Multi-criteria analyses of two solvent and one low-temperature concepts for acid gas removal from natural gas

Simon Roussanaly[a,*], Rahul Anantharaman[a] and Karl Lindqvist[a]

[a] *SINTEF Energy Research, Sem Sælandsvei 11, NO-7465 Trondheim, Norway*
* Corresponding author. Tel.: +47 474 41 763; fax: +47 735 97 250; *E-mail address:* simon.roussanaly@sintef.no.

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Abstract

This paper evaluates three acid gas removal concepts studied in the project "A Green Sea". Two solvent concepts (aMDEA/MDEA and Selexol) and a low-temperature concept are modeled and assessed, taking different raw natural gases and natural gas product requirements into consideration. The analyses and comparisons of the concepts and cases consider nine criteria in order to include both energy efficiencies and compactness.

The assessment shows that acid gas removal using aMDEA/MDEA technology seems to perform well in terms of energy efficiency, volume and weight for low CO_2 removal. However, for high CO_2 content or strong polishing requirements, the chemical solvent technology loses its efficiency in terms of weight and volume. The assessment shows that the Selexol concept is an inefficient option in terms of energy efficiency, volume and weight, especially when large quantities of CO_2 have to be removed from the gas stream. The assessment also shows that the low-temperature technology can be a compact and energy efficient option, both in the case of strong polishing requirements and high bulk removal of CO_2. However, the higher the amount of CO_2 to be removed, the less energy-efficient is the low-temperature technology.

The case evaluation underlines the fact that the aMDEA/MDEA solvent concept exhibits the best or close to the best key performance indicators (KPIs) for all parameters for the RNG1 Pipe case (raw natural gas specification 1 to pipeline quality specification) and therefore appears to be the best technology option. For this case, the two other technologies are slightly less energy-efficient than the aMDEA/MDEA, but both are significantly less compact. For the RNG1 LNG (raw natural gas specification 1 to LNG quality specification) case, the aMDEA/MDEA and low-temperature concepts have similar KPIs. The chemical solvent technology, however, is slightly more energy-efficient and compact and would therefore be preferred for the RNG1 LNG case. Finally, the RNG2 Pipe (raw natural gas specification 2 to pipeline quality specification) case shows that the low-temperature technology can be a compact option for acid gas removal, which is a critical factor in the case of offshore applications for both the equipment costs and the weight constraints on the platform. Despite its lower energy efficiency, it is therefore likely that the low-temperature technology will be selected in the RNG2 Pipe case. This choice is strengthened by some regulations which recommend that solvents such as MDEA and aMDEA should be phased out for offshore applications, as is seen e.g. in Norway. In addition, if stricter regulations are also enforced for onshore applications, this might also argue in favor of the low-temperature technology or other chemical solvents that are otherwise less efficient than aMDEA/MDEA.

Finally, the potential of hybrid concepts is discussed and suggested for future works, in order to combine the advantages of the different technologies, such as the energy-efficient performances of the aMDEA/MDEA concept and the compactness of the low-temperature concept.

Keywords: Acid Gas Removal (AGR); Natural gas; Evaluation; Chemical solvent; Physical solvent; Low-temperature.

Abbreviations: AGR, Acid gas removal; aMDEA, activated N,N-dimethylethanolamine; BTEX, Benzene, toluene, ethylbenzene, and xylenes; CCS, CO_2 capture, transport and storage; CP, CO_2 products; CR, CO_2 remaining; DMEPG, dimethyl ethers of propylene glycol; DMMEA, N,N-dimethylethanolamine; FPSO, Floating production storage and offloading; HOCNF, Harmonized Offshore Chemical Notification Format; LNG, Liquified natural gas; MDEA, N-methyl-diethanolamine; MS, Methane slip; PSA, Pressure swing absorption; Pipe, Pipeline; RNG, Raw natural gas.

1 Introduction

Natural gas represented 24% of global primary energy consumption in 2012 [1] and is expected to grow by between 1.6 and 1.9% per year until 2035, according to the World Energy Outlook [2]. However, as illustrated in Table 1, natural gas resources are often not located close to markets, and large-scale transport of natural gas is required between countries. Furthermore, to meet the growing demand, new natural gas fields with higher CO_2 and H_2S content will also be developed (Table 2). Natural gas product quality specifications for pipelines are typically 2-3% CO_2, and 50-100 ppm CO_2 for Liquified Natural Gas (LNG) [3]. For fields with CO_2 concentrations in natural gas greater than these limits, Acid Gas Removal (AGR) is therefore a requirement, rather than an option.

CO_2 removal from natural gas to meet transport specifications can, in principle, be achieved by various acid gas removal technologies [4] such as chemical and physical absorption [5], membrane separation [6], pressure-swing adsorption (PSA) [7, 8], membrane contactors [9], cryogenic/low-temperature separation [10] or separation by hydrates [11]. Chemical solvents are currently the most common for acid gas removal from natural gas, and these are expected to remain important in the near future for large-scale gas processing applications [4]. Membrane separation for bulk CO_2 removal from natural gas is increasingly used [12]. The low-temperature and adsorption concepts are emerging technologies that are expected to become alternatives to solvents for natural gases with high CO_2 content [4]. However, the choice of technology depends on several case-specific criteria such as natural gas feed conditions and product specifications, the location and size of the natural gas treatment plant, plant economics, ambient conditions and environmental aspects, and process control and operation.

The most widely used technologies for CO_2 removal from natural gas are chemical and physical absorption. However, most of the amine-based solvents used for acid gas removal have significant environmental impacts and are expected to be phased out in the near future, for example, under the Harmonized Offshore Chemical Notification Format (HOCNF) implementation in Norway. Furthermore, the handling of acid gases like CO_2 and H_2S needs to be integrated into the process in order to avoid their emission to air. The objective of the project "A Green Sea" is therefore to identify and evaluate mature as well as new technologies and concepts for acid gas removal to achieve required product specifications and also prevent the use of chemicals that are harmful to the environment.

This paper presents the evaluation of three acid gas removal concepts studied in the project "A Green Sea". Two solvent concepts (aMDEA/MDEA and Selexol) and a low-temperature concept are modeled and assessed, considering a range of raw natural gases, and natural gas product requirements. The analyses and comparisons of the concepts and cases are performed using multi-criteria analyses [13, 14] in order to include different Key Performance Indicators (KPIs) ranging from energy efficiencies to the compactness of the processes under consideration.

The methodology, including the cases considered in this study, and an overview of acid gas removal technologies and the KPIs for the concept evaluation is presented. The cases are evaluated for each of the AGR technologies and compared using the KPIs described in the methodology section. The assessment results are then discussed from the technology point of view and the case perspective in order to provide recommendations. The potential impact of current and future regulations is finally discussed before concluding.

Table 1: Volumes of natural gas produced and consumed (in billions of cubic metres) by respectively top natural gas producing and consuming countries in 2012 [1]

Top ten natural gas producers			Top ten natural gas consumers		
Rank	Country	Annual production	Rank	Country	Annual consumption
1	United States	681.4	1	United states	722.1
2	Russian federation	592.3	2	Russian Federation	416.2
3	Iran	160.5	3	Iran	156.1
4	Qatar	157	4	China	143.8
5	Canada	156.5	5	Japan	116.7
6	Norway	114.9	6	Saudi Arabia	102.8
7	China	107.2	7	Canada	100.7
8	Saudi Arabia	102.8	8	Mexico	83.7
9	Algeria	81.5	9	United Kingdom	78.3
10	Indonesia	71.1	10	Germany	75.2

Table 2: Example of natural gas reservoirs compositions (in %vol) [15, 16]

	Reservoir				
Component	Groningen (Netherlands)	Ardjuna (Indonesia)	Uthmaniyah (Saudi Arabia)	Lacq (France)	Uch (Pakistan)
CH_4	81.3	65.7	55.5	69	27.3
C_2H_6	2.9	8.5	18	3	0.7
C_3H_8	0.4	14.5	9.8	0.9	0.3
C_4H_{10}	0.1	5.1	4.5	0.5	0.3
C_{5+}	0.1	0.8	1.6	0.5	-
N_2	14.3	1.3	0.2	1.5	25.2
H_2S	-	-	1.5	15.3	-
CO_2	0.9	4.1	8.9	9.3	46.2

2 Methodology

To ensure a consistent and transparent evaluation of the different technologies, a systematic methodology for evaluation is required. An overview of the technology evaluation methodology is shown in Fig. 1 below. The framework for the methodology can be divided into three parts:

1. Fuel and product specification, or the boundary conditions, for process evaluation.
2. Operational and economic parameters of the different AGR technologies.
3. Definition of Key Performance Indicators that use information from (1) and (2) to provide consistent evaluations.

