Evaluating technology options to mitigate greenhouse gas emissions

IEAGHG Technical Report

2017-04

February 2017

CO_2 Capture in Natural Gas Production by Adsorption Processes for CO_2 Storage, EOR and EGR

IEA GREENHOUSE GAS R&D PROGRAMME

International Energy Agency

The International Energy Agency (IEA) was established in 1974 within the framework of the Organisation for Economic Co-operation and Development (OECD) to implement an international energy programme. The IEA fosters co-operation amongst its 28 member countries and the European Commission, and with the other countries, in order to increase energy security by improved efficiency of energy use, development of alternative energy sources and research, development and demonstration on matters of energy supply and use. This is achieved through a series of collaborative activities, organised under more than 40 Implementing Agreements. These agreements cover more than 200 individual items of research, development and demonstration. IEAGHG is one of these Implementing Agreements.

DISCLAIMER

This report was prepared as an account of the work sponsored by IEAGHG. The views and opinions of the authors expressed herein do not necessarily reflect those of the IEAGHG, its members, the International Energy Agency, the organisations listed below, nor any employee or persons acting on behalf of any of them. In addition, none of these make any warranty, express or implied, assumes any liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product of process disclosed or represents that its use would not infringe privately owned rights, including any parties intellectual property rights. Reference herein to any commercial product, process, service or trade name, trade mark or manufacturer does not necessarily constitute or imply any endorsement, recommendation or any favouring of such products.

COPYRIGHT

Copyright © IEA Environmental Projects Ltd. (IEAGHG) 2017.

All rights reserved.

ACKNOWLEDGEMENTS AND CITATIONS

This report describes research commissioned by IEAGHG. This report was prepared by:

SINTEF Materials and Chemistry & SINTEF Energy Research

The principal researchers were:

- Rahul Anantharaman
- Richard Blom
- Carlos Grande
- Karl Lindqvist
- Simon Roussanaly

To ensure the quality and technical integrity of the research undertaken by IEAGHG each study is managed by an appointed IEAGHG manager. The report is also reviewed by a panel of independent technical experts before its release.

The IEAGHG manager for this report were:

- Prachi Singh & Jasmin Kemper

The expert reviewers for this report were:

- Hyungwoong Ahn, University of Edinburgh
- Gelein de Koeijer, Statoil

The report should be cited in literature as follows:

'IEAGHG, "CO$_2$ capture in natural gas production by adsorption processes for CO$_2$ storage, EOR and EGR", 2017/04, February, 2017.'

Further information or copies of the report can be obtained by contacting IEAGHG at:

IEAGHG, Pure Offices, Cheltenham Office Park
Hatherley Lane, Cheltenham,
GLOS., GL51 6SH, UK

Tel: +44 (0)1242 802911 E-mail: mail@ieaghg.org Internet: www.ieaghg.org

CO_2 CAPTURE IN NATURAL GAS PRODUCTION BY ADSORPTION PROCESSES FOR CO_2 STORAGE, EOR AND EGR

Key Messages

- The aim of this study is to evaluate pressure swing adsorption (PSA) processes for removal of CO_2 from natural gas (NG). For this, the study performs a techno-economic comparison of PSA with an amine based solvent process and discusses candidate materials for the PSA process.

- CO_2 capture from NG can be done by several technologies, e.g. solvent scrubbing, membranes, adsorption or cryogenic processes. The future demand in NG might trigger development of NG fields with high CO_2 partial pressure, for which PSA processes could be more suitable. Besides, PSA processes have the potential to reduce energy consumption and costs. Hence, there is a requirement to evaluate the feasibility of PSA processes for CO_2 capture from NG at high pressures.

- An iterative pathway was applied to find a PSA cycle design with maximum CO_2 purity. The final design consists of a 12-column multi-feed cycle with around 85% CO_2 purity and is the first reported design for the separation of CO_2 and CH_4 at a pressure of 70 bar and flowrates of 500 000 Sm^3/h.

- The final PSA design has about 50% higher costs of CO_2 removal (including CO_2 conditioning, transport and storage) and NG sweetening than the reference amine process. However, the process is not yet optimised, so there is ample room for improvement.

- Data availability for suitable adsorbent materials is severely limited. This study used a carbon molecular sieve (CMS) and identified other materials worthwhile of investigation, such as certain zeolites, titanosilicates, metal organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs) and honeycomb monoliths.

- A combined approach of material and process optimisation could significantly reduce the cost of the proposed PSA design, potentially even below the cost for the reference case of amine scrubbing.

- Improving the feasibility of the PSA process for CO_2 capture from NG requires more work in several areas. This includes optimisation of the PSA cycle to minimise NG losses, investigation of novel cycle concepts (e.g. hybrid of single and dual PSA), evaluation of advanced adsorption materials and data for suitable adsorbents at high pressure. This is basic research and modelling work that should be mainly undertaken by related research groups from academia and industry.

Background to the Study

Natural gas (NG) is the fossil fuel with lower emissions of CO_2 per kilowatt of energy produced. Furthermore, the discovery of new gas reserves and utilisation of unconventional sources could expand the NG market up to 60% in 2035.
While NG demand is expected to expand in every region between 2010-2035, growth is nearly three times faster in non-OECD countries (2.3% per year) than in the OECD (0.8%) based on IEA's World Energy Outlook 2012.

NG, when extracted from the wellbores, is composed of several hydrocarbons, which give its calorific value and its recognition as a high-energy fuel. There are several components that are associated with the extraction of NG that have to be removed in order to transport the gas from the production site to the end-users. The most important components to be removed are acid gases (especially SO_2, H_2S and CO_2) and water. Sulphur compounds have to be removed to the ppm level due to their toxicity and corrosive nature in presence of water. In case of transporting NG through pipelines, the CO_2 specifications depend on each country but are usually around 2-4%. If NG contains more than this percentage, CO_2 removal is necessary. This removal will also enhance the energy content (calorific value) of NG with a consequent decrease of the volume of NG to be transported. Thus, removal of CO_2 has both direct and indirect contributions to the control of CO_2 emissions from NG production.
CO_2 capture in NG production has been successfully demonstrated in several projects like Sleipner, Snøhvit and In Salah, for CO_2 storage and enhanced oil recovery (EOR). The NG extracted in those locations contains variable amounts of CO_2 ranging from 8% to 14%. It has been reported that some NG fields in Southeast Asia (Indonesia, Vietnam, Thailand & Brunei) contain high CO_2 concentrations up to 80%. Future demand in NG will initiate development of these fields in South-East Asia. Therefore, it is necessary to evaluate different CO_2 capture technologies to reduce CO_2 emissions in NG production.

CO_2 capture from NG can be performed by several techniques like solvent scrubbing, membranes or cryogenic distillation. CO_2 capture by adsorption process has a potential in reducing energy requirement and operational costs due to smaller energy consumption and low maintenance requirements. Physical adsorbents and pressure swing adsorption (PSA) process are considered to be suitable for CO_2 capture at higher CO_2 partial pressure. At lower CO_2 partial pressure, adsorbents with strong basic functionalities and temperature swing adsorption (TSA) are favourable. Currently, a wide variety of solid sorbents are being developed to separate CO_2 from flue gas, like zeolites, activated carbons, calcium oxides, hydrotalcites, supported amines and metal-organic frameworks (MOFs). The PSA technology for NG upgrading is not commercial and is only in R&D stage. The high pressure and high flows used in this application are not similar to other PSA applications.

IEAGHG commissioned the analysis of this technology to SINTEF Chemistry & Materials and SINTEF Energy Research.

Scope of Work

The aim of this study is to evaluate the utilisation of a PSA process for CO_2 removal from NG production. The unit design will not include final and detailed process optimisation. The PSA unit performance of NG upgrading with simultaneous CO_2 recovery for CO_2 storage, EOR or enhanced gas recovery (EGR) will be evaluated in terms of costs, performance, energy consumption and size.

Innovation of this work:

According to the knowledge of the authors, this is the first publicly available study that will analyse a PSA process for upgrading NG at 70 bars with the aim of producing high purity of both product streams, i.e. CH_4 and CO_2. The study used novel data on a commercial carbon molecular sieve (CMS) for the analysis.

Findings of the Study

Summary of existing technologies for CO_2 capture from NG

The following technologies are currently used for CO_2 separation from NG:

- Membranes: Several technologies are available in the market. The two major configurations are hollow fibre modules and flat sheet spiral modules, with the latter being more resistant to fouling. The main advantage of membrane technologies is the modular design, enabling straightforward scale-up, expansion and start-up. However, for NG processing this can be a disadvantage, due to the lack of large-scale efficiency. Energy demand and footprint can be small, making the process favourable for subsea applications. In addition, 1-stage membranes do not need mobile parts or additional chemicals. One disadvantage is the requirement of potentially expensive pre-treatment for particulates and liquids.
- Cryogenic distillation: This is a well-known process. Challenges are to avoid freezing of CO_2 at temperatures below the triple point, the azeotrope formation of CO_2 and C_2H_6, and the energy consumption and pinch point of CO_2 and H_2S separation. Further disadvantages are the cost of separation and volume of equipment. However, when applied to liquefied natural gas (LNG) processes, the cost penalties due to energy requirement for cryogenics might be less pronounced. Advantages include delivery of NG at pipeline or LNG specification, flexibility in configuration and suitability for C_{4+}-rich NG.
- Solvent scrubbing: This process will be the reference case for this study. In short, advantages are that the process is well known among the NG industry, proven for a wide range of conditions and is able to remove CO_2 and H_2S to ppm levels. Disadvantages include mainly the high energy requirement for regeneration of the solvent and the need for reclaiming due to the build-up of heat stable salts.
- Adsorption: The most common processes are TSA and PSA. The focus in this study is on PSA, which currently is not a commercially established process but rather is in R&D stage. Thus, the amount of available data is very limited. The only industrial applications are: (1) fast-cycling, offshore PSA unit for NG upgrading by XEBEC, operating at 16 bar and small flowrate, and (2) PSA unit for NG upgrading by Linde, without openly available information.

More information on each technology is available in the related sections of the report.

Conditions used in this study

The NG composition, see Table 1, is similar to the composition used in a previous large research project sponsored by the Research Council of Norway (coordinated by SINTEF and involving NTNU, Statoil, Gassco, Petrobras and initially Total). For the design of a PSA unit, some initial simplifications are required due to lack of data available for C_{2+}. When using kinetic adsorbents, nitrogen will not be adsorbed and heavier hydrocarbons will probably condense in the macropores of the adsorbent; however, specific data is not available.

Table 1 NG composition and feed conditions

Property	**Value**	**Value [PSA]**
Temperature [K]	313	313
Pressure [bar]	70	70
Flowrate [Sm^3/h]	500000	500000
y_{CH4}	0.8300	0.8300
y_{C2H6}	0.0460	0.0700
y_{C3+}	0.0240	
y_{CO2}	0.1000	0.1000

The study will consider all costs and performance of the PSA unit and compression train to produce pipeline-quality NG with less than 2.5% CO_2, as well as production and compression of the CO_2-rich stream.

All costs in this report are in euros for a reference year of 2014 with a plant location in The Netherlands. An exchange rate of 1.33 $/€ is considered to convert cost data available in US dollars.

The calculation of the total cost requirement (TCR) is estimated based on a bottom up approach (BUA) including:

- Total equipment cost (TEC) – using cost estimation software, quotations from equipment suppliers, power law method, and other available data.
- Total direct cost (TDC) –sum of TEC and installation costs, including piping/valves, civil works, instrumentations, electrical installations, insulations, paintings, steel structures, erections and OSBL (outside battery limits).
- Total plant cost (TPC) – sum of TDC and indirect costs, including yard improvement, service facilities, engineering/consultancy cost, building and contingency. The project contingency is added to the capital cost to give a 50% probability of a cost over-run or under-run.
- Total cost requirement (TCR) – sum of TPC, interest during construction, owner's costs, spare parts, working capital and start-up costs.

Additional costs normally associated with 1^{st}-of-a-kind commercial plants are excluded. The estimate accuracy is +35/-15% (AACE Class 4). In the first year, the gas processing facility will operate at 65%, while it will operate at 85% during subsequent years.

The fixed operating costs include (see also Table 2):

- Insurance and local property taxes – total of 1% of TPC.
- Maintenance cost – 2.2% of TPC for both solvent and sorbent based processes and a complete replacement of the PSA sorbent over 10 years.
- Labour costs – 5-shift working pattern, 'fully burdened' cost of labour at 60k€. Administrative and support labour is 30% of the operating and maintenance labour cost while maintenance labour is 40% of the overall maintenance cost.

Table 2 Utilities and material costs

Utilities, units	Cost
Electricity cost [€/MWh]	80
Natural gas price [€/GJ]	6
Carbon molecular sieve [€/t]	6,500
MDEA [€/kg]	43
Piperazine [€/kg]	58
Process water [€/m^3]	0.20
Sea water cooling [€/m^3]	0.03
CO_2 transport and storage [€/t]	10

The study uses the following three key performance indicators to evaluate and compare the reference solvent and PSA concepts for gas sweetening:

1. Sweetening cost to meet the pipeline transport requirement.
2. CO_2 removal cost with or without CO_2 conditioning, transport and storage.
3. CO_2 avoidance cost.

As in other IEAGHG studies, the default CO_2 transport and storage cost is 10 €/tCO_2. However, to represent the additional cost which could be associated with the small quantities considered here, sensitivity analyses on the transport and storage cost will be included. To reflect the impact of uncertainties in data and site specific characteristics, sensitivity analyses on the following parameters will be considered and with the variation presented in Table 3.

Table 3 Parameters and variation for sensitivity analysis

Criteria	Base case	Sensitivities	
Investment cost [%]	-	-35	+35
Fixed operating cost [%]	-	-35	+35
Variable operating cost [%]	-	-35	+35
Adsorbent cost [%]	-	-35	+35
Discount rate [%]	8	5	10
Utilization rate [%]	85	70	90
Plant life [years]	25	10	40
Electricity cost [€/MWh]	80	60	100
Natural gas price [€/GJ]	6	3	9
Steam availability [%]	0	-	100
Accounting of the lost gas sale [%]	100	0	-
Adsorbent replacement rate [%]	10	5	20
CO_2 transport and storage cost [€/t$_{CO2,stored}$]	10	0	20

Reference case: amine scrubbing

A chemical solvent based gas sweetening unit using an aqueous solution of N-methyldiethanolamine (MDEA) at 45 wt% to remove CO_2 from the NG stream 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. To ensure adequate reactivity, the solvent is activated by addition of 5 wt% of piperazine (PZ).

The process layout, see Figure 1, 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. Due to the high absorber pressure and large solvent circulation rate, a liquid turbine recovers power from the rich solvent stream after leaving the absorber.

The solvent concept considered here is evaluated for a raw natural gas of 500 000 Sm^3/h with 10 vol% of CO_2 and no significant heavy hydrocarbons. To avoid excessive co-absorption of potential 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. Table 4 contains further data on temperatures, pressures, solvent characteristics and main unit sizes.

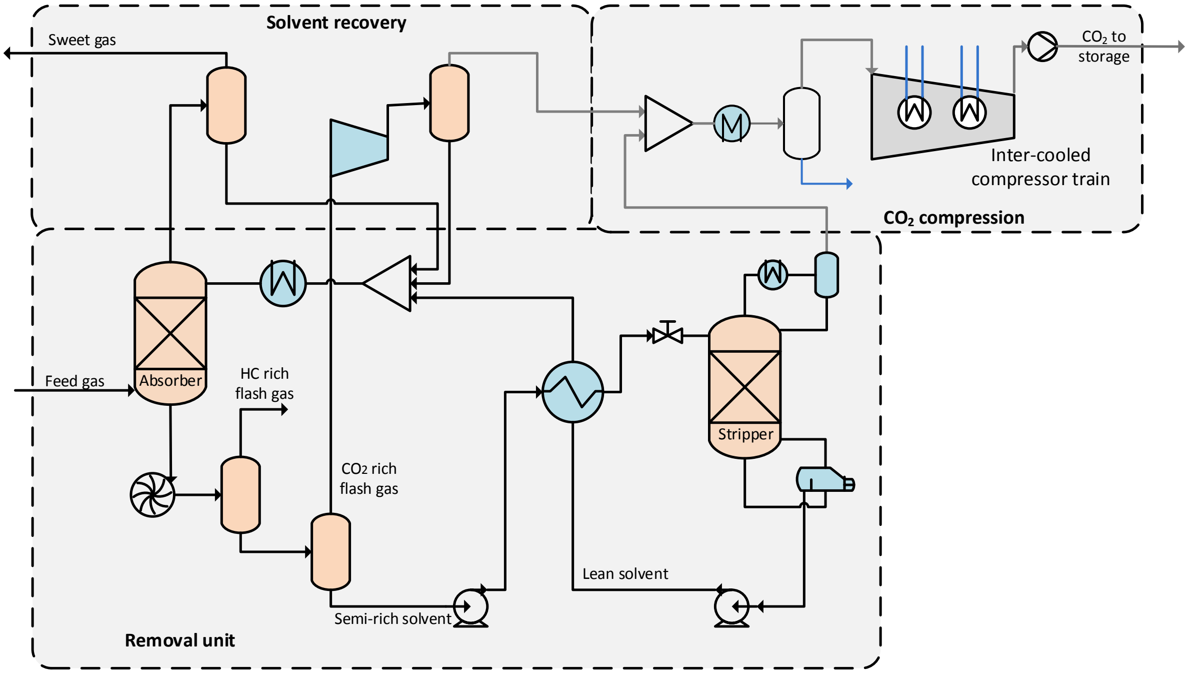


Figure 1 Process flow diagram of the aMDEA process

Table 4 Process parameters for aMDEA reference process

Parameter	**Value**
Raw NG conditions and composition	
Temperature [°C]	40
Pressure [bar]	70
C_1 [vol%]	88
C_2 [vol%]	2
CO_2 [vol%]	10
Sweet NG specifications	
Temperature [°C]	40
Pressure [bar]	70
Lower heating value (LHV) [MJ/kg]	39
CO_2 content [mol%]	≤ 2.5

CO_2 stream specifications	
Temperature [°C]	40
Pressure [bar]	110
CO_2 purity [%]	≥ 95
Solvent	
Lean solvent flow [kg/h]	987 000
Solvent make-up [kg/h]	1 810
Lean loading	0.06-0.07
Absorber	
Pressure [bar]	70
Lean solvent temperature [°C]	50
Column diameter [m]	4.2
Column height [m]	16.8
Stripper	
Pressure [bar]	1.8
Reboiler temperature [°C]	97-120
Column diameter [m]	3.1
Column height [m]	7.2
HC flash	
Pressure [bar]	5.0
CO_2 flash	
Pressure [bar]	1.1

Based on the input parameters presented in this section, Table 5 contains a summary of the resulting cost estimation for the aMDEA process. A detailed breakdown into units is available in the report.

