * y, a, f$					
24	Pressure Per	Pp	0,253	[bar]	con						
25	quadratic eq	a	-2,52	[-]	calc						
26		b	5,401	[-]	calc						
27		c	-2,09	[-]	calc						

Appendix C – Crossflow model codes from ACM

```

Model GasPermModule
/*
This model is of a gas permeation module model. It assumes:
- Cross flow with unhindered permeate withdrawal i.e. permeate is removed from each cell
  and mixed to form the module permeate. Retentate flows from one cell to the next.
- Isothermal conditions
- Ideal gas behaviour
- Constant permeabilities
*/
// Parameters and variables
NCells as IntegerParameter (Description:"Number of cross flow cells", 100);
A as Area (Description:"Total membrane area", Fixed); // (m2)
L(ComponentList) as Motype (Description:"Permeability in m3(STP)/(m2 h bar)", Fixed);
Lmol(ComponentList) as Motype (Description:"Molar permeability (kmol/(m2 h bar))");
PPerm as Pressure (Description:"Permeate pressure", Fixed); // (bar)
ACell as Area (Description:"Area per cross flow cell (m2)");
FRet([0:NCells]) as Flow_Mol (Description:"Retentate mole flow from cell"); // (kmol/h)
FPerm([1:NCells]) as Flow_Mol (Description:"Permeate mole flow from cell"); // (kmol/h)
ZRet(ComponentList,[0:NCells]) as Molefraction (Description:"Retentate mole fraction in cell");
ZPerm(ComponentList,[1:NCells]) as Molefraction (Description:"Permeate mole fraction in cell");
RhoRet as hidden Dens_Mol; // Retentate molar density (kmol/m3)
RhoPerm as hidden Dens_Mol; // Permeate molar density (kmol/m3)

// Ports
Inlet as Input MoleFractionPort;
Retentate as Output MoleFractionPort;
Permeate as Output MoleFractionPort;

// Convert permeability to molar basis
Lmol = L*1.01325 / (273.15*0.0831433);

// Retentate inlet conditions
FRet(0) = Inlet.F;
For comp in ComponentList Do
  ZRet(comp,0) = Inlet.z(comp);
EndFor

// Balance equations for each cell
ACell = A/NCells;
For k in [1:NCells] Do
  FRet(k-1) = FRet(k) + FPerm(k);
  For comp in ComponentList Do
    FPerm(k) * ZPerm(comp,k) = ACell * Lmol(comp) * (Retentate.P*ZRet(comp,k) - Permeate.P*ZPerm(comp,k));
    FRet(k-1)*ZRet(comp,k-1) = FRet(k)*ZRet(comp,k) + FPerm(k)*ZPerm(comp,k);
  EndFor
  sigma (foreach (comp in componentlist) ZPerm(comp,k)) = 1;
EndFor

// Retentate total flow and composition
Retentate.F = FRet(NCells);
For comp in ComponentList Do
  Retentate.z(comp) = ZRet(comp,NCells);
EndFor

// Permeate total flow and composition
Permeate.F = Sigma(FPerm);
For comp in ComponentList Do
  Permeate.F * Permeate.z(comp) = Sigma(Foreach (cell in [1:NCells]) FPerm(cell)*ZPerm(comp,cell));
EndFor

// Other outlet stream conditions
Retentate.T = Inlet.T;
Retentate.P = Inlet.P;
Permeate.T = Inlet.T;
Permeate.P = PPerm;

Call(Retentate.h) = pEnth_Mol_Vap(Retentate.T, Retentate.P, Retentate.z);
Call(Permeate.h) = pEnth_Mol_Vap(Permeate.T, Permeate.P, Permeate.z);

Call(RhoRet) = pDens_Mol_Vap(Retentate.T, Retentate.P, Retentate.z);
Call(RhoPerm) = pDens_Mol_Vap(Permeate.T, Permeate.P, Permeate.z);
Retentate.v = 1/RhoRet;
Permeate.v = 1/RhoPerm;

End