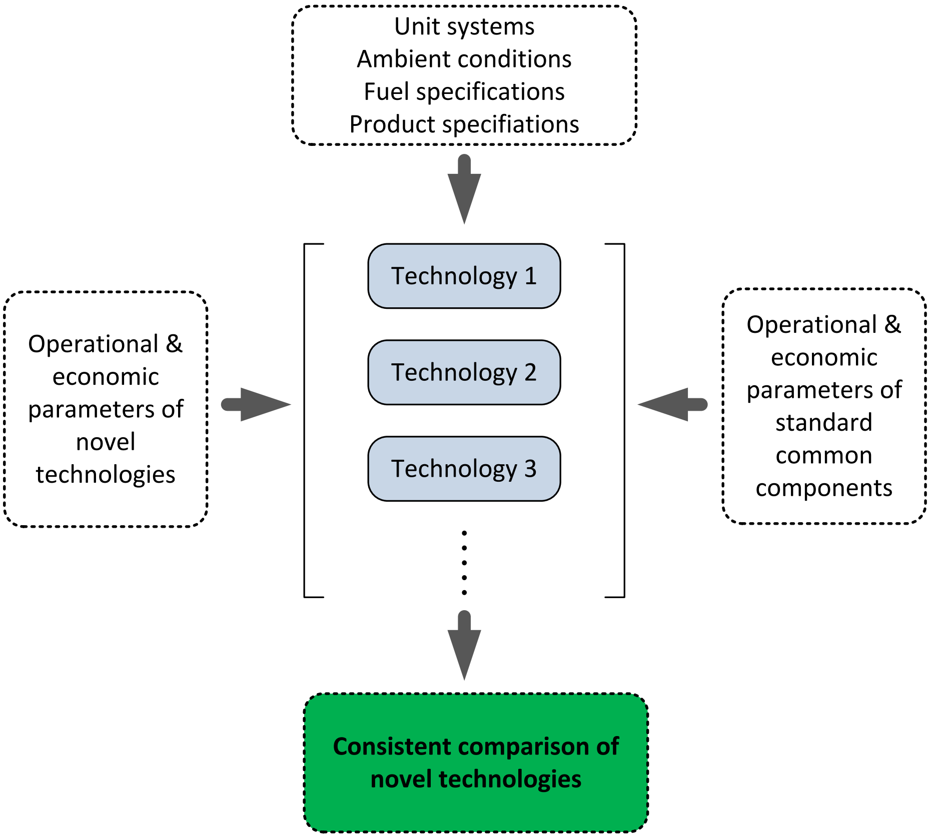

Fig. 1: Methodology for technology assessment

2.1 Acid gas removal cases

As several types of raw natural gas, natural gas product and CO_2 product compositions can be considered and combined to develop cases, this section details the feed and product specifications (as shown in Fig. 2). Based on this information, the cases which are considered for the comparisons of the different acid gas removal concepts are described.

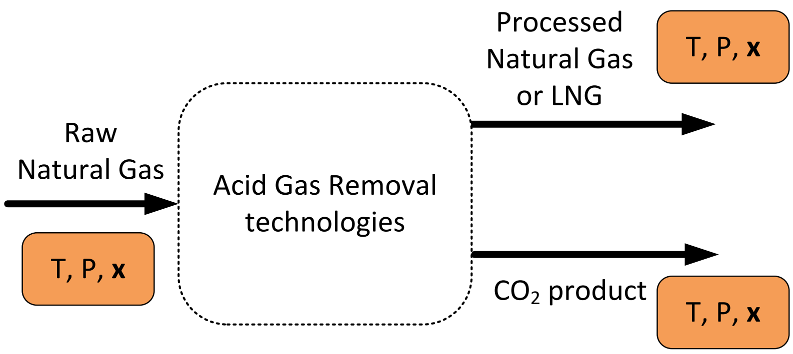

Fig. 2: Framework for technology evaluation

2.1.1 Raw Natural Gases

In order to compare the applicability of the various AGR technologies to different feed gas conditions, two very different raw natural gas (RNG) compositions are considered as feed streams for the case studies. Their characteristics and compositions are given in Table 3 and Table 4. RNG1 is a raw natural gas with 10%vol of CO_2 and no significant heavy hydrocarbons, while RNG2 is a raw natural gas with 50%vol of CO_2 and heavy hydrocarbons.

Table 3: Case study characteristics

	RNG1 Pipe	RNG1 LNG	RNG2 Pipe
Raw Natural Gas	RNG1	RNG1	RNG2
Temperature [°C]	40	40	40
Pressure [bar]	70	70	70
Flow rate [Nm^3/hr]	590 000	590 000	590 000
Flow rate [MSm^3/day]	15	15	15
Natural Gas product	NG Pipe	LNG	NG Pipe
Temperature [°C]	40	-162	40
Pressure [bar]	70	1	70
LHV [MJ/kg]	39	48	39
CO_2 content	2.5 *mol%*	50 *ppmv*	2.5 *mol%*
Sulphur [mg/Nm^3]	30	5	30
Max inerts [mol%]	3	1	3
CO_2 product	CP1	CP1	CP2
CO_2 purity [%]	95	95	70
Pressure [bar]	110	110	110
Temperature [°C]	40	40	40
Location	Offshore	Onshore	Offshore
Ambient seawater temperature [°C]	10	10	15

Table 4: Raw Natural Gas Composition

Composition [vol%]	RNG 1	RNG 2
C1	83	39.28
C2	4.6	3.5
C3	1.65	2.4
C4	0.3	1.8
C5	0.1	1.2
C6+	0.03	0.2
CO_2	10	50
Sulphur (eg. H_2S)	0	1
Organic sulphides	0	0.02
H_2O	0	0
N_2	0.32	0.5
BTEX	0	0.1

2.1.2 Natural Gas Products

Produced natural gas is typically available as pipe sales gas or as liquefied natural gas (LNG). The two natural gas products specifications considered for this work are therefore: "Pipe", corresponding to a specification for natural gas products to be transported by pipelines, and "LNG", corresponding to the natural gas product specification when transported in the form of LNG[1]. These specifications are given in Table 3.

[1] The LNG liquefaction train is not included in the current assessment.

2.1.3 CO_2 Product

In order to limit losses of valuable product, the CO_2 products (CP) are defined as having purities in the range of 70-95%. However, for the case study definition, two independent product purities are considered. The CO_2 product specification options are shown in Table 3.

2.1.4 Case definitions

Based on the different raw natural gases, natural gas products and possible CO_2 product characteristics, three case studies are defined, as shown in Table 3, along with their locations and associated characteristics. The RNG1 Pipe and RNG1 LNG cases consider a raw natural gas containing 10% CO_2 and no significant heavy hydrocarbons. For the RNG1 Pipe and LNG cases, the different acid gas removal processes considered are required to result in a natural gas product containing 2.5%vol and 50 ppmv of CO_2, while the CO_2 product is expected to have a purity of at least 95% in both cases. The RNG2 Pipe case considers a raw natural gas containing 50%vol CO_2 and heavy hydrocarbons. For the RNG2 Pipe case, the different processes are expected to result in a natural gas product containing 2.5%vol CO_2 while the CO_2 product is expected to have a purity of at least 70%.

2.2 Acid Gas Removal concepts

Three acid gas removal concepts are considered: an aMDEA/MDEA-based solvent concept, a Selexol-based solvent concept, and a low-temperature concept. These three concepts, as detailed below, are assessed for the three cases identified and defined above. However Selexol technology cannot reach the CO_2 requirements of the LNG specification and therefore cannot be used in the RNG1 LNG case.
It is also possible to consider a combination of these concepts in "hybrid" concepts. This is not included as part of this study, but is the focus of future work.

A pre-conditioning step has been assumed for all three concepts. Although these additional units may have non-negligible power consumption and weight, they have been excluded from the process evaluation. The rationale for focusing on CO_2 removal is that the H_2S and BTEX (Benzene, toluene, ethylbenzene, and xylenes) to CO_2 ratios are modest, such that CO_2 removal is anticipated to pose the greatest challenge for all considered processes.

2.2.1 aMDEA/MDEA based solvent concept (reference concepts)

Amine-based solvents are one of the most widely used solvents for CO_2 capture. A chemical solvent based gas sweetening unit using an aqueous solution of MDEA (45 wt%) to remove CO_2 from the natural gas streams is modelled in ProTreat v4.2. The relatively high partial pressure of CO_2 in the feed gas promotes the use of an MDEA based solvent, as it can be partly regenerated by pressure release [5]. To ensure adequate reactivity to CO_2, the solvent is activated by addition of 5 wt% of Piperazine.

The process layout shown in Fig. 3 is based on an absorber-stripper configuration with lean-rich solvent heat exchanger and includes flash tanks for partial release of absorbed components through pressure reduction. In addition, the RNG2 Pipe simulation includes a partial bypass of the stripper column, as the complete stripping of the absorbed species is not necessary to meet the sweet gas specification. Due to the high absorber pressure and large solvent circulation rate, a liquid turbine is used to recover power from the rich solvent stream after leaving the absorber. To avoid excessive co-absorption of heavy hydrocarbons, the temperature of the lean solvent entering the absorption column is set to be at least 10°C higher than the dew point of the sweet gas. Further data on temperatures, pressures and solvent composition are given in Table 5.