Table 5 Cost estimation of aMDEA reference process

Parameter	**Value**
Total equipment cost [k€]	13 523
Total direct cost [k€]	21 857
Total variable operating cost [k€/yr]	19 090
Sweetening cost [€/kSm$^3_{raw}$]	6.91
Sweetening cost [€/kSm$^3_{sweet}$]	7.47
CO_2 removal cost with T&S [€/t$_{CO2,captured}$]	50
CO_2 removal cost without T&S [€/t$_{CO2,captured}$]	30
CO_2 avoidance cost [€/t$_{CO2,avoided}$]	21

PSA process for CO_2 capture

Basic operation principles

PSA technology has been in the market of separation technologies for the last 50 years and can be used in a large variety of applications, with hydrogen purification and air separation being the most important ones. The main advantage of PSA technology is the low energy consumption when compared to other technologies.

A good PSA process results from the interaction between material science and engineering. This implies that general advances in PSA units can be divided in two main domains: (1) the utilization of new adsorbents or traditional adsorbents in non-classical shapes (material science) and (2) new and more efficient ways to use and regenerate the adsorbent (process engineering). Most of the applications of PSA technology focus on the purification of the less adsorbed gas. The utilisation of PSA for purification of the most adsorbed gas is still under development for many applications that include CO_2 capture from flue gases, olefin-paraffin separation, etc.

In addition, a PSA for NG upgrading cannot be a discontinuous or semi continuous process due to the large volumes involved, so the PSA will involve a series of columns running in parallel cycles of adsorption and desorption. A “cycle” is the sum of all the events, or “steps”, that will happen in a column. "Feed" is the step where CO_2 is adsorbed and sweetened NG is produced. This step is followed by changing the column pressure in the "depressurisation" or "pressure equalisation" steps. A recycle of the most adsorbed component can take place and this step is normally termed as "rinse". When the pressure is reduced and CO_2 is extracted from the column, the step is termed "blowdown" and when part of the produced NG is used for displacing CO_2 from the voids of the column, the column undergoes the "purge" step. Finally, the pressure in the column is restored in a step termed as "pressurisation". After some cycles, the PSA unit will reach cyclic steady state (CSS), i.e. its performance will be constant over time.

A basic cycle is the 2-column Skarstrom cycle. However, this cycle is semi continuous and thus not applicable to NG upgrading. In order to remove acid gases from NG continuously, a system with more than two columns is required to ensure that at least one column is receiving feed while the others are under regeneration. The section “*PSA cycle design*” will lay out the iterative pathway the contractors took when developing the final 12-column PSA design from a 4-column starting point.

Adsorbent selection

The adsorbent selection is the main and initial task in the specification of a PSA unit. In the last years, a lot of simplified equations or criteria for adsorbent selection have been published. Most of these simplified methodologies tend to provide imprecise results, as they fail in taking into account temperature fluctuations and tackling diffusion issues. Thus, a direct method of selecting an adsorbent is not available and is mostly based on experience.

Two important issues influence the selection criteria for acid removal from NG:

1. Low non-linear isotherms for CO_2. When the isotherm becomes more non-linear, regeneration has to be done at lower pressures (most times under vacuum) thus spending more energy to recover the CO_2.

2. Little or no adsorption of CH_4. The high partial pressure of CH_4 limits the choices of the adsorbents. Even if the adsorbent is more selective to CO_2, adsorption of large amounts of CH_4 will result in undesired thermal oscillations, reducing the cyclic loading of CO_2 in the column. If adsorption of CH_4 takes place, desorption time needs consideration, delaying the cycle time and thus making the columns larger.

The only possibility of severely limiting the amount of CH_4 adsorbed at high partial pressures is by preventing its entrance to the micropores of the adsorbent. Materials imposing size restrictions to targeted molecules are known as "kinetic adsorbents". E.g., Zeolite 4A is one standard zeolite material suitable for this application. However, based on existing data, the limitation of CH_4 diffusion through the pores is not satisfactory and thus large thermal variations may occur.

The following two commercial materials are more promising:

1. A titanosilicate material termed ETS-4, which is a molecular gate. In principle, the pores of the material can be tuned by heating at different temperatures until CH_4 cannot penetrate into the pores. The material is commercially available from BASF but it is not yet possible to get a sample of the material for detailed evaluation. For this reason, it was not considered in this report.
2. A carbon molecular sieve (CMS) is a readily available material, which is already used in several biogas upgrading plants (i.e. separation of CH_4-CO_2 at lower pressures and flow rates). Commercial materials are available from CarboTech and EnviroChemicals. The results provided in this report are based on the utilization of this material.

PSA modelling

Several commercially available software are available for simulation of PSA units, incl. Matlab, COMSOL Multiphysics, ProSim, Aspen Adsorption, gPROMS, Fluent and Inprocess. In all these programmes, it is possible to simulate the PSA performance by solving a model for one column. There are several approaches to simulate the performance of an entire PSA by solving only one column. The simplest alternative is to use average (fixed) gas compositions for all steps involving internal recycling. The second alternative is to create a virtual stream (buffer) storing part of the exiting gas of the feed step that will then be used for the purge. Another possible strategy for PSA simulation is to simulate the entire unit including the valves, dead volumes of the system and column headers (dead volume at the extremities of the columns). This is a more detailed way of describing the entire process with the penalty of having an increased computational effort but it has the benefit of knowing the entire dynamics of the system.

In this study, models for multiple-column PSA units were developed in gPROMS software (PSE Enterprise, UK). For a 12-column PSA unit, a minimum of 144 valves is necessary, including three storage tanks for light and heavy products and for rinse gas. All valves have only two stem positions: open and closed, with no intermediate opening allowed.

Due to the large amount of devices modelled, a simulation of a PSA unit takes around 20 hours until reaching CSS, solving around 50-70 cycles. Providing the right conditions for convergence is critical to the stability of the system, not only due to its complexity, but also because of the strong variation of conditions (pressure, temperature and flows) within the different steps. Despite the good numerical stability of the solvers embedded in the software, obtaining numerical stability of these systems is not straightforward.

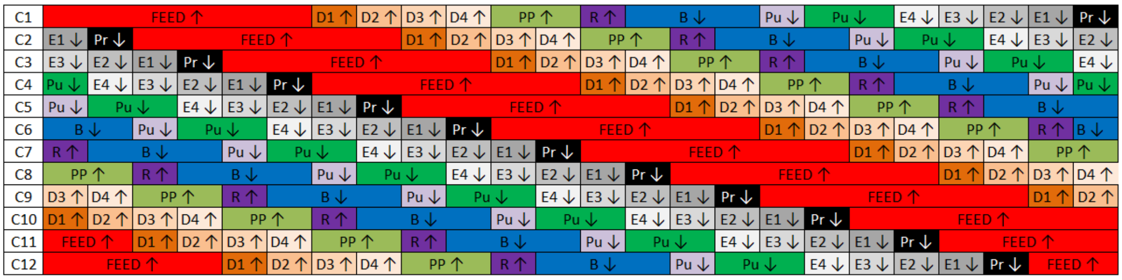
PSA cycle design

Since there is no detailed information about a commercial process to serve as reference, the final cycle configuration was iteratively achieved. To the knowledge of the authors, the final cycle has not been previously reported in the literature. This section will provide a short summary of the pathway to the final PSA cycle design. However, the final unit is not yet optimised, since this process will take more detailed engineering work than would be inside the scope of this study.

Pathway to final PSA cycle design:

1. Start with modelling a continuous feed 4-column cycle with adsorption at 70 bar and desorption at 1 bar, including two pressure equalisation steps. Simplified assumption that the binary system (90% CH_4 – 10% CO_2) is isothermal. Maximum purity of CO_2 is 60%.
2. 6-column cycle with three pressure equalisation steps. Maximum purity is 40% CO_2, thus requiring a second PSA unit (i.e. dual PSA consisting of rectifying and stripping PSA), which could bring the purity up to 90%. However, the requirement of two compressors for internal recycles involving large amounts of gas leads to a substantial energy demand rendering the design unviable for NG upgrading.
3. 7-column cycle with three pressure equalisation steps to improve the CO_2 purity in the rectifying PSA, leading to a slight increase in overall CO_2 purity. However, this design requires large column diameters, as long desorption times lead to a short “time on stream”.
4. 12-column cycle with three pressure equalisation steps and multiple feed concept (which is already common practice in H_2 purification but without the rinse step used here). Advantages of this design are: (1) 30-40% smaller column diameter compared to 6- or 7-column cycle, (2) lower adsorbent demand, (3) higher “time on stream” leading to a smaller PSA unit, (4) less flowrate variations due to two columns performing blowdown at the same time, and (5) system flexibility in terms of purge and rinse schedule. The proposed design needs at least 120 valves and reaches CSS after 20-25 cycles. For a stream of 88% CH_4 – 10% CO_2 – 2% C_2H_6, the PSA can achieve 69% CO_2 purity. This cycle has many variables that could be optimised in further work.
5. 12-column cycle with four pressure equalisation steps and multiple feed concept. Figure 2 and Figure 3 show the final cycle design. The cycle keeps the advantages of the previous design but adds another pressure equalisation and shortens the time for purging and rinsing. The pressure at the beginning of the provide purge step is ~14 bar, which has a great impact on the purity of the CO_2-rich stream, increasing its value to around 73%. However, adding extra pressure equalization steps will not solve the problem in a consistent way, since the pressure equalisations will be less and less effective. The main solution to reduce the content of CH_4 (and C_2H_6) in the CO_2-rich product is to remove an exit stream between the feed step and the blowdown step. Adding this extra recycle of light gas will increase the purity of CO_2 to almost 85%. As with the previous cycle, the final PSA cycle is not yet optimised. The evolution of the cycle development showed that the main challenge for achieving a high CO_2 purity is the large amount of paraffins in the gas phase of the column before the blowdown step.

Consequently, a significant portion of the cycle time is devoted to reduce the paraffin content by successive pressure equalisations.



C1	FEED ↑						D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓
C2	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓
C3	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓
C4	Pu ↓	E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓
C5	Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓		
C6	B ↓		Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓
C7	R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑	
C8	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	D4 ↑
C9	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑
C10	D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑					
C11	FEED ↑		D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑			
C12	FEED ↑				D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓		E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑	

Figure 2 Final 12-column multi-feed PSA design

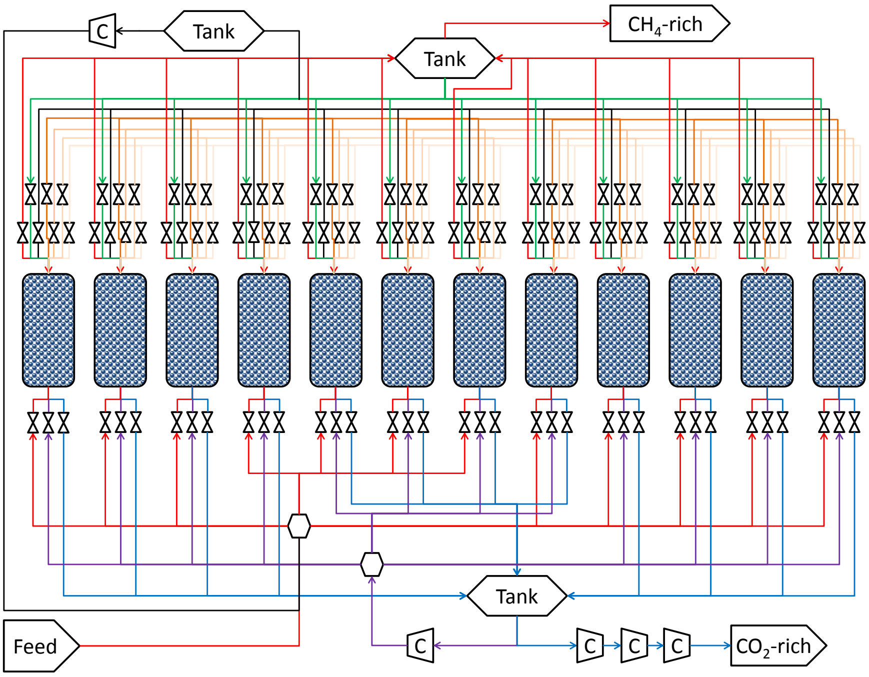


Figure 3 Process flow diagram of final PSA design including internal recycles and tanks

Cost estimation

A cost estimation similar to that for the reference amine process was carried out. Table 6 presents the results of this task.

Table 6 Cost estimation PSA process

Parameter	**Value**
Total equipment cost [k€]	32 633
Total direct cost [k€]	46 992
Total variable operating cost [k€/yr]	30 133
Sweetening cost [€/kSm$^3_{raw}$]	10.67
Sweetening cost [€/kSm$^3_{sweet}$]	11.78
CO$_2$ removal cost with T&S [€/t$_{CO2,captured}$]	72.5
CO$_2$ removal cost without T&S [€/t$_{CO2,captured}$]	45.1

CO_2 avoidance cost [€/$t_{CO2,avoided}$]	28.8

Compared to the solvent based case, the CO_2 stream in the adsorption case contains around 15.5% of CH_4 and C_2H_6 which are not produced and therefore lead to a 1.6% decrease of the amount of sellable NG. The estimation shows that the loss of revenues accounts for more than 55% of the total variable operating cost, or 42% of the total discounted cost (including CO_2 conditioning, transport and storage). The importance of the loss in NG revenue points out the potential of improving the process design and/or the sorbent selected in order to decrease the amount of NG present in the CO_2 stream, which could therefore significantly decrease the NG sweetening cost. The impact of this potential improvement on the process cost will be addressed through sensitivity analyses (see next section). Comparison of both processes shows, see Figure 4, that the adsorption based process leads to sweetening costs around 55% higher than the solvent based process for the reasons presented previously. CO_2 removal cost including transport and storage, CO_2 removal cost and CO_2 avoidance cost are respectively 45, 50 and 40% higher for the adsorption process.

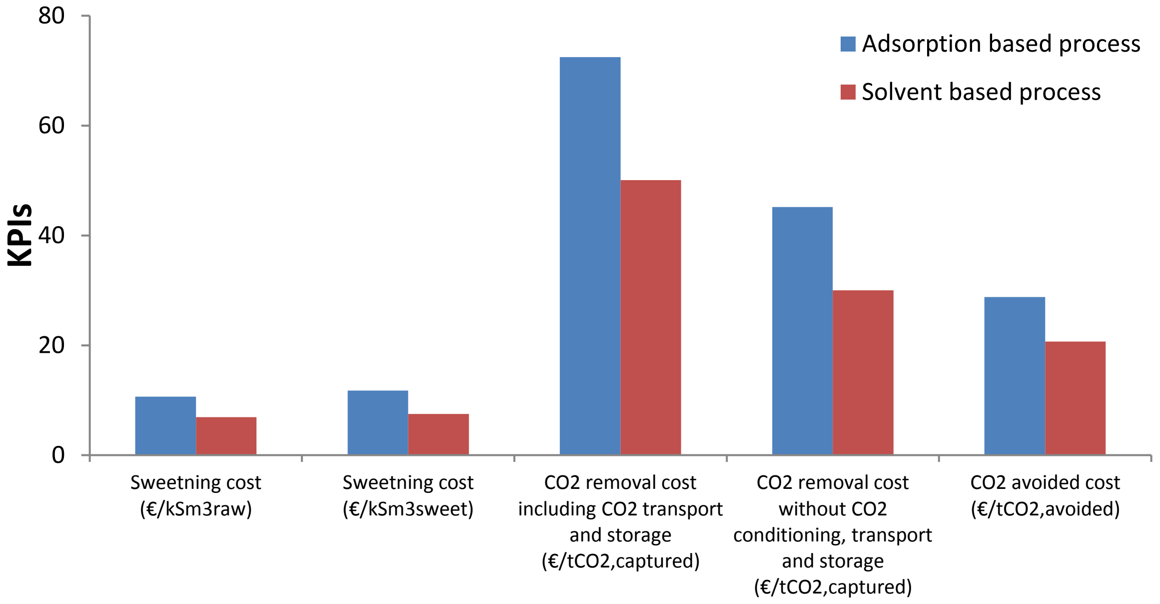


Figure 4 Cost comparison of solvent and adsorption based processes

Sensitivity analysis

First, a sensitivity analysis was undertaken on the CO_2 removal cost including CO_2 conditioning, transport and storage. The assessment shows that the cost uncertainties which influence both technologies the most are gas price (due to the steam consumption in the solvent based process and the losses in the CO_2 stream in the adsorbent based process), variable OPEX and transport and storage cost. On-site steam availability is also an important factor for the cost of the solvent based process. More importantly, the sensitivity analyses shows that the reduction of the amount of NG lost in the CO_2 stream represents a major opportunity to reduce the CO_2 removal cost of the adsorbent based process. This reduction could be achieved for example by process or material improvement or by adding purification of the CO_2 stream after the considered adsorption process.