```

Appendix D – Counter current model in Excel

	A	B	C	D	E	F	G	H	I	J	K	L
1	Example		a=CO2									
2			b=CH4									
3	Input Variables:											
4	Ff (feed rate)			83333	m ³ (STP)/h							
5	xf,a			0,8								
6	xr,a			0,08								
7	Ph (feed pressure)			4000	kPa							
8	Pl (Perm Pressure)			800	kPa							
9	Kp,a			2,33E-10	m ³ (STP)/S*m ² *Pa							
10	α a/b			62								
11	r= Pl/Ph			0,2								
12												
13	I	1	2	3	4	5	6	7	8	9	10	
14	I(x) xo,a	0,80	0,72	0,64	0,56	0,48	0,40	0,32	0,24	0,16	0,08	
15	a	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	
16	b	310,0	285,6	261,2	236,8	212,4	188,0	163,6	139,2	114,8	90,4	
17	c	-248,0	-223,2	-198,4	-173,6	-148,8	-124,0	-99,2	-74,4	-49,6	-24,8	
18	γ(I)	0,9947	0,9915	0,9871	0,9810	0,9718	0,9563	0,9262	0,8543	0,6720	0,3635	
19	γ(avg)		0,9931	0,9893	0,9841	0,9764	0,9640	0,9413	0,8903	0,7632	0,5178	
20	ΔV		24412,9	13494,3	8569,3	5939,8	4385,1	3416,4	2843,7	2688,7	3213,3	n (kmol)/h Lo
21	Ff(I)	83333,3	58920,4	45426,1	36856,9	30917,0	26532,0	23115,5	20271,8	17583,1	14369,9	641,15
22												
23	I		1	2	3	4	5	6	7	8	9	n (kmol)/h Vp
24	V(counter)	68963,5	68963,5	44550,6	31056,3	22487,0	16547,2	12162,1	8745,7	5901,9	3213,3	3076,98
25	γavg * ΔV	65517,1	65517,1	41273,1	27923,1	19490,3	13690,6	9463,2	6247,4	3715,6	1663,7	
26	γ(I) yp,a	0,9500	0,9500	0,9264	0,8991	0,8667	0,8274	0,7781	0,7143	0,6296	0,5178	
27												
28	Checks: (Counter)			Checks: (cocurr)								
29	Mass(in)	83333	m3/h		Mass(in)	83333	m3/h					
30	Mass(out)	83333	m3/h		Mass(out)	83333	m3/h					
31	[CO2]in	66667	m3/h		[O2]in	66667	m3/h					
32	[CO2]out	66667	m3/h		[O2]out	66667	m3/h					
33												
34	I		1	2	3	4	5	6	7	8	9	
35	V(cocurr)		24412,9	37907,2	46476,5	52416,3	56801,4	60217,8	63061,5	65750,2	68963,5	
36	γavg * ΔV		24243,9	37593,9	46026,8	51826,5	56053,9	59269,7	61801,4	63853,4	65517,1	
37	γ(I) yp,a		0,9931	0,9917	0,9903	0,9887	0,9868	0,9843	0,9800	0,9712	0,9500	
38												
39	Calculate the Area for each cell increment:											
40												
41	(x-ry')avg	0,5614	0,4821	0,4032	0,3247	0,2472	0,1717	0,1019	0,0474	0,0164	0,0037	
42	(Kp*Ph)	3,35										
43	ΔA	12897,3	8269,2	6246,4	5334,0	5107,3	5592,0	7416,9	12938,1	30208,7		
44	Total Area	94010,0										

Appendix E – Pressure drop by Hagen-Poiseuille

	A	B	C	D	E	F	G	H	I	J
2										Hagen- Poiseuille Eq.
3	$A_m = \pi * D_i * N_T(z_2 - z_1)$			$N_T = \frac{A_m}{\pi * D_i * (z_2 - z_1)}$						
4										
5	$\frac{\Delta P_h}{\Delta z} = \frac{-128 * Viscosity}{\pi D_i^4 N_T} (L \frac{T - P_s}{T_s P_{h avg}})$									
6										
7										
8										
9		Comp A:	CO2							
10		Comp B:	CH4							
11		(GasPerm) numbers								
12		Area	A	91020	m2					
13		Permeance	Kp,a	7,74E-04	[mole/(s*m2*bar)]					
14		Permeance	Kp,b	3,40E-05	[mole/(s*m2*bar)]					
15		Flux of A	N"a		[mole/(s*m2)]					
16		Flux of B	N"b		[mole/(s*m2)]					
17		Selectivity	α a/b	22,8	[-]					
18		Perm. frac.c	θ	0,85	[-]					
19		Flow Feed	n,f	1018,9	[mol/s]					
20		Vol flow	Q,f	0,6846	[m3/s]					
21		Frac A Feed	y,a,f	0,8	[-](mole)					
22		Frac B Feed	y,b,f	0,2	[-](mole)					
23		Pressure Fe	Pf	40	[bar]					
24		Temp Feed	Tf	50	Celsius					
25		Flow Ret	n,r	148,1	[mol/s]					
26		Frac A Ret	y,a,r	0,100	[-](mole)					
27		Frac B Ret	y,b,r	0,900	[-](mole)					
28		Pressure Re	Pr	38,8	[bar]					
29		Temp Ret	Tr	50,0	Celsius					
30		Flow Perm	n,p	865,3	[mol/s]					
31		Frac A Perm	y,a,p	0,924	[-](mole)					
32		Frac B Perm	y,b,p	0,076	[-](mole)					
33		Pressure Pe	Pp	8	[bar]					
34		Temp Perm	Tp	50,0	Celsius					
35		quadratic co	a	-21,8	[-]					
36			b	-5,89	[-]					
37			c	-11,39	[-]					
38			r	0,2	[-]					
39		Viscosity	μ CO2	1,61E-05	Pa*s					
40		Viscosity	μ CH4	1,19E-05	Pa*s					
41		Viscosity	μ mix	1,53E-05	Pa*s					
42		Lengt memb	Δz	1	m					
43		In diameter	Di	5,00E-05	m					
44		No. Straws	Nt	5,79E+08	[-]					
45			Q,f/Nt	4,25E-06	m3/h					
46			Q,f/A	7,52E-06	m/s					
47		Pressure los	Δp	1,18E+05	[Pa]					
48		Pressure los	Δp	1,177	[bar]					

Equation [edit]

In standard fluid-kinetics notation:^{[5][6][7]}

$$\Delta p = \frac{8\mu LQ}{\pi R^4} = \frac{8\pi\mu LQ}{A^2}$$

where:

- Δp is the pressure difference between the two ends,
- L is the length of pipe,
- μ is the dynamic viscosity,
- Q is the volumetric flow rate,
- R is the pipe radius,
- A is the cross section of pipe.