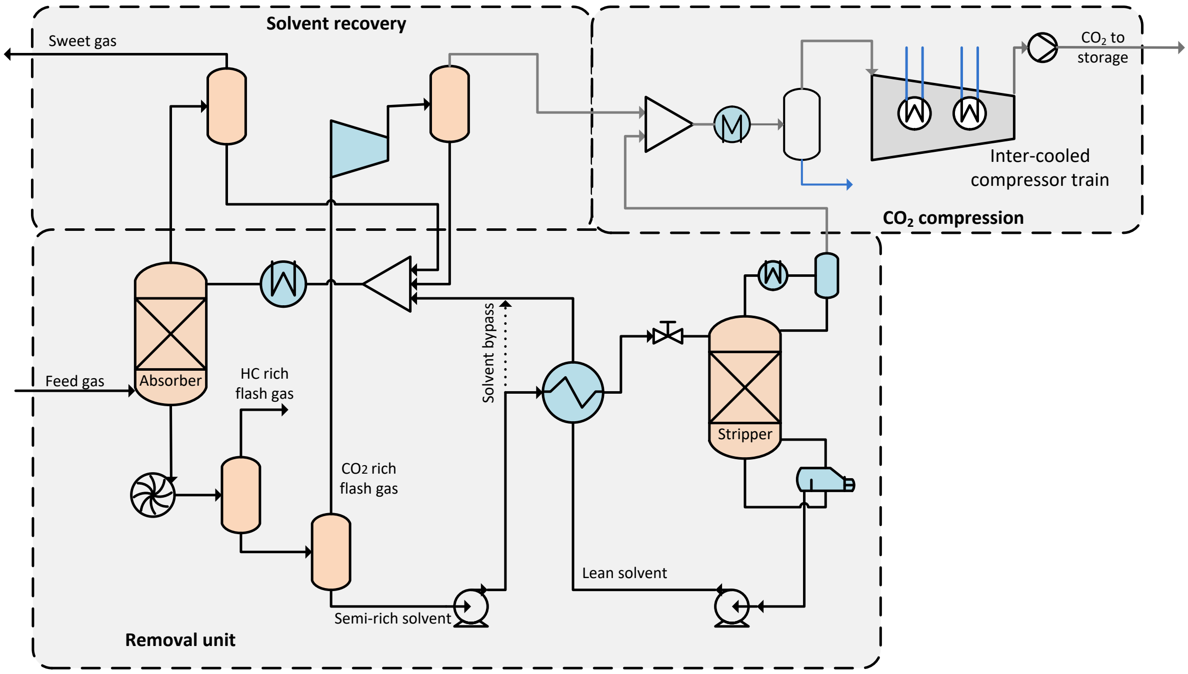

Fig. 3: Principal process flow diagram of the aMDEA/MDEA based solvent concept for RNG1 and RNG2 feed gas cases

Table 5: Process parameters for aMDEA/MDEA based solvent concept

Solvent	Lean loading [-] MDEA [wt%] Piperazine [wt%]	0.06-0.07 45 5
Absorber	Pressure [bar] Lean solvent temperature [°C] Packing type Flooding factor [-]	70 50 Nutter Ring 2 3/8 0.7
Stripper	Pressure [bar] Reboiler temperature [°C] Packing type Flooding factor [-]	1.8 97-120 Nutter Ring 2 3/8 0.6
HC flash	Pressure [bar]	5
CO_2 flash	Pressure [bar]	1.1

2.2.2 Selexol based solvent concepts

A physical solvent based gas sweetening unit using dimethyl ethers of propylene glycol (DMEPG) to remove CO_2 from the natural gas streams is modelled in ProTreat v4.2. The chosen configuration relies solely on pressure swing for release of the absorbed species as shown in Fig. 4. Three pressure levels are chosen in order to recycle some of the absorbed hydrocarbons, obtain part of the acid gases at elevated pressure, and reduce the methane slip and energy consumption for acid gas compression. It is worth noting that most of the acid gases are released in the low pressure step. Further data on temperatures and pressures are given in Table 6.

In this configuration, the absorber temperature is significantly lower than the dew point of the feed gas. This is required in order to minimize the solvent recirculation rate and methane slip, as a low solvent temperature

promote high solubility and selectivity of acid gases [5]. An auxiliary propane refrigeration cycle is used to cool the feed gas and lean solvent before entering the absorber. As a consequence, the majority of the heavy hydrocarbons (C3+) are co-absorbed by the solvent and released with the acid gases in the intermediate- and low pressure steps. While these components can be recovered from the water knock-out steps in the CO_2 compression train, this procedure is not explicitly considered in the scope of this work.
Liquid turbines are used in the pressure reduction steps, rather than valves, for the same reason mentioned for the chemical solvent process.

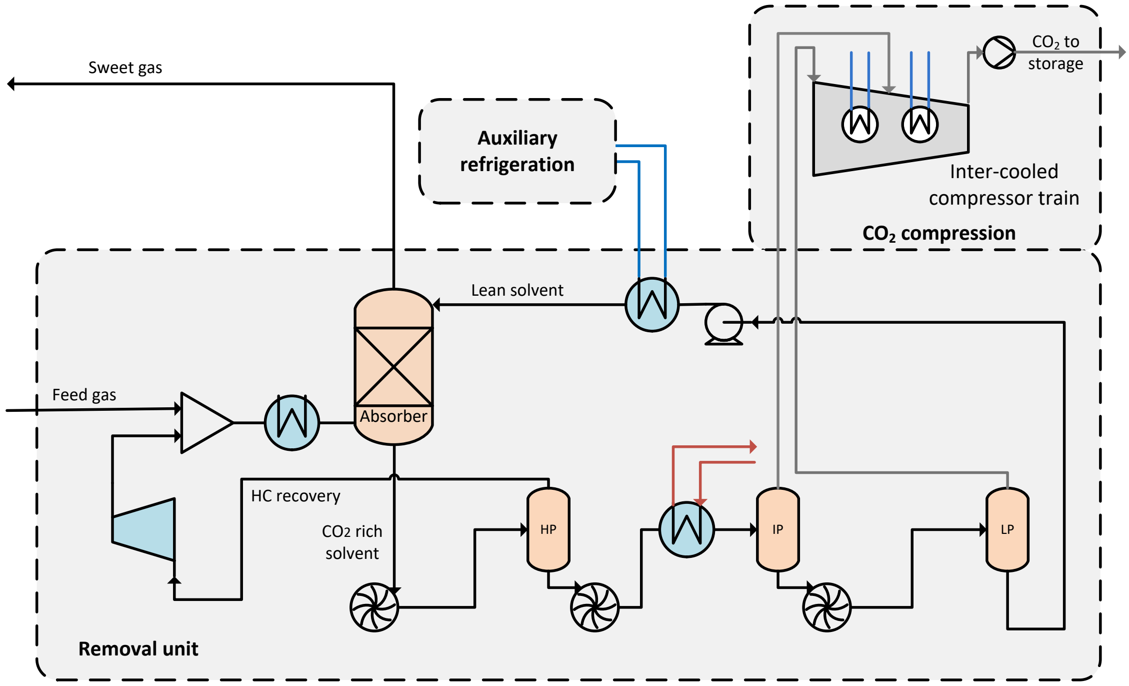

Fig. 4: Principal process flow diagram of the Selexol based solvent concept for RNG1 and RNG2 feed gas cases

Table 6: Process parameters for Selexol based solvent concept

Absorber	Pressure [bar] Lean solvent temperature [°C] Feed gas temperature [°C] Packing type Flooding factor [-]	70 5 25 Intalox Metal Tower Packing 50 0.7
Flash vessel HP	Pressure [bar]	28
Flash vessel IP	Pressure [bar]	13
Flash vessel LP	Pressure [bar]	1.1

2.2.3 Low-temperature concepts [10]

A low-temperature separation unit to remove CO_2 from the natural gas is modelled in Aspen HYSYS. Fig. 5 and Fig. 6 show the process layout of the RNG1 cases and the RNG2 Pipe case, respectively, including the main methane column(s), CO_2 purification column(s) and a section producing freeze-out inhibitor for the methane column(s). The process layout and operational parameters are adjusted according to the feed gas composition and products specification.