Second, the influence of cost uncertainties on CO_2 avoidance cost was analysed. Uncertainties that have the most influence are CO_2 transport and storage cost, electricity cost and variable OPEX.

In addition, the sensitivity analyses show that CO_2 avoidance cost associated with the adsorption based process will remain higher than with the solvent based process, even when considering the cost uncertainties. This is mainly due to higher electricity consumption in the CO_2 stream conditioning of the adsorption based process, as the CO_2 stream after removal is delivered at 1 bar instead of 1.9 bar in the solvent process and the CO_2 stream mass flow is higher due to the presence of 15% CH_4 and C_2H_4.

Candidate materials for kinetic adsorbents

Some candidate materials that are not commercial but might show kinetic limitation to CH_4 adsorption include the following:

- Zeolites, e.g. 4A modified to $[Na_{12-x}K_x]$-LTA, DD3R, chabazites, Si-CHA, rho and natural zeolites. However, all of these materials would require vacuum regeneration. Further increasing the Si:Al ratio can help overcome this issue.
- Titanosilicates, e.g. ETS-4 and UPRM-5. However, equilibrium data is only available for up to 7 bar.
- MOFs, e.g. $Cu(hfipbb)(H_2hfipbb)_{0.5}$[$H_2$hfipbb = 4,4'-(hexafluoro-isopropylidene) bis(benzoic acid)] and MOF-508b. However, the first material has a low adsorption capacity and kinetic selectivity, and the second a relatively low density.
- Zeolitic imidazolate frameworks (ZIFs), e.g. ZIF-9. However, data for most of these materials is not yet available for CH_4-CO_2.

Expert Review Comments

IEAGHG invited expert reviewers to provide comments on the draft report. The authors have addressed several of those comments in the final version of the report. One reviewer asked to consider sulphur species. This was not taken into account due to a lack of adsorption equilibrium data and non-ideality of these mixtures, the assessment of which is far outside the scope of this study. Likewise, cases where the stream exiting the PSA column during the rinse step is recycled to the feed were not considered, as it would add significant additional costs to the system. Using the stream for light reflux, as in this study, is already done in some existing large-scale H_2 PSA units. However, it is currently not possible to find published citable material on this topic. Another reviewer asked to evaluate the role of drying and its economic implications in more detail. Because this problem will be present in all NG streams, a short discussion was added, mainly to the future recommendations section. Besides, the authors added a paragraph regarding CO_2 capture pilots dealing with adsorption processes. Finally, some comments regarding the cost analysis were taken into account. For example, the authors have increased the cost factor to include higher process and project contingencies (in line with NETL guidelines) for the adsorption section and updated the methodology to reflect these changes.

Conclusions

This study is the first report that designs a PSA process for the separation of CH_4 and CO_2 using a feed pressure of 70 bar and with high flowrates as in the NG industry. This report provides a short summary of the available technologies to perform this separation and uses amine scrubbing as a reference case of a mature technology to benchmark a PSA unit that was specifically designed for this report. In addition, it provides a small list of possible candidate materials that can be used for this application and result in improved unit performance.

The PSA unit was designed to upgrade NG with a composition of 83% CH_4, 10% CO_2 and 7% C_2H_6 available at a temperature of 313 K and an inlet flowrate of 500,000 Sm^3/h. Due to the lack of existing data at the pressure levels, unpublished adsorption equilibrium and kinetic data of CMS available in SINTEF was used for designing the PSA unit. A PSA unit with 12 columns using a multi-feed principle (3 columns processing the feed gas at the same time) with 15 steps including a rinse of CO_2 was necessary to produce pipeline-quality NG and CO_2 with a purity of 84.5%. In order to minimize gas losses with the CO_2 stream, the number of pressure equalisations has to be significantly increased (a maximum of 4 was used in this study). A cost comparison between the existing amine scrubbing process and the designed PSA unit indicates that the cost of CO_2 removal (including transport and storage) is 72.5 €/$t_{CO2,captured}$ compared with 50.1 €/$t_{CO2,captured}$ obtained in the amine scrubbing process. The main contributor for the higher cost of the PSA unit is the amount of NG losses with the CO_2 stream. In the case that a PSA unit can significantly reduce the NG losses, costs can be reduced to around 40 €/$t_{CO2,captured}$.

Recommendations

Recommendations for future work include the following:

- As the data availability for suitable adsorbent materials at 70 bar is limited, it will be highly desirable to extend the databases and explore new materials to have a selection of possible materials.
- The most important factor for the cost of gas clean-up were the gas losses along with the CO_2. Thus, further optimisation of the proposed PSA cycle will be worthwhile.
- A hybrid between a single PSA and dual PSA could be a very good alternative for mixtures with higher CO_2 concentration and could be an interesting topic for further investigation.
- Honeycomb monolith adsorbents might be able to significantly reduce both cycle time and column size, so should be a focal point of future research.

CO_2 Capture in Natural Gas Production by Adsorption Processes for CO_2 Storage, EOR and EGR

FINAL Report

Coordinating person:
Carlos A. Grande

Main authors of this report:
Carlos A. Grande and Richard Blom. SINTEF Materials and Chemistry, Forskningsveien 1, Oslo, Norway;
Simon Roussanaly, Rahul Anantharaman and Karl Lindqvist. SINTEF Energy Research AS, Sem Sælands vei 11, Trondheim, Norway.

Project managers at IEAGHG:
Prachi Singh and Jasmin Kemper

Executive summary

Adsorption-based processes are used in industry for gas separation and purification for over 50 years. Main applications are air separation (production of oxygen and / or nitrogen) and hydrogen purification from hydrocarbon reforming. Most common adsorption processes are Temperature Swing Adsorption (TSA) and Pressure Swing Adsorption (PSA). TSA is mostly used for purification when the contaminant to be removed is less than few percent of the stream while PSA process are more suitable for bulk separations.

In this study, we have evaluated the feasibility of using a PSA process for the removal of carbon dioxide from natural gas. This process is not commercially available yet and thus faces several challenges regarding the utilization of proper materials and efficient regeneration schemes. The main challenges in process design are the high flow rates involved and the high pressure of the feed stream.

The study considered the utilization of kinetic based adsorbents to reduce the amount of methane adsorbed at high pressures. To present a design of a process that can operate at similar conditions as other standard technology, this study used data from a commercial carbon molecular sieve sample, already existing in the market. We also present a status on potential next-generation adsorbents.

The study covers the possibility of using different process designs and the impact of design in the PSA performance shows that a significant work of engineering is required to improve the process.

The effect of different PSA process operation modes has been evaluated to remove 10% of CO_2. A new 12-column PSA cycle using multi-feed principle has been used for obtaining pipeline-grade methane (amount of CO_2 < 2.5%) and CO_2 purity ~ 84.5%. The remaining 15% of the CO_2-rich stream is 8% CH_4 and 7.5% C_2H_6. The cost of CO_2 removal including transport and storage is 77 €/ton$_{CO2,captured}$, compared with 50 €/ton$_{CO2,captured}$ obtained from a benchmark case using amine absorption. A major contributor to the cost is the loss of revenue from gas sales, a cost that has the potential of being significantly reduced with a more efficient PSA cycle. Honeycomb materials also may play a significant role in improving the PSA performance and size. Moreover, PSA technology may present better performance for more concentrated streams since the losses in the CO_2-rich stream should be minimized.

Contents

1: Introduction 4
2: Summary of existing technologies for CO_2 capture from NG 5
  2.1 Membranes 5
  2.2 Cryogenic distillation 7
  2.3 Solvent scrubbing 8
  2.4 Adsorption processes 10
3: Conditions used in this study 15
  3.1 Natural gas composition 15
  3.2 Conditions and boundaries used in this study 15
  3.3 Economic framework 16
  3.3.1 Economic boundary conditions 16
  3.3.2 Capital investment 17
  3.3.3 Main operational parameters 18
  3.3.3.1 Maintenance, Insurance and labour costs 18
  3.3.3.2 Chemicals, consumables and CO_2 transport and storage cost 18
  3.3.4 Main economic Key Performance Indicators (KPI) 19
4: Reference case: amine scrubbing 20
  4.1 Introduction 20
  4.2 Process and technical modelling 20
  4.3 Cost estimation 22
5: Pressure Swing Adsorption process for CO_2 capture 24
  5.1 Basic PSA operation principles 24
  5.2 Adsorbent selection 27
  5.3 Mathematical modelling 28
  5.4 Implementation of model equations 33
  5.5 PSA cycle design 34
  5.6 Cost estimation 46
  5.7 Sensitivity analysis 48
  5.8 Process benchmarking 50
6: Available kinetic adsorbents: data inventory 52
7: Final remarks 54
  7.1 Conclusions 54
  7.2 Future recommendations 54
8: References 56
Appendix A. Summary of economic parameters 63
References: 64
Appendix B. Boundary condition equations for PSA model 65
Appendix C. Equations of ancillary components of the PSA 69

1: Introduction

Natural gas (NG) is the fossil fuel with lower emissions of CO_2 per kilowatt of energy produced. Furthermore, the discovery of new gas reserves and utilization of unconventional sources will make possible to expand the NG market up to 60% in 2035.

While the natural gas demand is expected to expand in every region between 2010-2035, growth is nearly three times faster in non-OECD countries (2.3% per year) than in the OECD (0.8%) based on IEA World Energy Outlook 2012 [1].

Natural gas when extracted from the wellbores is composed by several hydrocarbons which give its calorific power and is the main reason of being a high-energy fuel. Unfortunately, there are several components that are associated to the extraction of natural gas that have to be removed in order to transport the gas from the production site to the end-users. The most important components to be removed are acid gases (especially SO_2, H_2S and CO_2) and water. Sulphur compounds have to be removed to the ppm level due to its toxicity and to their corrosive nature in presence of water. In the case of transporting the natural gas through pipelines, the CO_2 specifications depend on each country but are around 2-4%, so in case that the natural gas contains more than this percentage, CO_2 has to be removed to meet specifications. Removal of CO_2 will also enhance the energy content (calorific value) of NG with a consequent decrease of the volume of NG to be transported through pipeline and cylinders. Thus removal of CO_2, which is the most prominent greenhouse gas on earth, has both direct and indirect contribution to the control of CO_2 emission from NG production.

CO_2 capture in NG production has been successfully demonstrated in several projects like Sleipner [2], Snøhvit [3] and In Salah [4], for CO_2 storage and EOR purpose. The NG extracted in those locations contains variable amounts of CO_2 ranging from 8% to 14%. It has been reported that some NG fields in Southeast Asia (Indonesia, Vietnam, Thailand & Brunei) contain high CO_2 concentrations up to 80%. Future demand in NG will initiate development of these natural gas fields in South-East Asia. Therefore, there is a requirement to evaluate different CO_2 capture technologies to reduce CO_2 emission in NG production.

CO_2 capture from NG can be performed by several techniques like solvent scrubbing, membranes or cryogenic distillation. CO_2 capture by adsorption process has a potential in reducing energy requirement and operational costs due to smaller energy consumption and low maintenance requirements. Physical adsorbents and Pressure Swing Adsorption (PSA) process are considered to be suitable for CO_2 capture at higher CO_2 partial pressure. Whereas at low CO_2 partial pressure, adsorbents with strong basic functionalities and temperature swing adsorption (TSA) are favourable.

Currently, a wide variety of solid sorbents are being developed to separate CO_2 from flue gas like zeolites, activated carbons, calcium oxides, hydrotalcites, supported amines, metal-organic framework (MOF) materials.

The PSA technology for this application is not commercial and is only in R&D stage. The high pressure and high flows used in this application are not similar to other applications where PSA is widely used. The aim of this study is to evaluate the utilization of a PSA process for CO_2 removal from natural gas production. The unit design is not yet optimized and the performance obtained can indeed be improved if some specific R&D is performed. The PSA unit performance in NG upgrading with simultaneous CO_2 recovery for CO_2 storage, EOR and EGR will be evaluated in terms of costs, performance, energy consumption and size.

2: Summary of existing technologies for CO_2 capture from NG

2.1 Membranes

A membrane is a selective barrier that allows a selective passage of some of the components of the gas mixture through it, obtaining two independent and purified streams. In the case of removing acid gases from NG, both CO_2 and H_2S normally "permeate" through the membrane while leaving a concentrated mixture of hydrocarbons (termed as "retentate").

Membrane materials can be divided into organic and inorganic materials. Among the inorganic membranes we can divide them into porous membranes and dense membranes. The porous membranes are normally a thin film (micro-meter scale) supported on a porous support to provide mechanical strength. Such membranes can be all types of solid materials that can differentiate sizes of separating molecules such as CO_2 from other gases in NG. Gas separation in porous membranes is achieved by molecular sieving accompanied by surface diffusion. The channels and cages that make up the pore structure have the ability to separate gases based on their kinetic diameters. In the case of CO_2, separation is enhanced at lower temperatures due to preferential adsorption. There have been some works in membranes with high flux and very high selectivity by avoiding methane to go through the pores of the membrane. The support has to provide mechanical strength without affecting significantly the diffusion of the species and can be even porous stainless steel. Dense membranes are made of non-porous material, normally palladium or palladium alloys that can be applied to hydrogen and oxygen separation and do not have a market in natural gas so far.

The important materials in upgrading of NG are polymeric membranes [5, 6]. The polymeric materials can be used above or below their glass transition temperature. Glassy membranes (working below the glass transition temperature) are rigid and glass-like while rubbery membranes (working above the glass transition temperature) are flexible and soft. Most polymers used as membranes for natural gas upgrading (NGU) are glassy. The industrial standard is cellulose acetate polymer. The cellulose acetate membranes are 0.1 to 0.5 μm thin placed over a thicker layer of a porous support to provide the necessary mechanical strength (composite membrane). The thin thickness of the membrane aims to maximize flux with minimized resistance, hence to minimize the total necessary membrane area and cost of the process. The separation with dense polymeric membranes is dominated by the difference of "permeability" of the gases through the membrane. The main mechanism of this membrane is solution-diffusion type which means that the species (gas) is first dissolved in the membrane and then transported through it by suitable driving force such as concentration difference, pressure difference. The permeability is defined as the product between the dissolved amount of a permeant in the membrane (solubility) multiplied by its ability to permit through the membrane (diffusivity). It is desired that a membrane possesses do not have only high selectivity but also high permeability at the same time.

However, cellulose acetate is sharing the market with other membranes like polyimides or perfluoro polymersor polysulfone. A summary of the selectivity of glassy polymeric membranes can be found in literature [7, 8].

There are several membrane technologies available in the market. The technology for CO_2 capture from natural gas is commercially available since the early 80's and major players in this area are Air Products, Air Liquide, UOP, UBE and ABB/MTR [9].

There are two major technological configurations of NGU membranes. They are available as hollow fiber module or as flat sheets wrapped into spirally wound module. The hollow fiber membrane (largest share of the market [10]) can have two different process technologies for low and high pressures, the latter being the standard in NGU. In the high-pressure modules, the permeate flows into the hollow fiber from the outside (called shell side by resemblance with heat exchanger layouts). The NG stream can have some particulates and oil mist that is trapped in the stagnant areas of the module making the membrane more susceptible to plugging (or fouling) and thus some pre-treatment of the gas is required. The spiral configuration is more resistant to components that generate fouling and also allow more membrane materials to be used. However, they are more expensive to fabricate.

A membrane process produces two streams. The retentate is obtained at a similar pressure as the feed and is composed mainly by the gas with less permeation through the membrane (hydrocarbon components). The permeate is obtained at a lower pressure and is composed mostly by gases with higher permeability, thus the acid gases. Depending on the selectivity and permeability of the membrane more than one membrane stage is required. If the membrane allows 10% of the methane in natural gas to permeate, a second stage should be used to recover it. For this reason, the pressure in the permeate has to be increased again and thus more equipment (compressors) are necessary. A scheme of a membrane process is shown in Figure 1 [11].

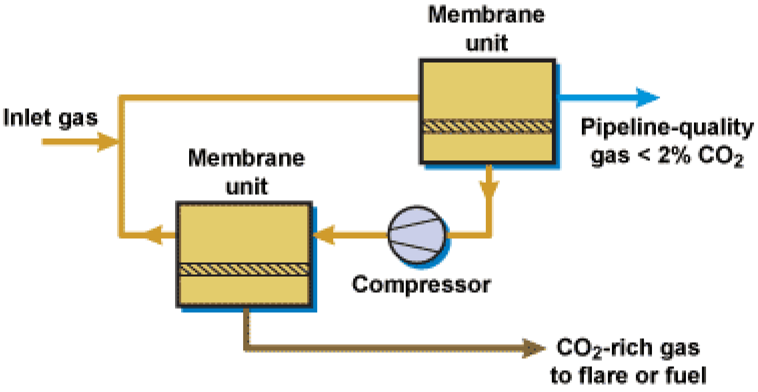


Figure 1. Scheme of dual-stage membrane process for natural gas sweetening [11].

Perhaps the main simplicity of membrane technology is its modular design which allows straightforward scale-up. This allows an easy expansion and an easy start-up. However, such an easy scale-up by adding more modules in parallel would be deemed as disadvantageous to the membranes for NGU since many other processes benefit from a large scale efficiency.

Provided that the membrane has a high selectivity and a high permeation flux, the energy and area occupied by the process can be small. In such cases, they can offer a valid solution for subsea applications at least for pre-treatment or pre-conditioning the natural gas.