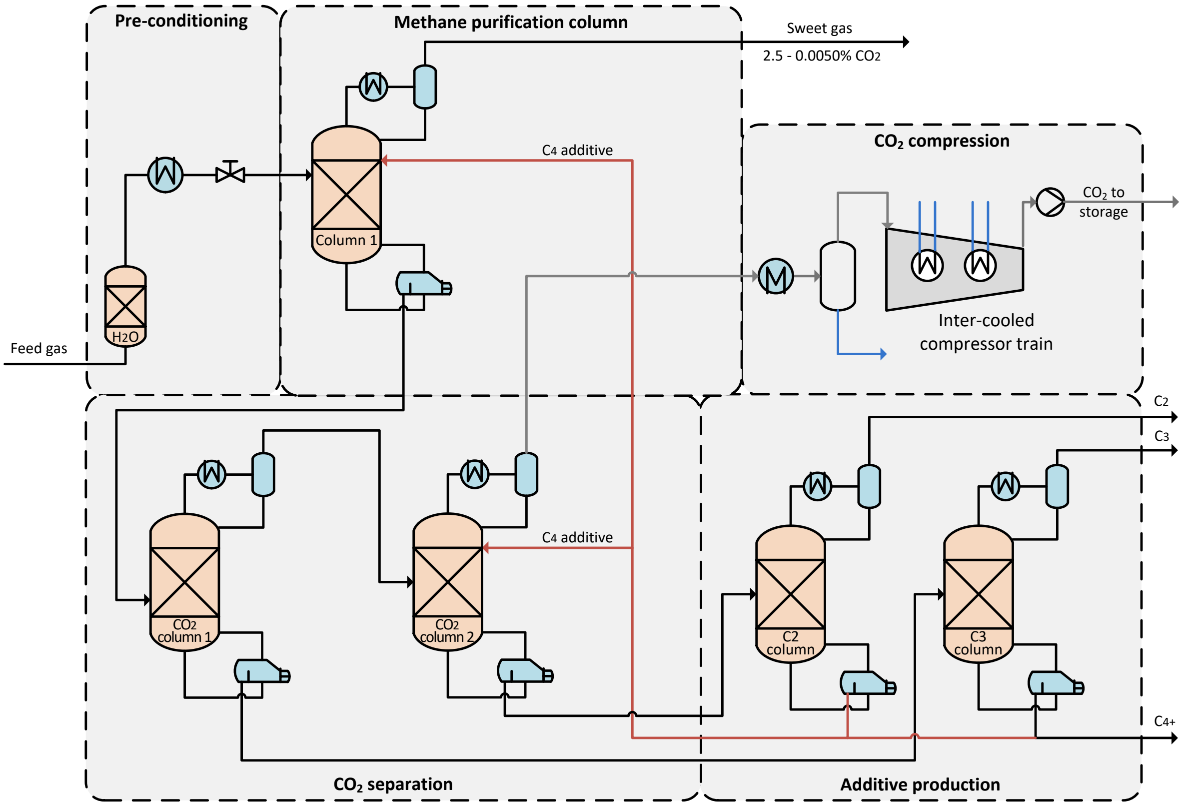

Fig. 5: Principal process flow diagram of the low-temperature concept for RNG1 feed gas cases

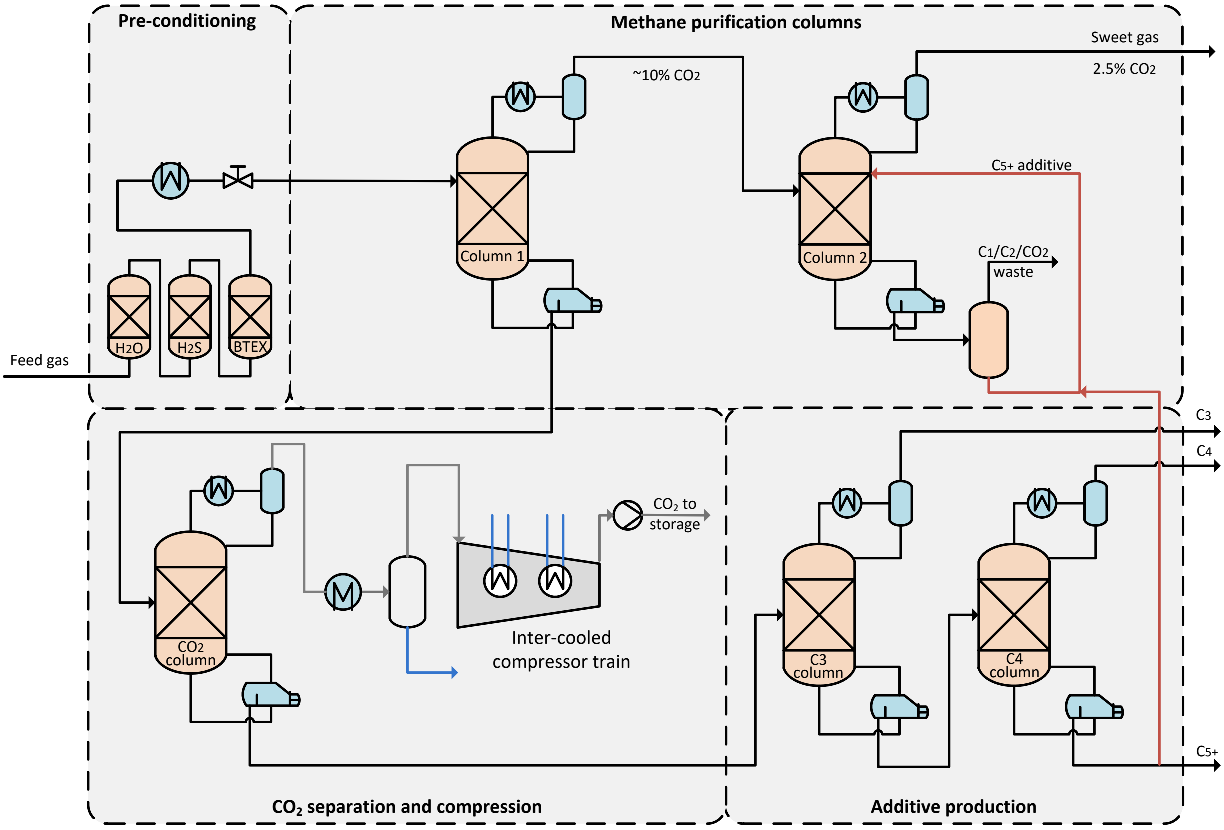

Fig. 6: Principal process flow diagram of the low-temperature concept for RNG2 Pipe feed gas case

An auxiliary refrigeration system supplying cooling for the column condensers, not illustrated here, and consisting of a propane-ethylene cascade is also modelled. Even if the refrigeration system is not optimized with regards to refrigerant selection, power consumption or equipment weight, it is still assumed that the model gives a reasonable estimate of the power consumption required to supply the refrigeration duties associated with feed gas pre-cooling and condenser duties. Furthermore, it is deemed likely that the gas processing unit will be part of a larger installation, such as an FPSO (Floating production storage and offloading) or an LNG liquefaction plant, such that steam utility streams and sea water for the column reboilers are readily available.

The pinch temperature for heat transfer is set to 3°C for all low-temperature heat exchangers, except for the propane-ethylene interface heat exchanger which has a 4°C pinch temperature. This choice represents a trade-off between refrigeration power consumption and heat exchanger size. Further data on temperatures, pressures and top product CO_2 composition are given in Table 7.

Table 7: Process parameters for low-temperature concept

		RNG1		RNG2
		Pipe	LNG	Pipe
Methane column 1	Pressure [bar]	40	40	40
	Condenser temperature [°C]	-81.4	-85.1	-67.5
	Reboiler temperature [°C]	35.9	30.2	7.51
	Top product CO_2 concentration [mol%]	2.50	0.005	10.3
Methane column 2	Pressure [bar]	X	X	40
	Condenser temperature [°C]	X	X	-84.8
	Reboiler temperature [°C]	X	X	0.00
	Top product CO_2 concentration [mol%]	X	X	2.50
CO_2 column(s)	Pressure [bar]	30	30	30
	CO_2 product purity [mol%]	96.7	97.6	90.9
C2 column	Pressure [bar]	24	24	X
C3 column	Pressure [bar]	20	20	16
C4 column	Pressure [bar]	X	X	10

The risk of CO_2 solidification is minimized either by operating a column at temperatures that avoided solidification or by adding a CO_2 solidification inhibitor. The first methane column in the RNG2 case is operated at conditions sufficiently far from the CO_2 freezing point. The secondary column(s) require addition of an additive stream consisting of pentane and hexane components in order to be operated at the desired temperature. In the RNG1 case, relatively pure propane is used for freezing point inhibition both in the methane column and the second CO_2 purification column. In all cases, the inhibitors were produced from the bottom product of the CO_2 purification column(s) as it made the system self-sustaining with regards to column additive. As a side effect, the heavier hydrocarbons from the feed gas were produced as valuable product streams, aside from the waste streams of CO_2/hydrocarbon mixtures.

2.3 Key Performance Indicators

To enable consistent comparisons between different concepts, a system for evaluation is required. Key Performance Indicators (KPIs) are developed and defined to enable these consistent comparisons to be made. The KPIs can be classified into quantitative and qualitative KPIs. Based on these criteria, multi-criteria analyses [13, 14] can be performed to compare the technologies over the different cases.

2.3.1 Quantitative KPIs

Quantitative KPIs are indicators where the number evaluated can be directly used for comparing the different process concepts. These KPIs are defined in such a way that no subsequent interpretation or judgment call is required. The quantitative KPIs developed for comparing the concepts in this study are CO_2 recoveries, methane slip, system penalties and system efficiencies.

2.3.1.1 CO_2 Remaining

CO_2 remaining indicates the amount of CO_2 not removed from the raw natural gas feed, and is defined as the ratio of CO_2 not captured compared to the amount initially present in feed natural gas.

$$\mathbf{CR} = \frac{\textbf{Amount of } \mathbf{CO_2} \textbf{ in the raw natural gas} - \textbf{Amount of } \mathbf{CO_2} \textbf{ captured}}{\textbf{Amount of } \mathbf{CO_2} \textbf{ in the raw natural gas}} \quad (1)$$

2.3.1.2 Methane slip

Methane slip (MS) indicates the fraction of methane from the raw natural gas that is lost during the removal of CO_2 from natural gas. This is a simplistic indicator of the thermal losses (heating value losses) in the system due to CO_2 removal. It is defined as:

$$\text{Methane slip} = 1 - \frac{\text{CH}_4 \text{ in the sweet gas}}{\text{CH}_4 \text{ in the raw natural gas}} \quad (2)$$

2.3.1.3 System Penalties

System penalties are an indicator of the overall energy penalty in the process. The system penalty can be defined in terms of the processed natural gas product or the captured CO_2. The two definitions of system penalties are the following:

- Natural gas energy penalty (π_{NG}): is the energy penalty to produce 1 MWth of natural gas product at defined specifications (*in MW/MW$_{th}$*).

$$\pi_{\text{NG}} = \frac{(\text{MW}_{\text{th,Raw NG}} - \text{MW}_{\text{th,NG product}}) + \text{MW}_{\text{el}}}{\text{MW}_{\text{th,NG product}}} \quad (3)$$

- CO_2 energy penalty (π_{co2}): is the energy penalty to capture 1 kg of CO_2 (*in MJ/kg*).

$$\pi_{\text{co2}} = \frac{(\text{MW}_{\text{th,Raw NG}} - \text{MW}_{\text{th,NG product}}) + \text{MW}_{\text{el}}}{\text{Amount of CO}_2 \text{ captured}} \quad (4)$$

2.3.1.4 System Losses

The system losses provide an indication of how efficient the process is for producing the specified natural gas product. Natural gas is a fuel and hence the losses of a process (π_{th}) can be thought of in terms of losses in the total heat content in the course of the removal of CO_2. This is defined as the fraction of thermal energy lost during the CO_2 removal compared to the amount of energy available in the feed natural gas:

$$\pi_{\text{th}} = \frac{\text{MW}_{\text{th,Raw NG}} - \text{MW}_{\text{th,NG Product}}}{\text{MW}_{\text{th,Raw NG}}} \quad (5)$$

However, the above definition ignores other energy input to the process for removing the CO_2. To provide a more complete picture for comparison, the following equation defines system losses (π_{sys}) as the ratio of thermal energy lost during the CO_2 removal compared to the total energy input:

$$\pi_{\text{sys}} = \frac{\text{MW}_{\text{th,Raw NG}} - \text{MW}_{\text{th,NG Product}}}{\text{MW}_{\text{th,Raw NG}} + \text{MW}_{\text{el}}} \quad (6)$$

2.3.2 Qualitative KPIs

The main qualitative KPIs consider cost-related indicators. Even if no cost estimation is considered, dry weight, internal volume and heat exchange area of key equipment provide indications of equipments costs and can be used as a basis to discuss and compare the three acid gas removal technologies. It is worthwhile to note that the qualitative KPIs are not specific values in that they are not evaluated in per kg of CO_2 or in per $kW_{th}h$ of NG produced terms.

Section 7 provides an overview of the sizing and weight estimation methodologies used to assess the qualitative KPIs of the different concepts.

2.3.3 Multi-criteria analyses

The nine quantitative and qualitative Key Performance Indicators are considered to benchmark the three acid gas removal technologies for the three cases. In each case, these indicators are pictured in a spider diagram as shown in Fig. 7. In this system, the highest value among the three technologies' KPIs is set to the border, so that the closer a KPI is to the border, the less attractive is the technology. The theoretically ideal and worst technologies are illustrated in Fig. 7 as an example.

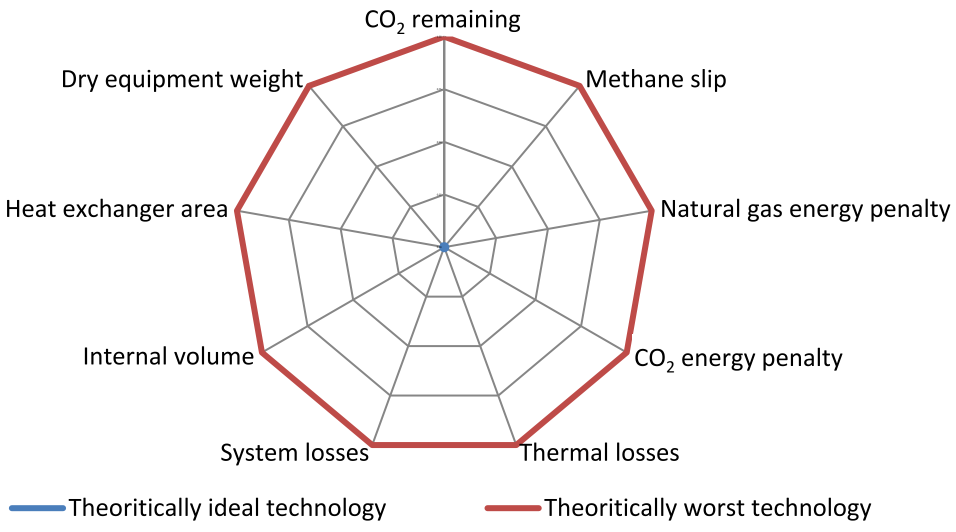

Fig. 7: Multi-criteria analysis structure for evaluation of the three concepts

3 Results

3.1 Quantitative and qualitative KPIs evaluation

The results of the evaluation of the quantitative and qualitative key performance indicators of the three acid gas removal concepts for the three cases are summarized in Table 8 and Table 9.

The KPIs evaluation shows that the aMDEA/MDEA technology, with rather low methane slip, low energy penalties and high efficiencies performs quite well in terms of energy efficiency. It is however worth noting that the RNG1 LNG and RNG2 Pipe system efficiencies are respectively 0.9 and 2.6 points lower than the RNG1 Pipe, due to the higher CO_2 energy penalty incurred in the first case and the higher methane slip in the second. Regarding the qualitative KPIs, the aMDEA/MDEA technology is very compact in the RNG1 Pipe case. However, in the RNG1 LNG case, the volume and weight of the aMDEA/MDEA concept rise by 50% and 60% respectively compared to the RNG1 Pipe, due to the additional 30% CO_2 removal from the raw natural gas as per the LNG specifications. In the RNG2 Pipe case, the weight and volume are almost triple that of the RNG1 Pipe case, while the amount of CO_2 removed from the raw natural gas is approximately six times higher. The solvent required in the aMDEA/MDEA capture system increases with the amount of CO_2 to be removed and impacts the weight and volume of the system similarly. However, as CO_2 separation from higher concentrations is more efficient, a scale effect is observed when capturing CO_2 from the RNG2 case, due to the increase in the CO_2 partial pressure [4].

Table 8: Quantitative KPIs of the three acid gas removal concepts for the three cases

	CO_2 remaining [%]	Methane slip [%]	Natural gas energy penalty [MW/MW_{th}]	CO_2 energy penalty [MJ/kg_{CO2}]	Thermal losses [%]	System losses [%]
aMDEA/MDEA-based solvent						
RNG1 Pipe	21	0.06	0.004	0.85	0.05	0.38
RNG1 LNG	0.04	0.09	0.02	4.08	0.11	2.25
RNG2 Pipe	1.8	0.26	0.04	0.98	1.3	4.0
Selexol-based solvent						
RNG1 Pipe	18.5	2.73	0.08	15.76	6.42	7.20
RNG1 LNG	X	X	X	X	X	X
RNG2 Pipe	2.5	3.87	0.46	7.87	29.7	31..7
Low-temperature						
RNG1 Pipe	21.6	0	0.03	5.82	0.64	2.53
RNG1 LNG	0.2	0	0.04	6.77	1.13	3.72
RNG2 Pipe	2.1	0	0.22	4.50	15.2	18.1

Table 9: Qualitative KPIs of the three acid gas removal concepts for the three RNG cases