In the case of single-stage membranes, there are no mobile parts associated and no additional chemicals are needed.

The process can require some expensive pre-treatment for particulates and liquids generated by Joule-Thomson effect when crossing a pressure differential.

It is generally accepted that membranes can work well for bulk removal of gases. Since the H_2S and CO_2 permeate at about the same rate, additional measures have to be made to meet H_2S specifications.

2.2 Cryogenic distillation

Distillation is the most well-known separation process available in chemical industries. It is based on the relative volatility of the different species constituting the mixture. Since the partial pressures and the boiling temperature of the components are quite different, it seems natural to use this process. The main problems are that the CO_2 phase freezes at significant concentration at temperatures below the CO_2 triple point, and also that CO_2 and ethane are difficult to separate since they form an azeotrope (same gas and liquid equilibrium composition). Moreover, distillation of CO_2 and H_2S presents a pinch point increasing the distillation difficulty and energy consumption.

The Ryan/Holmes approach to the problem is the most common solution. The simplified scheme of the Ryan/Holmes unit is shown in Figure 2 [12]. This is an extractive distillation process using a heavier hydrocarbon as additive (C_4 and heavier) to change the thermodynamic behaviour of the multicomponent system avoiding the freezing of CO_2 at the demethanizer and disrupting the ethane/CO_2 azeotrope at the ethane recovery column. The heavy hydrocarbons (C4+) are then recovered from the light hydrocarbons and H2S in a separate distillation train and recycled to the main separators. The amount and nature of these hydrocarbons depend on the amount of carbon dioxide present in the NG. Cryogenic distillation is beneficial particularly as a bulk separation process for gas mixtures with high CO_2 content, and can also in principle deliver natural gas at pipeline and LNG specification [13].

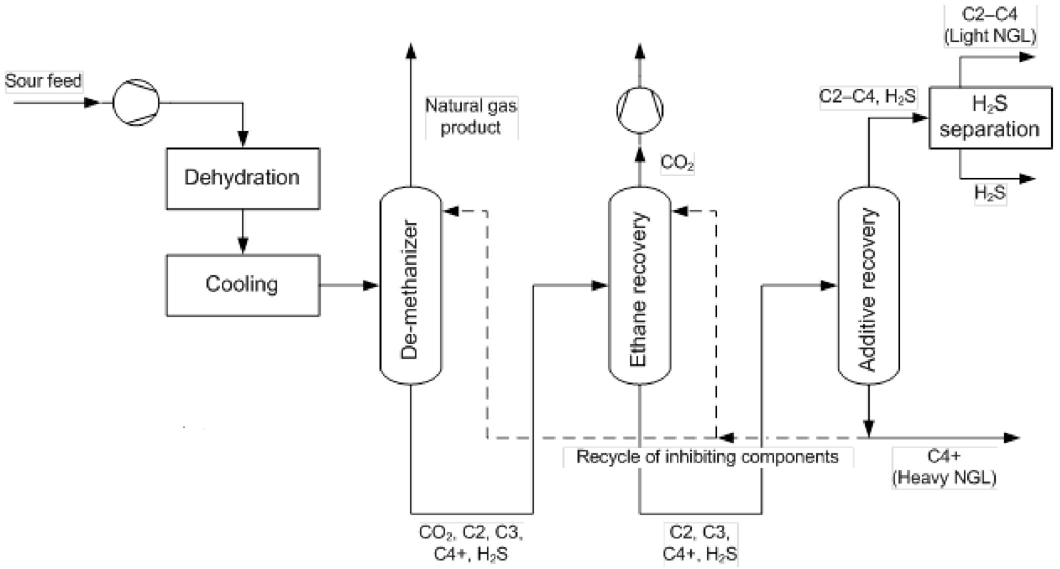


Figure 2. Ryan/Holmes scheme for separation of NG compounds by cryogenic distillation. Adapted from Reference [13].

Other processes that use low temperature concepts are available. In those processes, solid CO_2 (at least in some parts of the unit) is properly handled without the requirements of additions of hydrocarbons (e.g. ExonMobil CFZ, CryoCell and Sprex)

The main advantages of cryogenic processes are:

- The parts of equipment used are conventional and thus well-known.

- The configuration is flexible and can be used to very high concentration of acid gases.
- It is very well suited when NG is rich in C_{4+}
- Acid gases are recovered at high pressure.

On the other side, the main disadvantages are related to the cost of the separation and to the volume of equipment used. In the production of liquefied natural gas (LNG) the temperature of the whole stream has to be reduced anyway so this technology might have less cost penalties in this market, particularly when recover heavier components is important [14].

2.3 Solvent scrubbing

Absorption is the physical phenomena of a molecule of one compound entering a bulk phase of another compound (soda drinks are the daily example). In the case of acid gas removal from NG, the acid gases are absorbed in a liquid phase, which can be termed as a "physical" solvent since just weak interactions are linking the acid gases to the solvent. If the liquid phase is a liquid that further reacts with CO_2, the solvent can be called "chemical" solvent. The link acid gas – solvent is dependent of temperature; is stronger at lower temperatures and weaker at higher temperatures (denoting an exothermic interaction).

Once the acid gases are linked to a solvent (either physical or chemical) the solvent has to be regenerated at a higher temperature. So a gas mixture at a lower temperature (normally around 310 K) is putted in contact with the lean solvent and then the solvent loaded with CO_2 is routed to a higher temperature regeneration (around 390 K) where the desorbed acid gases are recovered.

Two major types of adsorbents are available: physical solvents and chemical solvents.

The physical solvents have weak interactions with the acid gases. The most well-known processes use solvents termed Rectisol (R) and Selexol (R).

Rectisol is a process that uses methanol as physical absorbent operating better at lower temperatures and higher pressures.

Selexol is a mixture of various dimethyl ether of polyethylene glycol, $CH_3O(C_2H_4O)_nCH_3$.

Absorption of CO_2 is around 15 times higher than methane while H_2S absorbs 134 times stronger [17]. Unfortunately, propane and higher hydrocarbons also adsorb (with similar or higher absorption constants as CO_2). Due to strong linking of the solvent to water, Selexol provides a first step of dehydration of the gas.

The most common chemical solvents are amines and to a much lesser extent, alkali salts. Hydrogen sulphide reacts with an amine via direct protonation reaction to form amine hydrosulphide:

$$R_1R_2R_3N + H_2S \leftrightarrow R_1R_2R_3NH^+HS^-$$

The reaction is shown for the tertiary amine, but it also applies for primary and secondary amines.

The reaction with CO_2 is more complex and involves more steps:

$$CO_2 + H_2O \leftrightarrow H_2CO_3\ (carbonic\ acid)$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \ (bicarbonate)$$

$$R_1R_2R_3N + \ H^+ \ \leftrightarrow R_1R_2R_3NH^+$$

$$CO_2 + H_2O + R_1R_2R_3N \leftrightarrow R_1R_2R_3NH^+ + HCO_3^-$$

This scheme of reactions takes place with diverse alkanolamines. However, the reaction is not very fast (as with H_2S) because carbonic acid dissociation to bicarbonate is relatively slow.

A secondary scheme of reactions is possible if there is a labile or reactive hydrogen in the structure of the amine. The second reaction forms an amine salt of a substituted carbamic acid (carbamate formation) and only takes place in primary and secondary amines:

$$CO_2 + R_1R_2NH \leftrightarrow R_1R_2N^+HCOO^-$$

$$R_1R_2N^+HCOO^- + R_1R_2N \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+$$

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NH_2^+ + R_1R_2NCOO^-$$

This reaction scheme is faster than the CO_2 hydrolysis scheme presented above, but still slower than the H_2S reaction. The carbamate scheme is limited to 0.5 mol CO_2 per mol amine.

The most employed amines are: MEA (monoethanolamine) as primary amine, DEA (diethanolamine) as secondary amine and MDEA (methyldiethanolamine) as tertiary amine.

Hot potassium carbonate can also be used for removing acid gases from natural gas. The lean alkali salt enters into contact with NG at 383 K and a pressure around 20 bars and then is regenerated at near atmospheric pressure in the stripper. This technology does operate by pressure variations eliminating the requirements of heat exchangers between the rich and lean solvent streams.

The acid gas removal by absorption is the standard technology to remove acid gases from natural gas. They are operating in different sites around the world from many years and thus are well-known. For this reason, there is also plenty of literature that can be accessed reporting the whole value-chain of the process from the development of amines to economic studies of its applications.

This process will be used as a reference process in the rest of the study [15-17]. The scheme of the process is represented in Figure 3. The lean water-amine solution enters into counter-current contact with the acid gas containing natural gas in the absorber or contactor. Some liquid distributors (structured packings) are placed in the absorber to increase the contact area between the falling liquid and the gas. The absorber can work at pressures as high as 70 bar. The temperature of the amine solution around the top of the absorber is 300-320 K and it is some degrees higher when removed from the bottom due to the heat of reaction of CO_2 with the amine. The absorption temperature varies with the amine used in the process and is around 333 K.

After the rich amine solution is taken from the bottom of the absorber, the pressure is reduced to 5-7 bars to flash the dissolved hydrocarbons which can be used as plant fuel.

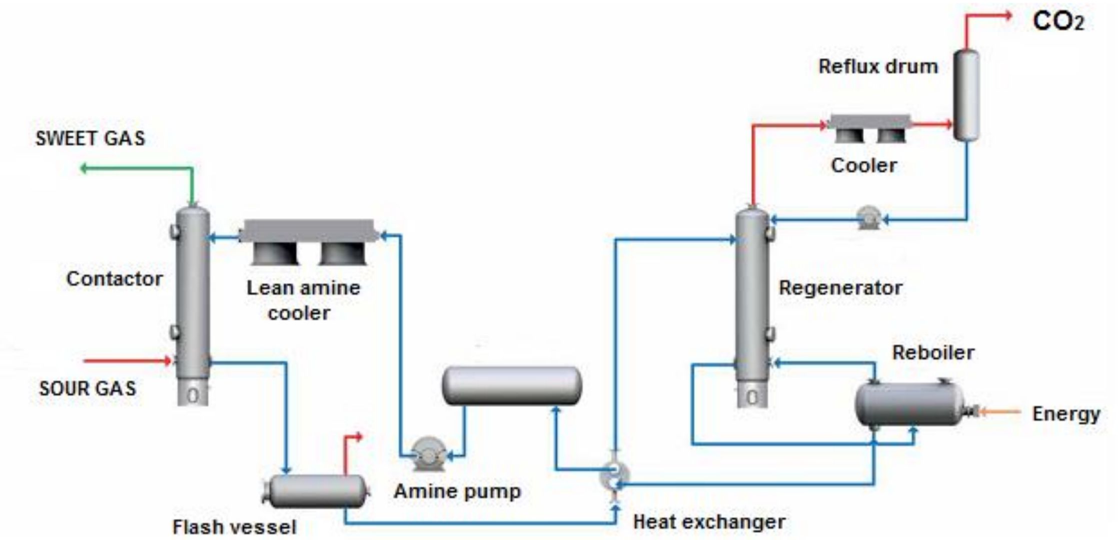


Figure 3. Reference process for natural gas processing with amine-based CO_2 capture

The regeneration of the rich amine is carried out in the stripper that operates at temperatures around 393-403 K which requires utilization of low-pressure steam. The CO_2 is stripped off the amine and is obtained at high purity at the top of the stripper. One important piece of equipment that is used in this process is the heat exchanger to integrate heat utilization between the lean and rich amine.

It has to be mentioned that around 1-3% of the flow of amines has to be reclaimed. Amines react with other components like oxygen and SOx to form heat stable salts (HSS) that should be removed by a reclaimer.

Utilization of physical and/or chemical solvents has to be evaluated depending on the conditions of the field. However, qualitatively, physical solvents are more appropriate when the concentration of acid gases is higher and when not so stringent product specifications are required. Amines are preferred when less amount of acid gases is present in the NG.

The major advantage of this process is that it is well-known among major players in the NG industry. It is proven for a wide range of conditions and can remove CO_2 and H_2S to ppm levels. It has though some known disadvantages like the high energy requirement for regeneration (remember that the amine is dissolved in water so a lot of heat is employed to heat the amine solution) and the utilization of chemicals.

2.4 Adsorption processes

Adsorption is the spontaneous phenomenon of attraction that a molecule from a fluid phase (gas or liquid) experiences when it is close to the surface of a solid, named adsorbent [18-21]. By using a high surface area solid, this phenomenon can be enhanced per unit volume constituting the principle of an adsorption-based separation process. When the adsorbent is putted in contact with a fluid phase, an equilibrium state is achieved. This equilibrium establishes the amount of fluid that can be adsorbed (how much fluid can be attached to the surface) for a given fluid phase composition, temperature and pressure. Information about the adsorption equilibrium of the different species is vital information to design and model adsorption processes.

In physical adsorption, the amount of gas adsorbed increases with pressure and decreases with temperature. The adsorption behaviour of a porous material is normally assessed by measuring the amount adsorbed at equilibrium state (thermodynamic data) at different pressures at constant temperature; the so-called "adsorption equilibrium isotherms". The shapes of these isotherms vary depending on the type of binding that the gas molecules have to the surface as shown in Figure 4.

Isotherms Type I are the most common ones for adsorption processes. When water adsorption is considered, other isotherms (e.g. Type IV) are common depending on the interactions between water and the surface of the material [22].

For utilization in PSA units, linear isotherms are better. When isotherms are strongly non-linear, a large extent of the adsorption capacity is achieved even at low pressures. Then in order to regenerate the adsorbent and desorb the loaded gases vacuum has to be employed, increasing the energy consumption of the process and thus reducing the economic viability of the technique. An example is provided in Figure 5 where two isotherms representing the behaviour of two different materials at the same temperature are displayed. In this case, the material 1 (red isotherm) presents a higher loading but with a more non-linear isotherm. The isotherm of material 2 achieves less total capacity, but it is less steep. If we assume that the cyclic capacity of the material will be calculated as the adsorption capacity at the feed pressure (A) minus the capacity at the regeneration pressure (B), the cyclic capacity ($\Delta q = q_A - q_B$) of the second material (green isotherm) is higher, although the isotherm presents a smaller overall capacity. In order to exploit the capacity of the first material, lower pressures should be used at desorption, normally requiring vacuum and thus being more energy intensive.

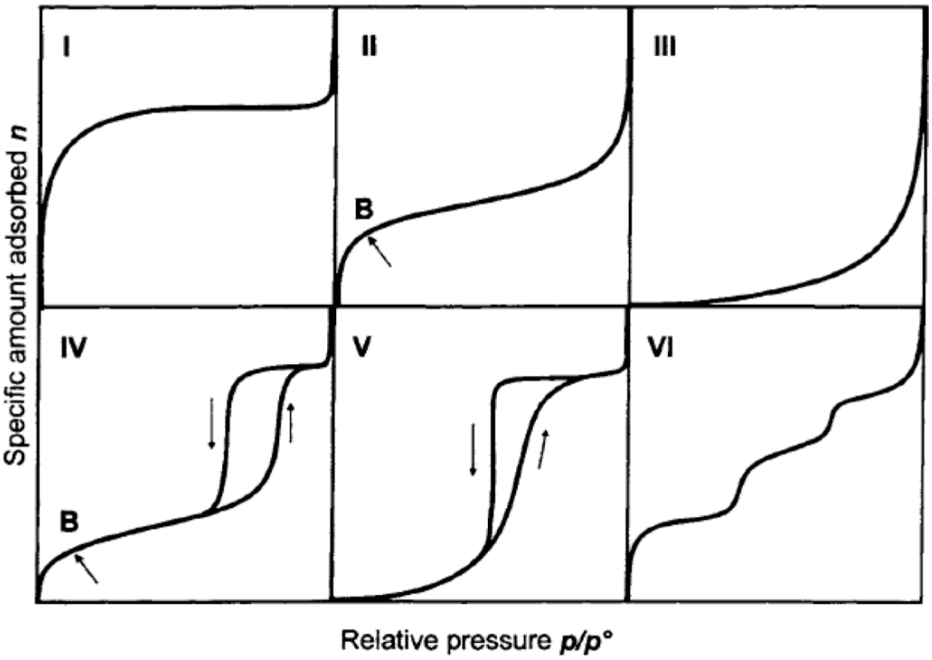


Figure 4. Different types of adsorption isotherms.

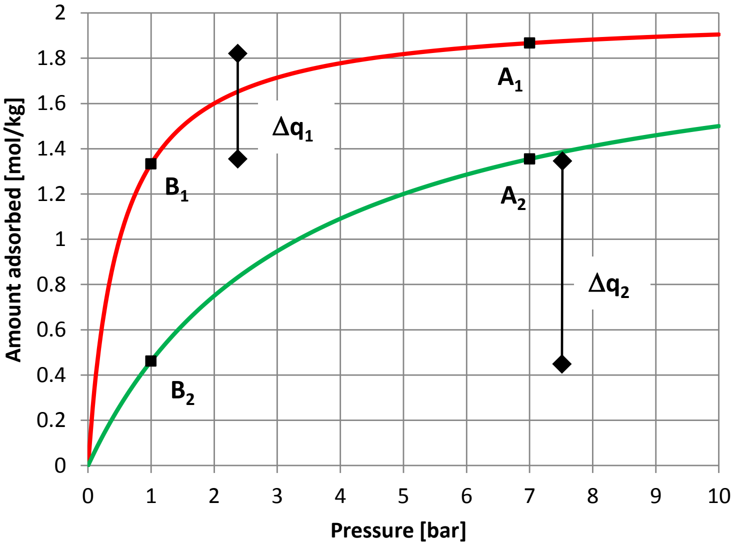


Figure 5. Cyclic capacity of two different materials at a constant temperature showing the effect of isotherm non-linearity.