	Concept volume [m^3]	Concept heat exchanger area [10^3 m^2]	Concept weight [t]
aMDEA/MDEA-based solvent			
RNG1 Pipe	659	7.5	550
RNG1 LNG	1018	13.8	898
RNG2 Pipe	1884	3.1	1584
Selexol-based solvent			
RNG1 Pipe	1798	4	1136
RNG1 LNG	X	X	X
RNG2 Pipe	2570	9.7	1669
Low-temperature			
RNG1 Pipe	974	17.5	1032
RNG1 LNG	1149	22.6	1177
RNG2 Pipe	1241	17.6	1125

The assessment shows that for the RNG1 Pipe case, the Selexol concept is not very energy-efficient compared to the other technologies. For the RNG2 Pipe case, the Selexol technology is even less energy-efficient and has a system efficiency of only 68.3%. In both cases, the low efficiencies are due to the hydrocarbon slip. Regarding the qualitative KPIs, the Selexol technology is not a compact option for either of the RNG1 and the RNG2 Pipe cases. Indeed weight and especially the volume of the Selexol technology are already high for the RNG1 Pipe case, and both increase by around 50% in the RNG2 Pipe case. The high volume and weight of the Selexol technology is due to significantly lower kinetics of absorption and desorption of CO_2 by Selexol, leading to large plant footprint compared to chemical solvents such as aMDEA/MDEA. Moreover, the driving force of desorption is mainly pressure-based, while less heat is used than in the chemical solvent case [4]. It is worth noting that due to the poor energy and compactness performances of the Selexol technology, the RNG1 LNG case was neither modelled nor evaluated.

For the low-temperature technology, the evaluation demonstrates rather high energy efficiency for the RNG1 cases; this is largely due to the absence of methane slip. The CO_2 energy penalty of the low–temperature concept, however, was seven times as high as for the aMDEA/MDEA for the RNG1 Pipe case. This difference is lower in the two other cases, where it is 65% and 350% higher in the RNG1 LNG and the RNG2 Pipe cases respectively. The system efficiency of the low-temperature technology drops to 82% in the case of the RNG2 Pipe case as there is a significant loss of hydrocarbons as can be seen from the Natural Gas Energy Penalty parameter.

The weight and volume evaluation of the low-temperature concept shows that it appears to be a quite compact option for acid gas removal. Indeed, except in the RNG1 Pipe case, in which volume and weight are 50 to 90% higher than using the aMDEA/MDEA methods, the low-temperature technology is similar to or more compact than the aMDEA/MDEA concept in the RNG1 LNG and RNG2 Pipe cases respectively. It is even 30% more compact than the aMDEA/MDEA technology in the RNG2 Pipe case. It is worth noting that the low-temperature technology is less affected in terms of weight and volume by an increase in the quantity of CO_2 to be captured, both in the case of stronger polishing requirement as in the RNG1 LNG case, and high bulk removal of CO_2 as in the RNG2 Pipe case. This effect is especially noteworthy when the RNG1 Pipe and RNG2 Pipe cases are compared, where the weight and volume increase by 30 and 10% respectively, while the quantity of CO_2 to be removed from the raw natural gas is multiplied by approximately six. Such small differences might seem surprising. Two main reasons might explain this: first, the temperatures used in the refrigeration cycles of the RNG2 Pipe case are lower than in the RNG1 cases, which allow the overall weight of the concept to be reduced. This has not been possible in the RNG1 cases as initially suggested, due to the freeze-out temperature. Secondly, the fact that the CO_2 separation is split into two columns, one of which is doing a bulk removal while the second column performs the polishing, also plays a part in the small discrepancy between the results of the RN2 Pipe and RNG1 cases. Indeed, the first column can "easily", i.e. in a small volume, remove a significant part of CO_2 in the natural gas due to the high CO_2 concentration, while the second column size is also small because its inlet flow is already significantly reduced, as most of the CO_2, which represented 50% of the raw natural gas, is removed in the first column.

The specific energy requirement for CO_2 removal merits some discussion and gives a flavour of the difference in capture technologies used. The energy penalty for the RNG1 Pipe and RNG2 pipe cases using aMDEA/MDEA are similar while it is significantly higher for the RNG1 LNG case. This indicates that the energy requirement depends on the natural gas product specification rather than the feed composition. It is expected that at these high partial pressures the penalty for capture is pretty constant (leading to similar penalties for the Pipe cases), but the extent of CO_2 removal for the aMDEA/MDEA technology has a larger impact on the penalty. The LNG case involves a deeper CO_2 removal than the Pipe case and hence the significantly higher energy penalty of capture.

The energy penalty for capture using the low temperature process shows a very different trend than that of the aMDEA/MDEA solvent process. The low temperature process separate CO_2 from natural gas by partial condensation of CO_2, and the energy penalty for CO_2 removal is thus very dependent on the feed CO_2 concentration. Hence, the penalty for CO_2 capture for the RNG2 Pipe case is lesser than the RNG1 Pipe case. The penalty for capture in the RNG1 LNG case is slightly higher than the RNG1 Pipe case as the specific energy requirement increase nearly linearly with increasing CO_2 purity requirement in the product as compared to exponentially in the aMDEA/MDEA case.

In the case of Selexol, which is a physical solvent, the CO_2 loading increases linearly with the feed CO_2 partial pressure, and the penalty decreases with the feed partial pressure. Thus the penalty for the RNG2 Pipe case is much lower than the RNG1 Pipe case for Selexol.

3.2 Multi-criteria analysis

Based on the KPIs assessments, the three acid gas removal technologies are compared for each of the three cases (RNG1 Pipe, RNG1 LNG and RNG2 Pipe) in order to provide recommendations for each of the cases.

3.2.1 RNG1 Pipe

As shown in Fig. 8, the aMDEA/MDEA solvent concept exhibits the best or close to the best KPIs for all parameters and seems therefore to be the best technology option for the RNG1Pipe case. The low-temperature technology reaches energy efficiencies 2.1 pt lower than the aMDEA/MDEA concept but its volume and weight are 45 and 85% higher respectively than the aMDEA/MDEA concept. The low-temperature concept can therefore be expected to suffer from higher investment costs and slightly higher operating costs. Finally, the Selexol technology exhibits close to all the worst parameters, except in the heat exchange areas. For example, its volume and weight are respectively 170 and 105% higher than the aMDEA/MDEA, while its system efficiency is 6.8 point per cent lower.

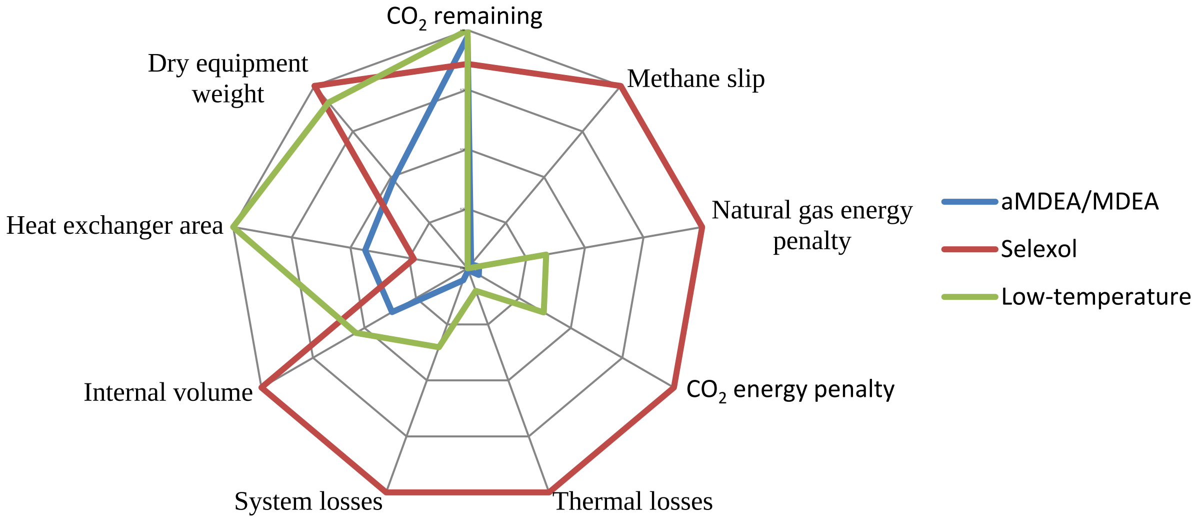

Fig. 8: Multi-criteria analysis of the RNG1 Pipe case

3.2.2 RNG1 LNG

It is first important to remember that no Selexol case was modelled for the RNG1 LNG case, due to the already poor performance of this technology in the RNG1 Pipe case, and which would be even stronger for the RNG2 LNG case.

As shown in Fig. 9, the aMDEA/MDEA and low-temperature concepts have similar key performance indicators in the RNG1 LNG case, especially due to larger increases in terms of weight and volume compared to the RNG1 Pipe for the aMDEA/MDEA than for the low-temperature concept. However, the low-temperature technology is still 15% larger and 30% heavier than the solvent-based concept, which should lead to higher investment costs for the low-temperature technology in the RNG1 LNG case. In spite of the absence of methane slip, the low-temperature option displays a system efficiency that is 1.4 point lower than the solvent concept, due to the higher energy penalties involved. The aMDEA/MDEA can therefore be expected to be more investment-efficient, to have slightly lower operating costs and therefore to be slightly more cost-effective than the low-temperature concept for the RNG1 LNG case.