Since the adsorbent materials are highly porous materials, the adsorption sites are not directly available and the molecules have to diffuse through a pore system. This diffusion process determines the time required to achieve equilibrium and depends on many factors like the size of the molecules and the pore system and their specific interactions. In some materials like extrudates of zeolite 13X, the process is so fast that sometimes it is impossible to measure with macroscopic techniques and microscopic techniques should be used [23]. In other cases, the process is extremely slow and it might take several days to reach adsorption equilibrium [24]. This property can be actually used for gas separation, provided that one gas achieves equilibrium much faster than the other. It is the principle of operation of nitrogen separation from air by carbon molecular sieves (CMS) for example [25]. Most commercial PSA units for biogas upgrading also use "kinetic adsorbents" like CMS or ETS-4 based on the fact that carbon dioxide is adsorbed much faster than methane [26-30]. An example of the time required to reach adsorption equilibrium of carbon dioxide and methane on a CMS sample is shown in Figure 6.

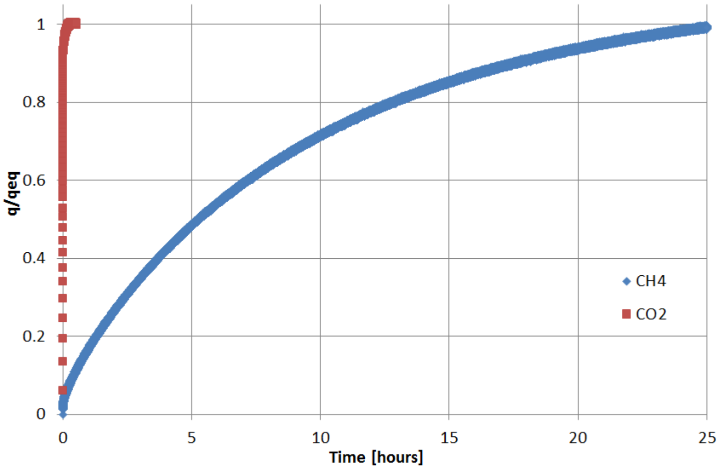


Figure 6. Time required to reach adsorption equilibrium in carbon molecular sieve sample MSC 3R-172 from Japan EnviroChemicals.

When a multicomponent gas phase is put into contact with a certain surface of a solid, the molecules that are less adsorbed, can be separated from molecules that are more adsorbed. The adsorbent is normally porous in order to enhance the surface available per unit volume to retain gases. The interactions between the solid surface and the gas molecules can be diverse, but the ones used for separation by adsorption processes are the bonds that correspond to physical adsorption which are lower than 50 kJ/mol. The physical adsorption is spontaneous and thus exothermal, releasing energy. It also means that to desorb a molecule, energy has to be provided to the system and this normally corresponds to the energy expenditure of the adsorption processes.

Adsorption processes are used in NG industry for water removal by molecular sieves (zeolites) and for H_2S removal. The most common adsorbent for H_2S removal is zeolite 4A. Regeneration of zeolite 4A after H_2S removal is at high temperatures (> 500 K) which produces COS (carbonyl sulphide). There are data of adsorption of H_2S in literature but they are quite limited to design a cyclic adsorption process due to lack of data at high temperatures. Therefore itis also not possible to fully design a temperature swing adsorption (TSA) process without making some assumptions.

Adsorption processes, particularly Pressure Swing Adsorption (PSA) and Vacuum Swing Adsorption (VSA) are already on demonstration stages for CO_2 capture from the production of hydrogen in refineries [31] and for steel production [32].

The removal of CO_2 from natural gas by adsorption is not a commercial process and is in research stage. Although many adsorbent materials have been tested for CO_2 removal, most of the experimental works available are related to removal of CO_2 from flue gases [33-38] or from biogas. In both of these mixtures, the partial pressure of CO_2 is lower than its partial pressure in natural gas, thus data available normally does not cover the whole pressure range. Moreover and most importantly, the partial pressure of methane is much higher than in biogas and thus the data available for methane is far away from the conditions of natural gas upgrading.

In the high pressure range, there is limited amount of data that can be used for the design [39-42]. The data on higher hydrocarbons (C_{2+}) in the same materials exists only in limited number of cases.

The only industrial application known involving utilization of a PSA process for natural gas upgrading is by XEBEC Inc. (Canada) in an off-shore facility in California (USA) [43]. The unit has been selected due to the compact size and is used to recover stranded gas. The technology uses a fast-cycling PSA operated by a rotary valve. It must be mentioned however that this unit operates with a relatively small flowrate and at a total pressure of 16 bars, which makes it impossible to assume straightfowardly that the technology can be used as stand-alone process for NGU at much higher flows and pressure level. Moreover, the only specification to be met in the XEBEC process is to produce pipeline-quality NG and not to produce a high-purity CO_2 stream. Linde Engineering also has a solution PSA unit for NGU but since it is not its core product, brochure information is not available.

Innovation of this work

To the knowledge of the authors, this is the first time that a PSA process is presented in literature to process a natural gas stream at 70 bar with the aim of having high purity and recovery on both CH_4 and CO_2 product streams.

Based on our previous experience, only kinetic separation adsorbent materials were considered since equilibrium separation materials that adsorb significant amounts of methane will invariably present strong undesired thermal oscillations. The report will be based on novel data on a commercial sample of carbon molecular sieve

(CMS).

The report also presents the effect of different PSA cycles in the total performance of the total upgrading unit. Several PSA cycles were idealized in order to increase the separation of both streams while keeping energy consumption to minimum levels.

The final PSA process involved a 12-column process with a multi-feed principle, several pressure equalizations and recycle of light (purge) and heavy (rinse) gases. Important criteria were to increase the purity of CO_2 and simultaneously the hydrocarbon recovery keeping in mind that unit size will be a strong limitation.

After the evaluation of several cycles it was possible to process a stream of 0.5 NMm^3/h with 10% of CO_2 to obtain a pipeline quality NG with a CO_2 content of 2.2% and a stream of CO_2 with a purity of 84.5%. C_{2+} is almost equally distributed in the two streams.

The PSA cycle is not yet optimized and probably better performance can be obtained with different cycle configurations. However, we believe that most of the principles discussed here will serve and be the basis for a faster technology readiness for commercialization. Despite the large size of the unit, a very high energy efficiency is obtained. The main reason for the large size if the number of columns required to accomodate intense pressure variations of the cycle.Improving the materials used in PSA units (using honeycomb monoliths for example), the cycle time can be significantly decreased and thus the size can become much smaller.

3: Conditions used in this study

3.1 Natural gas composition

Natural gas was formed by layers of organic matter exposed to heat and pressure over several thousands of years. Since the composition of the organic matter and formation conditions are different, the composition of natural gas is variable.

Natural gas is a mixture of hydrocarbon gases. It is composed primarily of methane and also includes ethane, propane, butane, pentane and other hydrocarbons. Furthermore, it can also contain undesired components like oxygen, inert gases (nitrogen and noble gases) and acid gases (hydrogen sulphide and carbon dioxide).

In order to study the application of a new technology, a gas composition and operating conditions have to be fixed. In this study we have used the conditions listed in Table 1. The composition is similar to a composition used in a previous study [44]. This composition was used in a large research project sponsored by the Research Council of Norway, coordinated by SINTEF and involving NTNU, Statoil, Gassco, Petrobras and initially Total. For the design of a PSA unit, some initial simplifications have to be made due to lack of data available for C_{2+}. Using kinetic adsorbents it is expected that nitrogen will not be adsorbed and will exit the PSA unit with methane. Regarding the heavier hydrocarbons, ethane might be recovered but higher chains will probably condense in the macropores of the adsorbent; however specific data is not available.

Table 1 – Natural gas composition and feed conditions used in this study

Property	Value	Value [PSA]
Temperature [K]	313	313
Pressure [bar]	70	70
Flowrate [Nm^3/h]	500,000	500,000
y_{CH4}	0.8300	0.8300
y_{C2H6}	0.0460	0.0700
y_{C3+}	0.0240	
y_{CO2}	0.1000	0.1000

3.2 Conditions and boundaries used in this study

The study will consider all the costs and performance of the PSA unit and compression train to produce pipeline-quality natural gas with less than 2.5% CO_2 content and also to produce and compress a CO_2-rich stream. The boundaries considered in this study are shown in Figure 7.

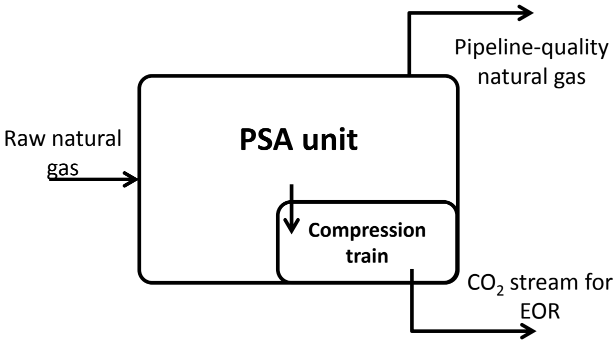


Figure 7. Boundaries of this study.

3.3 Economic framework

The competitiveness of the two acid gas removal concepts cannot only be evaluated based on technical performances but also strongly depends on their respective economic performances. Based on the cost methodology presented below, the economic performances of the two acids gas removal concepts are evaluated and compared in term of CO_2 captured cost. Finally sensitivity analyses are performed in order to illustrate the impact of uncertainties data and the site specific characteristics on the CO_2 capture cost.

The following sections describe the methodology used to assess the capital and operating costs and to compare the two acid gas removal technologies considered in this report while a summary of the economic parameters with considered references is presented in Appendix A.

3.3.1 Economic boundary conditions

All cost reported in this report are given in euros and are based on a reference year of 2014 for a plant to be built in the Netherlands. Investment costs are updated according to the Chemical Engineering Plant Cost Index (CEPCI) [45]. A summary of the CEPCI values from 1950 to 2014 is presented in Figure 8. An exchange rate of 1.33 $/€ is considered to convert cost available in US dollars [46].

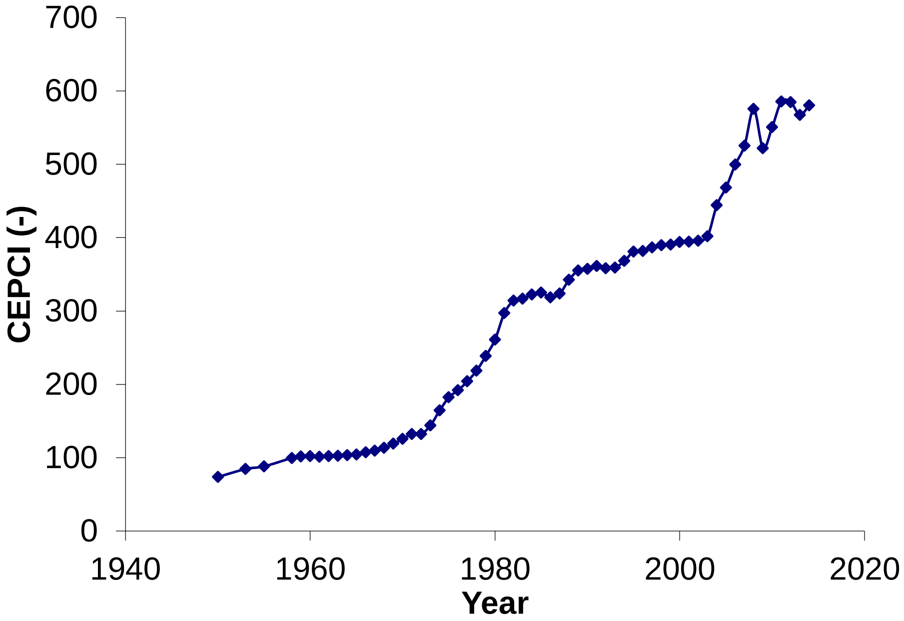


Figure 8: Chemical Engineering Plant Cost Index from 1950 to 2014

3.3.2 Capital investment

The calculation of the Total Cost Requirement (TCR) is estimated based on a bottom up approach (BUA):

- *Equipment Costs* – Estimation of equipment costs for each equipment is made using cost estimation software, quotation from equipment suppliers, power law method, and other available data. The *Total Equipment Cost (TEC)* is the sum of all equipment costs.
- *Total Direct Cost (TDC)* – The Total Direct Cost is the sum of the equipment costs and the installation costs which include costs associated with piping/valves, civil works, instrumentations, electrical installations, insulations, paintings, steel structures, erections and OSBL (outside battery limits).
- *Total Plant Cost (TPC)* – The Total Plant Cost is the sum of the direct costs and the indirect cost (which include yard improvement, service facilities, engineering/consultancy cost, building and miscellaneous), and contingency. The project contingency considered are added to the capital cost to give a 50% probability of a cost over-run or under-run.
- *Total Cost Requirement (TCR)* – The Total Cost Requirement is the sum of TPC, interest during construction, owner's costs, spare parts, working capital and start-up costs.

The cost estimates are for 'nth plants' based on current knowledge of the technology, i.e. they are commercial plants built after the initial technology demonstration plants. Additional costs normally associated with First Of A Kind (FOAK) commercial plants shall be excluded. However the cost estimates reflect the differences in maturity between the two technologies [47]. The estimate accuracy is expected to be +35/-15% (AACE Class 4).

3.3.3 Main operational parameters

3.3.3.1 Maintenance, Insurance and labour costs

The fixed operating costs are costs which are independent of the amount of natural processed and include:

- *Insurance and local property taxes:* The total annual cost of insurance, local property taxes and miscellaneous regulatory and overhead fees is to be a total of 1% of TPC.
- *Maintenance cost:* Maintenance costs include cost of preventive maintenance, corrective maintenance (repair and replacement of failed components) and periodic replacement of sorbent. A maintenance cost corresponding to 2.2% of the TPC for both the solvent and sorbent based processes and a complete replacement of the PSA sorbent over 10 years. The sorbent (Carbon Molecular Sieve) cost considered for both evaluation of investment and maintenance cost is presented in Table 2.
- *Labour costs:* Labour costs include operating labour, administrative and support labour. A 5 shift working pattern shall be assumed to evaluate the operating labour cost. The 'fully burdened' cost of labour, including social security payments is assumed to be 60 k€. Administrative and support labour are also included and assumed to be 30% of the operating and maintenance labour cost while maintenance labour are assumed to be 40% of the overall maintenance cost.

3.3.3.2 Chemicals, consumables and CO_2 transport and storage cost

The variable operating costs are costs which are dependent of the amount of natural processed and include utilities consumption such as electricity, natural gas internal consumption, process water, chemicals. In addition, as the adsorption based process lead to a lower natural gas production than the solvent based process, this difference in production is included by considering the revenues losses associated to natural gas losses for the sorbent based process. In addition, the cost associated with CO_2 transport and storage will also be considered here as a variable operating cost. The utilities costs are calculated based on the process simulation and the utility costs presented in Table 2.

Table 2: List of utilities and material costs

Utilities, units	Cost
Electricity cost [€/MWh]	80
Natural gas price [€/GJ]	6
Carbon Molecular sieve [€/t]	6,500
MDEA [€/kg]	43
Piperazine [€/kg]	58
Process water [€/m^3]	0.20
Sea water cooling [€/m^3]	0.03
CO_2 transport and storage [€/t][1]	10

The process is designed to operate at base load design. However in practice, the first year of operation often shows a downtime in operating hours due to technical issues. It

---

[1] A CO_2 transport and storage cost of 10 €/tCO_2 stored is normally considered in IEAGHG studies, here as the CO_2 stream may also include significant amount of natural gas(up to 15%vol), this cost is considered to be equal to 10€/$t_{CO2\text{ and natural gas stored}}$.

is therefore assumed that during the first year the gas processing facility will operate at 65% while it will operate at 85% during subsequent years.

3.3.4 Main economic Key Performance Indicators (KPI)

Three key performance indicators are here used in order to evaluate and compare the reference solvent and the Pressure Swing Adsorption concepts for gas sweetening:

- The unitary sweetening costs which correspond to the cost of sweetening the natural gas stream to meet the pipeline transport requirement divided by the amount of raw or sweet natural gas in normal conditions. The sweetening cost includes the costs associated with CO_2 removal, compression, transport and storage.
- The unitary cost of CO_2 removal which correspond to the cost of removing the CO_2 from the natural gas, without or with the CO_2 compression, transport and storage in the case of CCS, reported to the amount of CO_2 captured.
- The CO_2 avoided cost corresponds to the cost which shall be included for the valuation of a CCS project associated with the removal of CO_2 from the natural stream. Indeed in practice, the removal of CO_2 from the natural gas stream is required to meet the natural gas transport specification regardless of the captured CO_2 to be either vented or processed further for its storage. Only the cost of conditioning, transport and storing the CO_2 after its removal shall be included in order to calculate the CO_2 avoided cost[2] [42]. The CO_2 avoided cost is therefore equal to the conditioning, transport and storage cost divided by the amount of CO_2 avoided. The amount of CO_2 avoided is defined as the amount of CO_2 removed minus the climate impact associated with electricity and steam consumption. A climate impact of 0.435 $kgCO_2/MWh$ of electricity and 0.236 $kgCO_2/MWh$ of steam consumed will be considered to calculate the amount of CO_2 avoided [47].

In addition, the complete CCS cost including capture transport and storage will also be reported as an indicative value. As in other IEAGHG studies, the default CO_2 transport and storage cost is assumed to be 10€/tCO_2. However to represent the additional cost which could be associated to the small quantities considered here, sensitivity analyses on the transport and storage cost will be included.

Table 3: Parameters and variation for sensitivity analyses

Criteria	Base case	Sensitivities	
Investment cost [%]	-	-35	+35
Fixed operating cost [%]	-	-35	+35
Variable operating cost [%]	-	-35	+35
Adsorbent cost [%]	-	-35	+35
Discount rate [%]	8	5	10
Utilization rate [%]	85	70	90
Plant life [years]	25	10	40
Electricity cost [€/MWh]	80	60	100
Natural gas price [€/GJ]	6	3	9
Steam availability [%]	0	-	100
Accounting of the lost gas sale [%]	100	0	-
Adsorbent replacement rate [%]	10	5	20
CO_2 transport and storage cost [€/$t_{CO2,stored}$]	10	0	20

---

[2] It is woth noting that this KPI is not exactly equal to the CO_2 removal with CCS minus the CO_2 removal without CCS. Indeed, this KPI includes the climate impact associated with electricity and steam consumption.

To reflect the cost accuracy, the impact of data uncertainties and the site specificity characteristics, sensitivity analyses on the following parameters will be considered and with the variation presented in Table 3: investment cost, operating cost, discount rate, plant life, electricity cost, adsorbent cost, CO_2 transport and storage cost.

4: Reference case: amine scrubbing

4.1 Introduction

The solvent concept considered here is evaluated for a raw natural gas of 500,000 Nm^3/h with 10 $\%_{vol}$ of CO_2 and no significant heavy hydrocarbons with the characteristics given in Table 4. After the CO_2 removal process, the sweet natural gas is expected to meet the natural gas sales specification for pipeline exported shown in Table 5 (a) as for example a CO_2 content is lower that $2.5\%_{mol}$.

In order to limit losses of valuable product, the CO_2 product is defined as having purities higher than 95%. The acid gas removal process also includes a conditioning section for the CO_2 stream to meet the specification required for pipeline export as shown in Table 5(b).

Table 4: (a) Raw natural gas characteristics (b) composition [42]

Parameter	Value
Temperature [°C]	40
Pressure [bar]	70

Component	Composition [$\%_{vol}$]
C_1	88
C_2	2
CO_2	10

Table 5: (a) Sweet natural gas characteristics (b) CO_2 stream characteristics after conditioning [42]

Parameter	Value
Temperature [°C]	40
Pressure [bar]	70
LHV [MJ/kg]	39
CO_2 content	≤ 2.5 *mol%*

Parameter	Value
CO_2 purity [%]	≥ 95
Pressure [bar]	110
Temperature [°C]	40

4.2 Process and technical modelling

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 [48]. To ensure adequate reactivity to CO_2, the solvent is activated by addition of 5 wt% of Piperazine.

The process layout shown in Figure 9 is based on an absorber-stripper configuration with a lean-rich solvent heat exchanger and includes flash tanks for partial release of absorbed components through pressure reduction. Due to the high absorber pressure and large solvent circulation rate, a liquid turbine is used to recover power from the rich solvent stream leaving the absorber. To avoid excessive entrainment of heavy hydrocarbons into the amine solvents, 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, solvent characteristics, main unit sizes are given in Table 6.

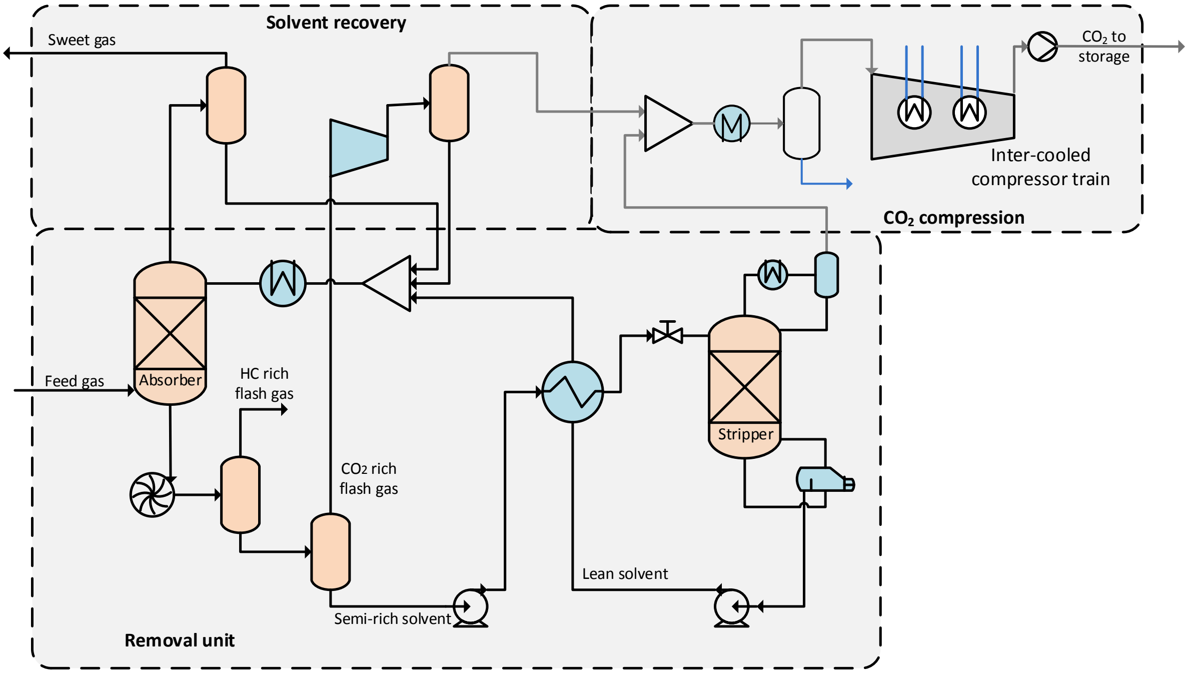


Figure 9: Principal process flow diagram of the aMDEA/MDEA based solvent concept [42]

Table 6: Process parameters for aMDEA/MDEA based solvent concept

Solvent	Lean loading [-]	0.06-0.07
	MDEA [wt%]	45
	Piperazine [wt%]	5
	Lean solvent flow [kg/h]	987,000
	Solvent make-up [kg/h]	1,810
Absorber	Pressure [bar]	70
	Lean solvent temperature [°C]	50
	Packing type	Nutter Ring 2 3/8
	Flooding factor [-]	0.7
	Column diameter [m]	4.2
	Packing height [m]	14.0
	Column height [m]	16.8
Stripper	Pressure [bar]	1.8
	Reboiler temperature [°C]	97-120
	Packing type	Nutter Ring 2 3/8
	Flooding factor [-]	0.6
	Column diameter [m]	3.1
	Packing height [m]	6.0
	Column height [m]	7.2
HC flash	Pressure [bar]	5
CO_2 flash	Pressure [bar]	1.1

4.3 Cost estimation

The cost breakdown of equipment and direct cost of the aMDEA/MDEA solvent based process are reported in Table 7. The evaluation show that the main separation units (absorber, desorber, hydrocarbon recuperation and CO_2 rich flash gas recovery) account for around 45% of the total direct cost, while the CO_2 conditioning section accounts for around 40% of the total direct cost while the solvent circulation equipment (pump, heat exchanger and cooler) account for the remaining part of the cost.

Table 7: Indicative equipment and direst costs breakdown of the aMDEA/MDEA solvent based process

Unit	Equipment cost [k€]	Direct cost [k€]
Absorber	3,800	5,000
Desorber	2,100	3,900
Hydrocarbons and Pressure recuperation[3]	800	1,500
CO_2 rich flash gas recovery[4]	800	1,100
Solvent circulation pump	500	1,300
Solvent lean cooler	500	1,600
Solvent heat exchanger	400	1,000
CO_2 conditioning for transport (1st stage)	1,700	2,500
CO_2 conditioning for transport (2nd stage)	1,300	1,900
CO_2 conditioning for transport (3rd stage)	1,400	2,000
CO_2 pumping for transport	1,800	2,800
Total	**15,300**	**24,600**

Regarding the annual fixed operating cost, the labour cost including supervision and administration is evaluated to 1,900 k€/y based on the methodology presented previously while the maintenance, insurance, local taxes and fees correspond to 1,000 k€/y. This results in a total fixed operating cost of 2,900 k€/y.

A summary of utilities and chemical consumption of the aMDEA/MDEA solvent based concept is provided in Table 8. The estimation of the different utilities and chemical consumption are based on the process simulation performed in ProTreat®. These utilities consumption lead to a total variable operating cost of 14,000 k€/y in which electricity and steam account respectively for 24 and 48% of the cost. In the base case, the steam was not assumed to be freely available on the gas processing site. However in practice at least a part of the steam might be available on site and could lower the steam cost in that case. This will be measured through sensitivity analyses.

Table 9 summarizes the results of the cost assessment of CO_2 removal from natural gas using an aMDEA/MDEA solvent based concept with the case and boundary conditions presented previously while Figure 10 presents the cost breakdown of the solvent based process. The evaluation shows that as expected for a solvent based CO_2 removal concept, the energy consumption through electricity and steam and the CO_2 transport and storage account for the main part of the overall capture cost, with respectively 17, 35 and 20%, while the total capital requirement and the fixed operating costs account for 15 and 11%.

---

[3] Include the hydrocarbons recovery flash and the liquid turbine.

[4] Include the CO_2 rich flash and the subsequent compressor.

Table 8: Cost of consumables the aMDEA/MDEA solvent based process

	Annual consumption	**Annual cost [k€/y]**
Electricity	57 [GWh/y]	4,600
Steam	1.0 [10^6GJ/y]	9,200
Cooling water	3,150 [m^3/y]	1
Solvent make up	17,200 [t/y]	100
CO_2 transport and storage	69 t/h	5,100
Total variable operating cost consumption	-	19,100

Regarding unitary key performance indicators, the sweetening cost is 6.9 and 7.5 €/kNm^3 of respectively raw and sweet natural gas. The CO_2 removal cost including CO_2 conditioning, transport and storage is equal to 50 €/$t_{CO2,captured}$ while the CO_2 removal cost without CO_2 conditioning, transport and storage is equal to 30 €/t/CO_2,captured.

As a consequence, the CO_2 avoided cost which correspond to the cost of CO_2 conditioning, transport and storage after removal form the natural gas is equal to 21 €/$t_{CO2,avoided}$. It is however important to note that the small quantities of CO_2 captured (558 kt_{CO2}/y) considered here may lead to a cost of transport and storage higher the 10 €/$t_{CO2,stored}$ considered here and correspond to the standard IEAGHG assumption.

Table 9: Overall cost KPIs of the aMDEA/MDEA solvent based process

	Cost
Discounted cost flow including transport and storage (k€)	264,800
Sweetening cost including transport and storage (€/kNm$^3_{raw}$)	6.9
Sweetening cost including transport and storage (€/kNm$^3_{sweet}$)	7.5
CO_2 removal cost including transport and storage (€/$t_{CO2,captured}$)	50
CO_2 removal cost without CO_2 conditioning, transport and storage (€/$t_{CO2,captured}$)	30
CO_2 avoided cost (€/$t_{CO2,avoided}$)	21

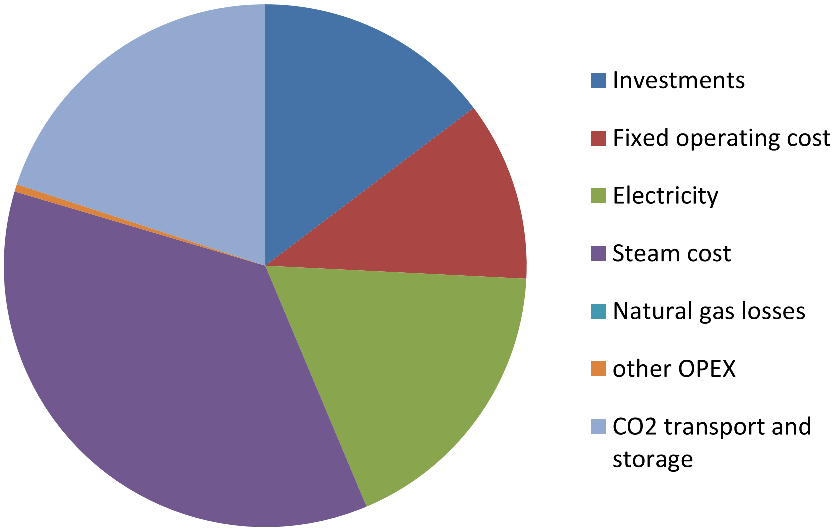


Figure 10: Break-down of the total discounted cost of the solvent based process including CO_2 conditioning, transport and storage

5: Pressure Swing Adsorption process for CO_2 capture

5.1 Basic PSA operation principles

In an adsorption process, the feed stream is putted into contact with the adsorbent that is normally packed in fixed beds. The less adsorbed (light) component will break through the column faster than the other(s) as shown in Figure 11 where a breakthrough experiment of CH_4-CO_2 in a fixed bed filled with carbon molecular sieve (CMS) [49].

In order to achieve separation, before the heavy or more adsorbed component(s) break through the column, the feed should be stopped and the adsorbent should be regenerated by desorbing the heavy compound, that can also be recovered. Since the adsorption equilibrium is given by specific operating conditions (composition, T and P), changing one of these process parameters it is possible to regenerate the adsorbent. When the regeneration of the adsorbent is performed by reducing the total pressure of the system, the process is termed Pressure Swing Adsorption (PSA); the total pressure of the system "swings" between high pressure in feed and low pressure in regeneration.

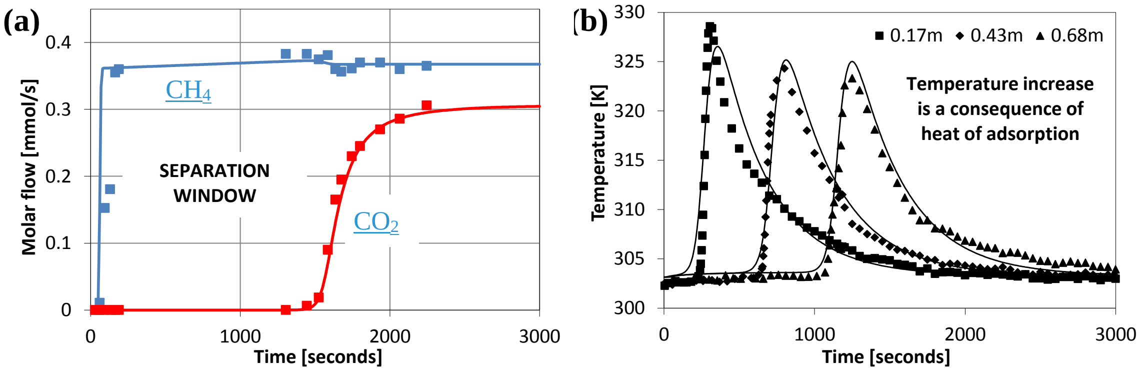


Figure 11. Example of a breakthrough curve of CH_4-CO_2 using carbon molecular sieve (CMS) adsorbent as an example of the performance of a kinetic adsorbent: (a) exit gas molar flow rate and (b) temperature evolution in three different positions of the column [49].

As shown in Figure 12, at the feed conditions, when a gas mixture CH_4 + CO_2 enters into contact with the adsorbent packed in a fixed-bed column, CO_2 is selectively removed from the feed gas while CH_4 is recovered at the other end of the column since it is much less adsorbed. The partial pressure of CO_2 is P_{ads} and it is loaded in the adsorbent until q_{ads}. Since the loading of component CH_4 is lower, this product can be recovered at high pressure. Once the column is saturated with CO_2, the adsorbent has to be regenerated by lowering the pressure to P_{des} and lowering its loading to q_{des}. After the high pressure is restored, the adsorbent can adsorb up to q_{ads} again and thus the cyclic loading (also termed as cyclic capacity) of the adsorbent towards carbon dioxide is (q_{ads} – q_{des}). Since adsorption is exothermic and desorption is endothermic, the cyclic capacity (q_{ads} – q_{des}) calculated from a single isotherm is only ideal while the real value is indeed lower; during adsorption, the heat released heats the bed up, reducing its capacity while during desorption the heat consumed cools it down, increasing the thermodynamic capacity. Based on this principle, the larger the temperature oscillations in the PSA unit, the poorer the performance.

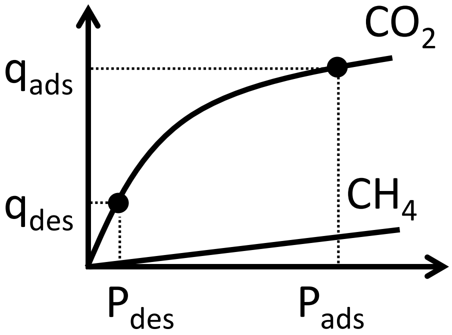


Figure 12. Adsorption equilibrium isotherms of CO_2 and CH_4 on a generic adsorbent. The solid points mark the cyclic capacity zone from the maximum loading during adsorption and the loading during the desorption step.

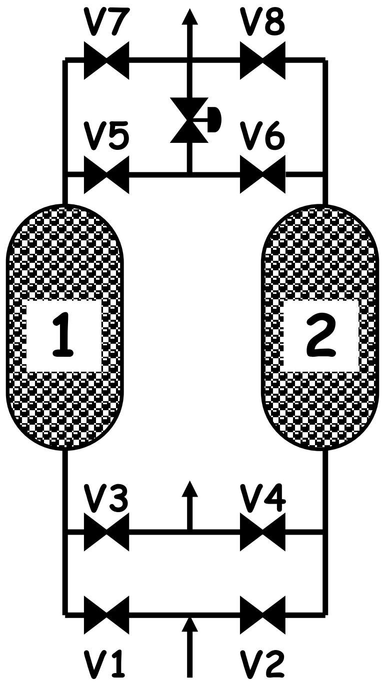
PSA technology is in the market of separation technologies for the last 50 years and can be used in a large variety of applications, such as hydrogen purification and air separation [50-52]. The upgrading of biogas is a fast-growing market where PSA units are taking an important share [53]. The main advantage of PSA technology is the low energy consumption when compared to other technologies.