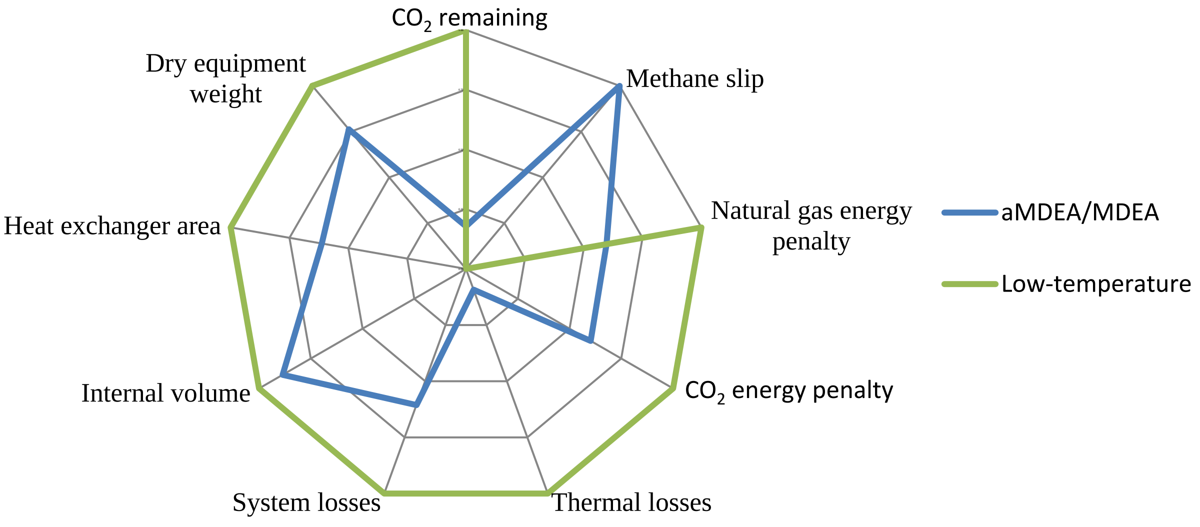

Fig. 9: Multi-criteria analysis of the RNG1 LNG case

3.2.3 RNG2 Pipe

As for the RNG1 Pipe, the assessment of the RNG2 Pipe case shows that the Selexol technology is the poorest in almost all parameters except for the heat exchange area. The Selexol concept is 110% larger and 50% heavier respectively than the low-temperature concept, and 14 points less energy efficient than the low-temperature concept and 28 points lower than the aMDEA/MDEA technology.

As Fig. 10 shows, the evaluation of the RNG2 Pipe case illustrates that the low-temperature option involves a process 35% more compact and 30% lighter than the chemical solvent concept. As the RNG2 Pipe case corresponds to an offshore application, the compactness of the system is critical, as it simultaneously reduces investment costs and the space and weight demands on the platform. Regarding the energy efficiency, the aMDEA/MDEA system is 14 points more energy-efficient and will therefore have lower operating costs than the low-temperature system. Due to the importance of the compactness in offshore applications, it is likely that the low-temperature technology will be selected in the RNG2 Pipe case.

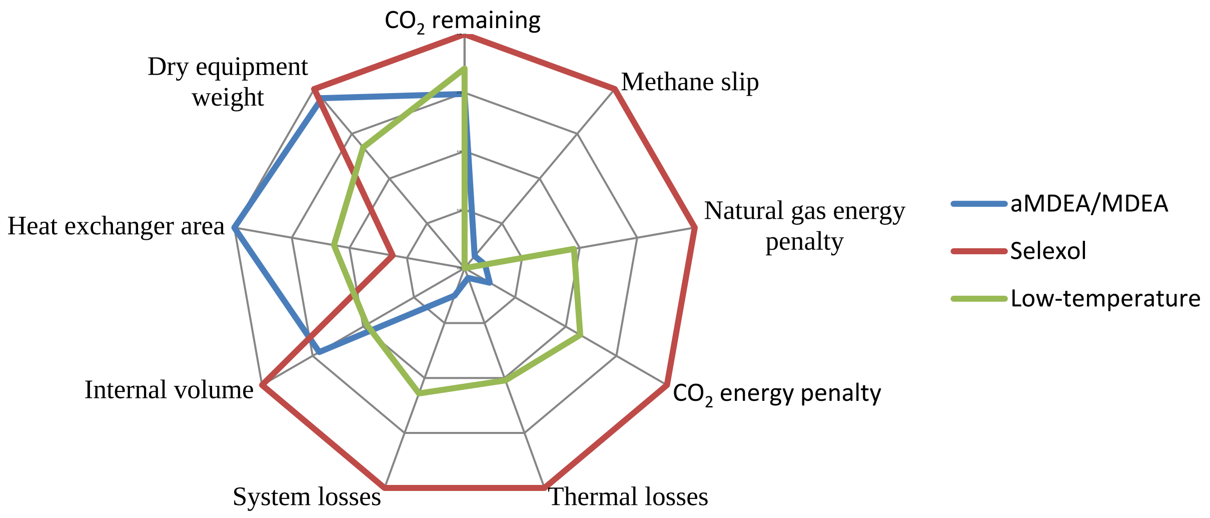

Fig. 10: Multi-criteria analysis of the RNG2 Pipe case

3.2.4 Impact of current and future regulations

The conclusions presented here are based purely on the energy and compactness performances of the three technologies. However current and future regulatory constraints might also influence the choice of technology for acid gas removal. As an example, the Norwegian authorities have a set of criteria for classifying chemicals used in offshore applications under the Harmonized Offshore Chemical Notification Format (HOCNF) implementation. While such criteria vary from country to country, the underlying principles for allowing emissions of chemicals are likely to be fairly similar. The Norwegian criteria focus mainly on the following aspects: toxicity, biodegradation and bioaccumulation. Based on this, four categories has been identified: "black" contains products which must not be discharged, "red" comprises chemicals which shall be phased out or replaced, "yellow" correspond to products which are acceptable, while "green" includes products that have no environmental impacts .

Due to their low biodegradability [17, 18], numerous amine-based solvents such as N-methyldiethanolamine (MDEA) and aMDEA are classified as red and are to be phased out. However, the Norwegian classification identifies other solvent options such as N,N-dimethylethanolamine (DMMEA) as yellow . These could be interesting alternatives and shall be investigated for offshore applications, as well as onshore applications in countries where regulations regarding onshore emissions are stricter.

The low-temperature concepts do not require chemicals other than alkane and alkene products which are already inherent to oil and gas production. The low-temperature concept can therefore be classified as green according to the Norwegian regulations on the use of chemicals in offshore applications.

Unfortunately, no data was available for Selexol, but due to its poor energy, volume and weight performances, regulatory constraints on the use of Selexol for acid gas removal will not influence the choice of technology.

Based on these aspects, the choice of the low-temperature technology for the RNG2 Pipe, offshore located, is strengthened for a Norwegian case as well as potentially for other countries. Moreover, if stronger regulations are also enforced for onshore applications, this might also play in favor of the low-temperature technology over other chemical solvents that are less efficient than aMDEA/MDEA.

4 Conclusions

This paper presents the evaluation of three acid gas removal concepts studied in the project "A Green Sea". Two solvent concepts (aMDEA/MDEA and Selexol) and a low-temperature concept are modeled and assessed, taking a range of raw natural gases and natural gas product requirements into consideration. The concepts and cases are analysed and compared, considering nine criteria in order to include both their energy efficiencies and compactness performances.

The assessment shows that acid gas removal using aMDEA/MDEA technology seems to perform well in terms of energy efficiency, volume and weight for low CO_2 content removal. However for high CO_2 content or strong polishing requirements, chemical solvent technology loses its efficiency in terms of weight and volume. The assessment shows that the Selexol concept is an inefficient option in terms of energy efficiency, volume and weight, especially where large quantities of CO_2 are to be removed from the natural gas stream. The assessment also shows that the low-temperature technology can be a compact and energy-efficient option for CO_2 removal. Indeed, except for the RNG1 Pipe case, in which its volume and weight are significantly higher than the aMDEA/MDEA concepts, the low-temperature technology has a similar to higher compactness than the aMDEA/MDEA concept for both the RNG1 LNG and RNG2 Pipe cases. The low-temperature technology is also less impacted in terms of weight and volume by increases in the amount of CO_2 to be captured, both in the case of more stringent polishing requirements and high bulk removal of CO_2. However, the higher the amount of CO_2 to be removed, the less energy efficient is the low-temperature technology.