A good PSA process results from the interaction between material science and engineering. Selecting proper adsorbent materials is very important, but also the way of configuring the cycle to enable continuous adsorption and regeneration is very important. The interdisciplinary approach required to maximize PSA performance implies that the general advances in PSA units can be divided in two main domains: utilization of new adsorbents or traditional adsorbents in non-classical shapes (material science) and more efficient ways to reactivate the adsorbent (process engineering). It should be noted that most of the applications of PSA technology are focused in the purification of the less adsorbed gas(es). The utilization of PSA for purification of the most adsorbed gas is still under development for many applications that include CO_2 capture from flue gases, olefin-paraffin separation, etc.

Adsorption is a spontaneous phenomenon. So, the "adsorption" step of the PSA unit normally termed feed, proceeds favoured by thermodynamics and only few solutions might be available to improve it. These solutions are normally related to heat management of the heat of adsorption [19, 54, 55]. A PSA for NGU cannot be a discontinuous or semi continuous process due to the large volumes involved, so the PSA will involve a series of columns running in parallel: when one column is saturated for feed, the feed should be immediately sent to another column previously conditioned. The flow change is performed using a set of valves that are associated to each column.

After regeneration is finished, the adsorbent is able to be used again, cyclically. The "cycle" is the sum of all the events that will happen in a column, that are defined as "steps". So, "feed" is the step where CO_2 is adsorbed and sweetened NG is produced. This step is followed by changing the column pressure within the "depressurization" or "pressure equalization" steps. A recycle of the most strongly adsorbed component can happen after the feed or in intermediate pressures and this step is normally termed as "rinse". When the pressure is reduced and CO_2 is extracted from the column, the step is termed "blowdown" and when part of the produced NG is used for displacing CO_2 from the voids of the column, the column undergoes the "purge" step. Finally the pressure in the column should be restored in a step termed as "pressurization".

The basic cycle is commonly termed as Skarstrom cycle, to honour its inventor, Charles Skarstrom. A scheme of the two-column PSA introduced in that patent is shown in Figure 13. The four steps of the "Skarstrom cycle" are also shown in Figure 13: feed, blowdown (or evacuation), purge and pressurization. Each of the steps is controlled with a set of valves that has to be specifically designed for the purpose of utilization of the unit and the cycle sequence that will be used.



C1	Feed	Blow	Purge	Press
	V1,V7	V3	V5,V3	V1
C2	Purge	Press	Feed	Blow
	V6,V4	V2	V2,V8	V4

Figure 13. Schematic design of a two-column pressure swing adsorption unit.

In the feed step of the Skarstrom cycle, NG is fed to the first column (C1) at the feed pressure which is the higher pressure of the system. The stream exiting the top of the column is upgraded NG. When the adsorbent packed in C1 is saturated with CO_2, the feed is directed to the second column (C2). In order to release part of the CO_2 adsorbed in C1, the flow direction is reversed and the total pressure of the column is reduced (opening valve V3). There are different terms to call this step, but blowdown is one of the most common and will be used here. To additionally remove CO_2 from the column, a purge step (or light gas recycle) is used. The purge is part of the sweetened NG from the other column which is flowing by the pressure differential between the two columns. After the adsorbent is ready to load more CO_2, the overall pressure of the system should be restored. That is done in the pressurization step using the NG feed.

After all these steps were finished, a complete cycle was completed. Even though each column is run batch-wise at each step, after some cycles it reaches a Cyclic Steady State, CSS. When CSS is achieved, the performance of the PSA is constant over the cycles. It should be noted that since this process sometimes involve substantial amount of heat generation, there can be multiple CSS [56].

Although the Skarstrom cycle shown in Figure 13 was used to explain the PSA operation, this cycle is semi-continuous and cannot be used for NGU. In order to continuously remove acid gases from NG, a system with more than two columns is required to ensure that always one column receivesfeed while the others are under regeneration.

The engineering choice is thus to select the most efficient cycle that maximizes the performance of the unit and also of the adsorbent so that less material is used.

5.2 Adsorbent selection

The adsorbent selection is the main and initial task in the specification of a PSA unit. There are several criteria to specify an adsorbent. One of the simplest ways to design an adsorber and select the adsorbent material was provided several years ago by Dr. Kent Knaebel [57, 58].

In the last years, a lot of "simplified equations or criteria" for adsorbent selection have been published. Many of them are only based on the adsorption equilibrium isotherms at a single temperature and / or on loadings collected at two different pressures aiming to establish the ideal cyclic capacity. Most of these simplified methodologies tend to provide imprecise results and there have been several presentation of world experts in the field evaluating many of them for different applications with random results. So far, they fail in taking into account temperature fluctuations and poorly tackling diffusion issues. Thus, a direct method of selecting an adsorbent is not available and unfortunately is mostly based on experience.

For CO_2 removal from NG, the selection criteria is based on two important issues:

a. Less non-linear isotherms for CO_2. When the isotherm becomes more non-linear, regeneration has to be done at lower pressures (mostly under vacuum) thus spending more energy to recover the CO_2. The general rule is: if adsorption becomes more favorable, desorption becomes more unfavorable and difficult.
b. Weaker adsorption of methane. The high partial pressure of methane limits the choices of the adsorbents. Even if the adsorbent is more selective to CO_2, adsorption of large amounts of CH_4 will result in undesired thermal oscillations, reducing the cyclic loading of CO_2 in the column. Also if adsorption of CH_4 takes place, its desorption time should be accounted for, delaying the cycle time and thus making the columns larger.

The only way of severely limiting the amount of methane adsorbed at such high partial pressures is limiting its entrance to the micropores of the adsorbent, where adsorption takes place. This is possible since the size of the CH_4 molecule is larger than the molecule of CO_2. The kinetic diameter of CH_4 is 3.8 Å while the kinetic diameter of CO_2 is 3.3 Å. The materials imposing size restrictions to targeted molecules are known as "kinetic adsorbents". There are several materials of which the pore sizes lie in that range. The most important examples are some 8-member zeolites, carbon molecular sieves, aluminosilicates and some metal-organic frameworks (MOFs).

Zeolite 4A is one standard zeolite material that can be used for this application. However, based on existing data, the limitation of CH_4 diffusion through the pores is not satisfactory and thus large thermal variations are expected.

There are two commercial materials that should be considered for this study.

1. A titanosilicate material termed ETS-4 known as molecular gate. In principle, the pores of the material can be tuned by heating at different temperatures until the point where CH_4 cannot penetrate into the pores. Some data has been published

[59-63] and the adsorbent is available commercially. The material is now commercialized by BASF and unfortunately is not yet possible to get a sample of the material for its detailed evaluation for this application. For this reason it was not studied in this report.

2. Carbon molecular sieve is a readily available material that can be used for this purpose [64]. This material is used in several biogas upgrading plants (separation of CH_4-CO_2 at lower pressures and flow rates). Commercial materials can be obtained by several companies, such as CarboTech from Germany (formerly known as Bergbau-Forschung) and Japan EnviroChemicals (formerly known as Takeda). The results provided in this report are based in the utilization of this material.

5.3 Mathematical modelling

The mathematical model of a PSA unit involves the description of mass, energy and momentum balances coupled with appropriate thermodynamic equations of state and adsorption equilibrium and kinetic models.

The following assumptions were made in order to derive the necessary conservation equations in each of the columns:

1. The behaviour of the gas mixture obeys the Benedict-Webb-Rubin equation of state [65].
2. The adsorbed phase composition is described by a theoretical extension of the single-component isotherms.
3. No mass, heat or velocity variations in the radial direction.
4. Axial dispersed plug flow.
5. External mass and heat transfer resistances can be estimated by a film resistance model.
6. Bidisperse adsorbent particle: macropore and micropore mass transfer resistances can be estimated by the Linear Driving Force (LDF) model. The resistance in the mouth of the micropores for CMS are lumped within the micropore diffusion term.
7. No temperature gradients inside each particle.
8. The column porosity is constant over the length of the bed.

The mass balance for each component in the gas phase of the column is given by:

$$\varepsilon_c \frac{\partial C_i}{\partial t} = \varepsilon_c \frac{\partial}{\partial z}\left(D_{ax} C_T \frac{\partial y_i}{\partial t} \right) - \frac{\partial \left(u_o\, C_i \right)}{\partial z} - \left(1-\varepsilon_c\right) \frac{a'\, k_{fi}}{Bi_i/5+1}\left(C_i - \overline{c_i} \right) \qquad [1]$$

where C_i is the gas-phase concentration, D_{ax} is the axial dispersion coefficient, ε_c is the column porosity, u_o is the superficial velocity, y_i is the molar fraction, k_{fi} is the film mass transfer resistance, Bi_i is the Biot number and $\overline{c_i}$ is the averaged concentration in the macropores, all valid for component i, while C_T is the total gas concentration and a' is the external adsorbent particle specific area.

A LDF model for the mass transfer rate from the gas phase to the macropores was assumed. The mass balances within the macropores of extrudates particles is given by:

$$\varepsilon_p \frac{\partial \overline{c_i}}{\partial t} + \rho_p \frac{\partial \left\langle \overline{q_i} \right\rangle}{\partial t} = \varepsilon_p \frac{8\, D_{p,i}}{R_p^{\,2}} \frac{1}{1+5/Bi_i}\left(C_i - \overline{c_i} \right) \qquad [2]$$

$$K_{P,i} = \frac{8D_{p,i}}{R_p^{\;2}} \tag{3}$$

where $D_{p,i}$ is the macropore diffusivity, R_p is the extrudate radius.

The LDF equation for the crystals averaged over the entire extrudates is expressed by:

$$\frac{\partial\left\langle \overline{q_i} \right\rangle}{\partial t} = K_{\mu,i}\left(q_i^{\,*} - \left\langle \overline{q_i} \right\rangle\right) \tag{4}$$

where the micropore diffusion constant is given by equation (5) for most microporous solids and by equation (6) for CMS materials (and for other adsorbents that present a diffusion resistance at the mouth of the pores [66, 67]:

$$K_{\mu,i} = \frac{15D_{\mu,i}}{r_c^2} \tag{5}$$

$$K_{\mu,i} = \frac{1}{\dfrac{1}{k_{b,i}} + \dfrac{r_c^{\;2}}{15D_{\mu,i}}} \tag{6}$$

where $D_{\mu,i}$ is the crystal diffusivity, r_c is the crystal radius, $k_{b,i}$ is the diffusion constant at the mouth of the micropore and q_i is the adsorbed phase concentration in the equilibrium state.

In the momentum balance it has been considered that the pressure drop and velocity change obey the Ergun equation, defined by:

$$-\frac{\partial P}{\partial z} = \frac{150\,\mu\left(1-\varepsilon\right)^2}{\varepsilon_c^{\;3} d_p^{\;2}} u_0 + \frac{1.75\left(1-\varepsilon\right)\rho_g}{\varepsilon_c^{\;3} d_p}\left|u_0\right| u_0 \tag{7}$$

where P is the total gas pressure, μ is the gas viscosity, ρ_g is the gas density and d_p is the particle diameter. It has been proved that the steady-state Ergun equation can be used, avoiding complex momentum balance [68].

The energy balance in the gas phase is:

$$\begin{aligned} &\frac{\partial}{\partial z}\left(\lambda \frac{\partial T_g}{\partial z}\right) - u_0\, C_{g,T}\, C_p \frac{\partial T_g}{\partial z} + \varepsilon_c\, R_g\, T_g \frac{\partial C_{g,T}}{\partial t} - \\ &\quad -\left(1-\varepsilon_c\right) a_p\, h_f\left(T_g - T_p\right) - \frac{4 h_w}{d_{wi}}\left(T_g - T_w\right) - \varepsilon_c\, C_{g,T}\, C_v \frac{\partial T_g}{\partial t} = 0 \end{aligned} \tag{8}$$

with T_g, T_p and T_w respectively as the gas, particle and wall temperatures; C_v and C_p as the gas molar specific heat at constant volume and pressure respectively; R_g as the ideal gas constant; d_{wi} as the wall internal diameter, λ as the heat axial dispersion coefficient. h_f is the film heat transfer coefficient between the gas phase and the particle and h_w is the film heat transfer coefficient between the gas phase and the wall.

Since it is assumed that there are no temperature gradients inside a particle, the solid phase energy balance for the column is given by:

$$(1-\varepsilon_c)\left[\rho_p \sum_{i=1}^{n} \overline{q}_i C_{v,ads,i} + \rho_p \hat{C}_{p,s}\right]\frac{\partial T_p}{\partial t} =$$

$$= (1-\varepsilon_c)\varepsilon_p R_g T_p \frac{\partial C_T}{\partial t} + (1-\varepsilon_c)\rho_p \sum_{i=1}^{n}(-\Delta H)_i \frac{\partial \overline{q}_i}{\partial t} + (1-\varepsilon_c) a_p h_f (T_g - T_p) \tag{9}$$

where ρ_b is the bulk density of the bed, $\hat{C}_{p,s}$ is the solid specific heat per unit sorbent mass and $(-\Delta H)_i$ is the isosteric heat of adsorption of component *i*.

Finally, for the energy balance of the column wall energy exchange with the gas phase inside the column and the external environment is considered:

$$\rho_w \hat{C}_{p,w} \frac{\partial T_w}{\partial t} = \alpha_w h_w (T_g - T_w) - \alpha_{w\ell} U (T_w - T_\infty) \tag{10}$$

where T_∞ is the external temperature, ρ_w is the wall density, $\hat{C}_{p,w}$ is the wall specific heat per mass unit, *U* is the overall heat transfer coefficient and α_w and $\alpha_{w\ell}$ are defined by:

$$\alpha_w = \frac{d_{wi}}{e(d_{wi}+e)} \quad ; \tag{11}$$

$$\alpha_{w\ell} = \frac{1}{(d_{wi}+e)\ln\left(\dfrac{d_{wi}+e}{d_{wi}}\right)} \tag{12}$$

where *e* is the wall thickness. In this case, *U* = 0 since the columns are considered to be adiabatic.

This mathematical model was developed in the group of Prof. Rodrigues at the University of Porto and has already been used in the simulation of fixed bed behaviour and Pressure Swing Adsorption (PSA) for several gas mixtures in PSA and VPSA applications [69-72].

To solve this theoretical model, some transport parameters are needed. They were calculated from the relations presented below.

The pore diffusivity was calculated with the Bosanquet equation:

$$\frac{1}{D_{p,i}} = \tau_\mathrm{p}\left(\frac{1}{\mathrm{D}_{\mathrm{m,i}}} + \frac{1}{D_{\mathrm{k,i}}}\right) \tag{13}$$

where $D_{m,i}$ is the molecular diffusivity, $D_{k,i}$ is Knudsen diffusivity, both for component *i* and τ_p is the pore tortuosity. The molecular diffusivity for the mixture was approximated with:

$$D_{m,i} = \frac{1-y_i}{\sum_{\substack{j=1 \\ j\neq i}}^{n} \dfrac{y_i}{D_{ij}}}$$

[14]

where the binary molecular diffusivity D_{ij} was calculated with the Chapman-Enskog equation [73]. The Knudsen diffusivity is calculated by

$$D_{k,i} = 9700\mathrm{r}_\mathrm{p}\sqrt{\frac{T_g}{M_w}} \tag{15}$$

where r_p is the mean pore radius (cm) and M_w is the molecular weight of the adsorbate.

The axial mass and heat dispersion coefficients as well as the mass transfer and heat transfer coefficients at the film were calculated using the Wakao and Funazkri correlations [74, 75]:

$$\frac{\varepsilon D_{ax,i}}{D_{m,i}} = 20 + 0.5 Sc_i Re \qquad [16]$$

$$\frac{\lambda}{k_g} = 7 + 0.5 Pr Re \qquad [17]$$

$$Sh_i = 2.0 + 1.1 Re^{0.6} Sc_i^{1/3} \qquad [18]$$

$$Nu = 2.0 + 1.1 Re^{0.6} Pr_i^{1/3} \qquad [19]$$

The axial coefficient relations are valid for the range 3<Re<10,000.

The internal convective heat transfer coefficient h_w between gas and the wall column can be estimated with Wasch and Froment correlation [76-78]:

$$\frac{h_w d_{in}}{k_g} = 140 + 0.013396 \frac{d_{in}^2}{d_p k_g} Re \qquad [20]$$

where h_w is expressed in W/m^{2}K, d_{in} is in m, k_g is the gas conductivity in W/mK and d_p is the pellet diameter in m.

where the sub-index *ex* represent the properties of the external gas surrounding the column. The Rayleigh number is defined by: $Ra = Gr\,\mathrm{Pr}$ and the Gr is the Grashof number. The properties of the external gas are evaluated at the film temperature: $T_{film} = (T_w - T_\infty)/2 \cdot$

General properties of the gases, like density, viscosity, and thermal conductivity were calculated according to Bird, Stewart and Lightfoot, 2002.

The dimensional parameters used for this model are defined by:

Biot number: $Bi_i = \dfrac{R_p k_{fi}}{\varepsilon_p D_{p,i}}$, [21]

Schmidt number: $Sc_i = \dfrac{\mu_g}{\rho_g D_{m,i}}$, [22]

Reynolds number: $Re = \dfrac{\rho_g u_i d_p}{\mu_g}$, [23]

Prandtl number: $Pr = \dfrac{\hat{C}_{pg} \mu_g}{k_g}$, [24]

Sherwood number: $Sh_i = k_{fi} d_p / D_{m,i}$ [25]

Nusselt number: $Nu = \dfrac{h_f d_p}{k_g}$, [26]

Grashof number: $Gr = \dfrac{g\beta(T_w - T_\infty)L^3}{\nu\alpha}$ [27]

where g = 9.8 m^2/s, ν is the kinematic viscosity of the external gas, α is the external thermal diffusivity and β is the thermal expansion coefficient. In these equations, d_p is the pellet diameter.