The case evaluations underline the fact that the aMDEA/MDEA solvent concept exhibits the best or close to the best KPIs for all parameters for the RNG1Pipe case and seems therefore to be the best technology option. For this case, the two other technologies are slightly less energy-efficient than the aMDEA/MDEA but significantly less compact. For the RNG1 LNG case, the aMDEA/MDEA and low-temperature concepts exhibits similar key performance indicators, especially due to greater increases in terms of weight and volume than the RNG1 Pipe, for the aMDEA/MDEA than for the low-temperature concept. However, the chemical solvent technology is slightly more energy-efficient and compact, and would therefore be preferred for the RNG1 LNG case. Finally, the RNG2 Pipe case shows that the low-temperature technology can be a compact option for acid gas removal, which is a critical factor in offshore applications, in terms of both equipment costs and weight constraints on the platform. In spite of its lower energy efficiency, it is therefore likely that the low-temperature technology will be selected in the RNG2 Pipe case, due to the importance of compactness in offshore applications.

Nevertheless, these results may be influenced by current and future regulatory constraints. As an example, the Norwegian authorities have a set of criteria for classifying chemicals used in offshore applications, according to which several amine-based solvents such as MDEA and aMDEA shall be phased out, while the low-temperature capture option does not raise issues; however, other solvent options that are likely to be less efficient may be used. This strengthens the case for low-temperature technology to be used for RNG2 Pipe cases located in waters in which amine-based solvents shall be phase out. Furthermore, if stricter regulations are also enforced for onshore applications, this might also play in favor of the low-temperature technology or other chemical solvents that are less efficient than aMDEA/MDEA.

However, it is important to note that the low-temperature processes are more recent concepts than the solvents and are therefore still significantly less optimized than the solvent concepts. The compactness and energy efficiency of the low-temperature concept are therefore likely to be improved in the future, for example, by optimizing the trade-off between the refrigeration cycle temperatures and use of additives or the gas/liquid separation in the refrigeration cycles.

The assessments presented in this paper consider only single-technology concepts. However, different technologies can be assembled into hybrid concepts in order to combine the advantages of each, such as the energy-efficient performance of the aMDEA/MDEA concept and the compactness of low-temperature concept. Therefore, future studies will investigate the potential of hybrid concepts for acid gas removal from natural gas, focusing on the RNG2 LNG case since, if hybrid concepts are to be better than single-technology concepts, this is most likely to be in cases with both high levels of CO_2 in the raw natural gas and stringent natural gas product specifications.

Finally, this paper does not look into the use of the CO_2 removed from the natural gas for CO_2 capture, transport and storage (CCS). However it is important to keep in mind that as CO_2 removal is here a necessary operation, the only additional cost associated with CCS would be CO_2 transport and storage costs. Therefore as CO_2 capture represents the main part of cost in "classic" CCS chains [19], CO_2 capture, transport and storage linked to CO_2 removal from natural gas can be expected to be a cost-efficient option to avoid CO_2 emissions to air.

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7 Appendix A: Sizing and weight estimation methodologies

This section provides an overview of the sizing and weight estimation methodologies. The processes described comprise absorbers, desorbers, flashes, distillation units, heat exchangers and rotating equipment (pumps, turbines, expanders and compressors). Various methods are used to estimate sizes and weights of these units.

7.1 Sizing methodology

Four methods, based on the process design literature [20-23], are used to estimate the internal volumes of the various types of equipment: packed columns, flash units, heat exchangers and rotating equipment.

7.1.1 Packed columns

Three types of packed columns are used in the solvents and low-temperature concepts: absorption, desorption and distillation units. The volumes of these packed columns are estimated using the internal column diameters and heights. In the case of the two solvent concepts assessed with ProTreat®, packing diameters and heights of absorption and desorption units can be obtained directly from simulations, while in the case of the low-temperature concept, the sizing of the packing volume is done using engineering common practices [24-26] and the HYSYS® simulation results. A summary of the distillation column sizing characteristics used for sizing is shown in Table 10.

For all three concepts, the inside diameter is assumed to be equal to the packing diameter while the column height is determined using a height-correction factor in order to include gas and liquid distribution beds, packing support and hold-down grids. For the design, the height of the column is assumed to be 20% higher than the packing height.

Table 10: Distillation packed columns design criteria

Parameter	Distillation column
Flooding factor [-]	0.7
Packing type	Mellapak® 250Y
Packing specific area [m^2/m^3]	250
Packing free volume [%]	95
F factor [-]	66

7.1.2 Flash units

Two parameters need to be evaluated in order to obtain a flash unit volume: its diameter and its height. Flash units sizing is done using engineering common practices [21-23] and the HYSYS® simulation results.

For vertical flash units, the diameter is based on the Souders-Brown equation [21], which gives the gas speed under conditions of flooding, and the flooding safety factor, while height can then be calculated using the diameter and the liquid residence time. Studies [22, 23] show that the ratio of the column height to the diameter of a vertical flash unit must be between three and five. If this ratio cannot be lower than 5, the flash is modelled as a horizontal flash.

Horizontal flashes are sized assuming a specific length to diameter ratio of five and a liquid residence time which leads to a gas speed that safely avoids flooding conditions (including a flooding safety factor).

A summary of design parameters of horizontal and vertical flash units is provided in Table 11.

Table 11: Vertical and horizontal flashes design criteria

Parameter	Vertical flash	Horizontal flash
Flooding factor [-]	0.7	0.7
Liquid residence time [min]	3 ≤…≤ 5	3 ≤…
Liquid level [%]	~50	~50
Height to diameter ratio [-]	3 ≤…≤ 5	5

7.1.3 Heat Exchange units

In order to obtain the volumes of heat exchange units (tube and shell heat exchangers, condensers and reboiler, as well as plate and shell condensers), their areas must first be assessed using the heat exchange relation, illustrated in equation 8, the heat transfer unit characteristics and the heat transfer design parameters. The volumes of conventional tube and shell heat exchangers are then estimated, assuming a specific area of 100 m^2/m^3, which corresponds to the most compact tube and shell heat exchangers [20]. For reboilers and condensers, specific areas of 75 and 225 m^2/m^3 are considered for tube and shell based units and plate and frame based units respectively, as additional volume is required to ensure splitting of the gas from the liquid. Sizing parameters of the different types of heat exchange units are summarized in Table 12.

$$A = \frac{q}{U \cdot LMTD} \qquad (7)$$

Table 12: Heat exchange units design criteria

Parameter	Tube & Shell heat exchanger	Kettle reboiler	Tube & Shell condenser	Plate & Frame condenser
U [$W.m^{-2}.K^{-1}$]	2000	800	1000	5000
Specific area [m^2/m^3]	100	75 [20][2]	75	225 [27][2]

7.1.4 Rotating equipment

The volumes of rotating equipment are estimated using weight estimates and assuming that half of the volume required by pumps and compressors is due to the steel volume. Therefore the overall density of a pump or a compressor is assumed to be 4,015 kg/m^3.

[2] Considering 25% lower specific area to include the additional volume required to ensure splitting of the gas from the liquid

7.2 Weight estimation methodology

Using the results of the sizing and the operating conditions obtained from simulations, dry equipment weights for the different concepts and cases can be estimated using Aspen Process Economic Analyzer® [28, 29]. The models selected in Aspen Process Economic Analyzer to represent the concept equipment are brought together in Table 13. For packed columns, the weights of the packing inside the columns are estimated using the appropriate packing volumes and the packing characteristics presented in Table 14.

Material characteristics represent an important variable for the assessment of the weights of the individual concepts. Here, by default, the equipment are assumed to be made of Stainless Steel 304 which has proven to be a good material for both ambient and low-temperature applications [8]. However, depending on the equipment conditions, different material alternatives are considered [30]. For equipment in contact with sea water, titanium is used as the base material in order to maintain equipment integrity over the time of use. For pressure vessels (packed columns and flashes) operating at pressures and temperatures above 20 bar and -35°C, 22 Chromium duplex stainless steel (SS2205) is used for the sake of its mechanical strength, which enables significant weight reductions compared to conventional stainless steel to be made.

Table 13: Models under Aspen Process Economic Analyzer®

Equipment	Modelling under Aspen Process Economic Analyzer®
Absorber	Packed tower with a single diameter
Desorber	Packed tower with a single diameter
Packed distillation column	Packed tower with a single diameter
Reboiler	Kettle reboiler with floating head
Shell & Tube condenser	TEMA shell and tube exchanger type BFU
Plate & Frame condenser	Plate and frame heat exchanger
Vertical flash drum	Vertical process vessel
Horizontal flash drum	Horizontal process vessel
Heat Exchanger	TEMA shell and tube exchanger type BFU
Compressor	Centrifugal gas compressor – horizontal
Liquid turbine	Centrifugal pump API 610
Expander	Turbo expander
Pump	Centrifugal pump API 610

Table 14: Packing characteristics [31]

Name	Density (kg/m^3)	Free volume (%)
Mellapak® 250Y	401	95
Nutter Ring 2 3/8	121	98
IMTP 50	166	98