The equations necessary to describe the thermodynamics of gas and solid phases are also required. In this work, the multi-site Langmuir model [79] was used to describe the multi-component adsorption equilibrium assuming that the multicomponent mixture can be described based on the parameters measured from single gas component isotherms. The multi-site Langmuir model is given by:

$$\frac{q_i^*}{q_{\max,i}} = K_i P y_i \left[1 - \sum_i \left(\frac{q_i^*}{q_{\max,i}}\right)\right]^{a_i} \quad [28]$$

where q_i^* is the amount adsorbed and $q_{\max,i}$, a_i and K_i are the maximum amount adsorbed, number of sites occupied per molecule and Langmuir isotherm constant, respectively. The Langmuir isotherm constant has an exponential dependence with temperature given by:

$$K_i = K_i^0 \exp\left(-\frac{\Delta H_i}{R_g T_s}\right) \quad [29]$$

where K_i^o is the pre-exponential factor and ($-\Delta H_i$) is the heat of adsorption of component *i*.

The Benedict-Webb-Rubin (BWR) equation of state was used to describe the multicomponent gas mixture. This model is given by:

$$P_T = RTC_T + \left(B_0RT - A_0 - \frac{C_0}{T^2}\right)C_T^2 + (bRT - a)C_T^3 + a\alpha C_T^6 + \frac{cC_T^3}{T^2}(1 + \gamma C_T^2)e^{-\gamma C_T^2} \quad [30]$$

The constants employed in the BWR equation are derived from pure gas data and then employed in the estimation of gas density using proper mixing rules. The constants of the BWR for CH_4 and CO_2 employed in this work are listed in Table 10. The mixing rules to estimate multicomponent behaviour are:

$$A_0 = \left[\sum_i y_i \left(A_{0,i}\right)^{1/2}\right]^2 \quad [31]$$

$$B_0 = \sum_i y_i B_{0,i} \quad [32]$$

$$C_0 = \left[\sum_i y_i \left(C_{0,i}\right)^{1/2}\right]^2 \quad [33]$$

$$a = \left[\sum_i y_i (a_i)^{1/3}\right]^3 \quad [34]$$

$$b = \left[\sum_i y_i (b_i)^{1/3}\right]^3 \quad [35]$$

$$c = \left[\sum_i y_i (c_i)^{1/3}\right]^3 \quad [36]$$

$$\gamma = \left[\sum_i y_i (a_i)^{1/2}\right]^2 \quad [37]$$

$$\alpha = \left[\sum_i y_i (\alpha_i)^{1/3}\right]^3 \quad [38]$$

Table 10. Constants of CH_4 and CO_2 in the Benedict-Webb-Rubin Equation of state.

	a	A_0	b	B_0	c x10^{-6}	C_0 x10^{-6}	α x10^{-6}	γ
CH_4	0.500	1.8791	0.034	4.26x10^{-2}	0.0026	0.0229	0.1244	6.0x10^{-3}
C_2H_6	0.350	415.56	0.011	6.28x10^{-2}	0.0332	0.1820	0.2434	9.2x10^{-3}
CO_2	0.052	2.7089	0.003	4.45x10^{-2}	0.0072	0.1148	0.1127	4.9x10^{-3}

The mathematical model provided by equations 1-39 is able to describe the operation of a fixed bed. In order to use this model into a PSA unit, the initial and boundary conditions should be provided. The initial conditions normally assume that the columns are filled with an inert gas that is not adsorbed and that the adsorbent does not have any of the gases adsorbed. The boundary conditions of the model depend on the PSA step that is being performed. The boundary conditions for the PSA steps that were used in this work are listed as Appendix B. The equations used to solve the ancillary parts of the PSA are also presented in Appendix C.

5.4 Implementation of model equations

There are several commercially available software that can be used to simulate a PSA unit: Matlab, COMSOL Multiphysics, ProSim, Aspen Adsorption, gPROMS, Fluent, Inprocess, etc. In all these programs it is possible to simulate the PSA performance by solving the model for one column. There are several approaches to simulate the performance of an entire PSA by solving only one column. The difference is mainly in the simulation of all steps that involve internal recycles: purge, rinse, pressure equalizations and pressurization steps. The simplest alternative is to use average (fixed) gas compositions for these steps. This procedure is relatively accurate when the purge and other steps are carried out with very small contaminations of the more strongly adsorbed gas. This approach is easier to apply and is useful to understand the basics of a new separation or adsorbent utilization. However, the results of this approach will be unrealistic for purge streams contaminated with the heavy gas. The second alternative is to create a virtual stream (buffer) storing part of the exiting gas of the feed step that will then be used for the purge. This strategy that mimics the bed interactions with other column is employed by several programs [80, 81].

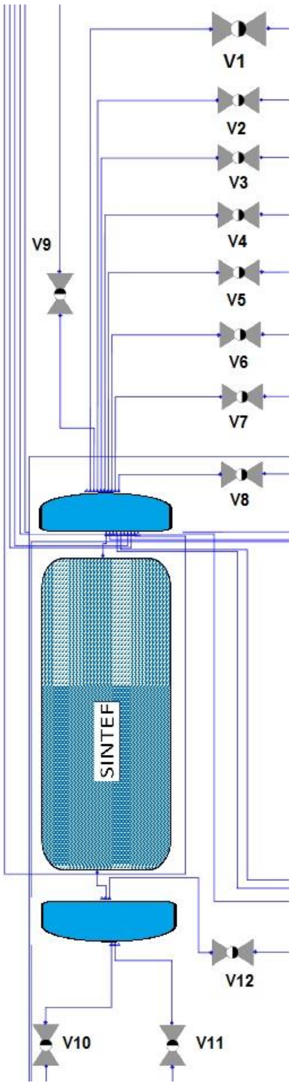


Figure 14. Column connections for multi-column PSA modelling.

Another possible strategy for PSA simulation is to simulate the entire unit including the valves, dead volumes of the system, column headers (dead volume at the extremities of the columns), etc. This is a more detailed way of describing the entire process with the penalty of having an increased computational effort. It also has the benefit of knowing the entire dynamics of the system. Efforts in this area were previously carried out [82-84]. If the multicomponent dynamic data has been verified with breakthrough curve measurements, using this strategy is possible to design a full unit without the requirements of having the experimental unit with a good accuracy. This is very important for PSA units composed of many adsorption columns of which the size is large. Another important advantage of this modelling approach is that with this model it is possible to identify if there are some steps that are or can be controlled by ancillary equipment (valves, tanks, etc.). Moreover, this type of modelling can have an important effect in understanding the entire dynamics of the PSA unit and particularly what happens in the initial cycles.

The model of a multiple-column PSA unit was developed using gPROMS software (PSE Enterprise, UK). The flowsheet of the unit was built by combining various models for individual significant piece of equipment. Each of the unit models has some inlet-outlet ports, used for communication between different modules. Thus the PSA model used was object-oriented written in an equation-oriented environment. The main advantage of this approach is that changing the cycle and configuration of the unit does not require rewriting the entire code since equations of columns, valves and tanks are identical. The mathematical models used for gas sources, valves, flow control, sink are described as process model libraries (PML).

Each of the columns is connected to a series of valves that will command its operation. All valves used in this study have only two stem position: open and closed and no intermediate opening is used. An example of one of the columns linked with the different valves is shown in Figure 14. In this example, the column is connected to 12 valves that open specifically to provide gas for different steps of the cycle. In the image, the valves are opened in the following scheduling: V1: first depressurization; V2: second depressurization, V3: third depressurization, V4, fourth depressurization; V5, V6: provide purge; V7: rinse exit; V8: provide pressurization gas; V9: light product production; V10: feed inlet; V11: rinse inlet; V12: blowdown exit (CO_2 recovery). There are also some lines that come to the column header. These lines are coming from other columns and have a corresponding valve linked to other column to control their flowrate and timing of gas delivery. Thus, for a 12-column PSA unit, a minimum of 144 valves should be used, including also three storage tanks for light and heavy products and for rinse gas.

Given the complexity of our model, a simulation of a PSA unit takes around 20 hours until reaching cyclic steady state (CSS). For the conditions used in this study, arriving to CCS means solving around 50-70 cycles. Providing the right conditions for convergence is critical to the stability of the system, not only due to its complexity, but also because of the strong variation of conditions (pressure, temperature and flows) within the different steps. It should be mentioned that despite of the good numerical stability of the solvers embedded in the software, obtaining numerical stability of this systems is not straightforward and many times the system has problems of convergence to achieve a result. Tighter conditions for integrating the partial differential equations or more accurate initial values for initialization are common measures for achieving convergence, but success is not entirely guaranteed *a priori* for a given set of conditions.

5.5 PSA cycle design

After deciding the adsorbent material to be used, the design of an efficient procedure to regenerate it is crucial for the total unit operation. Unfortunately (so far) there is no theoretical solution to decide the optimal sequence of steps that should be used for such a design. Normally the decisions on the order, sequence, duration, etc. of all the steps are done by experience in designing these systems. Alternatively, a super-sequence of steps can be provided to a mathematical optimization routine that will tell the user the conditions on how to run the cycle [85]. This approach also starts by assuming a fixed routine of the super-sequence. After defining which is the proper sequence of steps that one column has to undergo to complete a cycle, the number of columns has to be decided / adjusted to implement this strategy under the specific constrains imposed by the system. There are some procedures on how to do this including some graphical methods [86].

Since there was no detailed information about a commercial process to serve as reference, the final cycle configuration was determined by testing a number of arbitrary

PSA cycles. Some indications of how to obtain the final cycle will be discussed. Moreover, we do not guarantee that the final cycle configuration was well optimized, since that process will take more engineering work than the one used for this study.

It should be mentioned that the cycle has been a product of knowledge developed from PSA designs for different applications: CO_2 capture from flue gases, biogas upgrading and hydrogen purification. As shown in Table 11, all these applications have some similarities to the problem tackled here, but also clear differences from it. For example, CO_2 capture from flue gases concentrates on the selective removal of the most strongly adsorbed compound only while this work requires to produce both the least and most strongly adsorbed components at the same time.

Table 11. Adsorption processes considered for CO_2 capture from different sources that can serve as a basis to design a natural gas upgrading process.

Process	Similarities	Differences
Hydrogen purification	• "contaminants" to be removed are in the order of 20-40%. • Pressure can be up to 40 bar • Stream is available at high pressure (no compression)	• Hydrogen is slightly adsorbed in almost all materials • The scale of largest commercial unit is almost one order of magnitude smaller
Biogas upgrading	• Similar gas composition • Similar process requirements (low CH_4 slip means indirectly high CO_2 purity) • Loading of CO_2 can be significant	• Pressure is one order of magnitude smaller. • Flow rate is several orders of magnitude smaller • No worries in CO_2 capture
CO_2 removal from flue gases	• Flow rate	• Almost everything is different: pressure, gas composition, process requirements, loading of non-CO_2 gases, etc.

The cycle design was thus arranged in the following order of steps: feed, co-current column depressurizations, co-current provide purge, co-current rinse with CO_2-rich stream, counter-current blowdown, counter-current purge with CH_4-rich stream, counter-current pressure equalization and counter-current repressurization with the CH_4 product. All these steps have to be arranged in such a way to ensure that the feed stream is continuously processed.

An example of a continuous feed four-column cycle is shown in Figure 15. The image shows the time allocated to each of the steps of the cycle: co-current depressurizations (D1 and D2), co-current provide purge (PP), counter-current blowdown (BD), counter-current purge (PU), counter-current pressure equalization (E1 and E2) and counter-current repressurization (RE). These steps are continuously repeated with time. The requirements of the cycle are:

a- Feed should continuously switch from one column to the other so that it is continuously processed.

b- The gas exiting the co-current depressurization steps should be used in the counter-current pressure equalization. So at every time there is a column depressurization, there should also be a corresponding pressurizing pressure equalization step.

c- When there is a provide purge, the gas exiting this step should be fed to a purge step.

<table>
<tr><td>c1</td><td colspan="3">Adsorption ↑</td><td>D1↑</td><td>PP↑</td><td>D2↑</td><td>BD↓</td><td>PU↓</td><td>E2↓</td><td>E1↓</td><td colspan="2">RE ↓</td></tr>
<tr><td>c2</td><td>BD↓</td><td>PU↓</td><td>E2↓</td><td>E1↓</td><td colspan="2">RE ↓</td><td colspan="3">Adsorption</td><td>D1↑</td><td>PP↑</td><td>D2↑</td></tr>
<tr><td>c3</td><td>D1↑</td><td>PP↑</td><td>D2↑</td><td>BD↓</td><td>PU↓</td><td>E2↓</td><td>E1↓ (b)</td><td colspan="2">RE ↓</td><td colspan="3">Adsorption</td></tr>
<tr><td>c4</td><td>E1↓</td><td colspan="2">RE ↓</td><td colspan="3">Adsorption</td><td>D1↑</td><td>PP↑</td><td>D2↑</td><td>BD↓</td><td>PU↓</td><td>E2↓</td></tr>
</table>

Time →

Figure 15. Four-column cycle with two pressure equalization steps and a provide-purge step.

The system studied here will operate between 70 bar and 1 bar used for desorption, so the system will require a certain number of pressure equalization steps. The main objective of such steps is to remove most of the methane that is in the gas phase which is in great majority due to the high feed pressure of the system. Using a simplified calculation based on the assumption of a binary system (90% CH_4- 10% CO_2) and isothermal operation, it is possible to estimate the gas molecules remaning in the column at the ends of feed step and each of the three depressurizing pressurization steps. The obtained values are shown in Figure 16. The calculations include the amount of gas in the gas phase (inside the pores and outside the pores) and in the adsorbed phase. Despite the high kinetic selectivity of the material, the existence of so much CH_4 gas makes it difficult to extract high CO_2 purity fluid during the blowdown step. After the successive depressurizing pressure equalizations, it is possible to see that the amount of methane in the column is reduced from an initial value of almost 60% to a value of 41%. If blowdown is performed after the third depressurization, the maximum purity of CO_2 will be around 60%, although since not all CO_2 will desorb, the purity will be smaller than 60%. This means that additional steps are required in order to increase the purity of CO_2.

One attractive way to reduce the consumption of paraffin-rich stream is to use part of this gas in a provide purge step. This is a common measure in hydrogen purification and is useful in reducing the requirements of paraffins, thus increasing its recovery. Another strategy that is used to increase the purity of the most adsorbed compound is to use a rinse step. Although this step has been many times used at the same pressure of the feed step, the main purpose of the rinse step is only to displace the less adsorbed gas out of the column. If the rinse is performed with the most adsorbed component at a higher partial pressure than in the feed stream, it will adsorb, generating lots of undesired effects at the same time: requiring more gas, increasing the thermal swing of the system due to the released heat of adsorption and requiring more power to increase the pressure of the stream removed at the lowest pressure of the system. This is particularly important in this case where the content of CO_2 is only 10%.

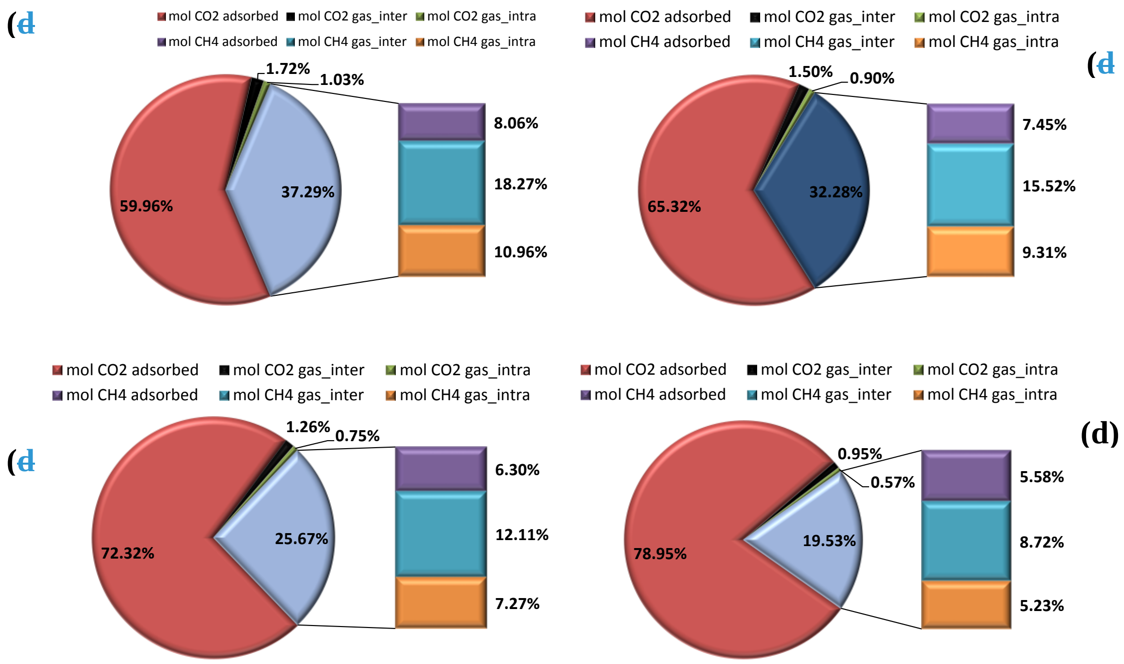
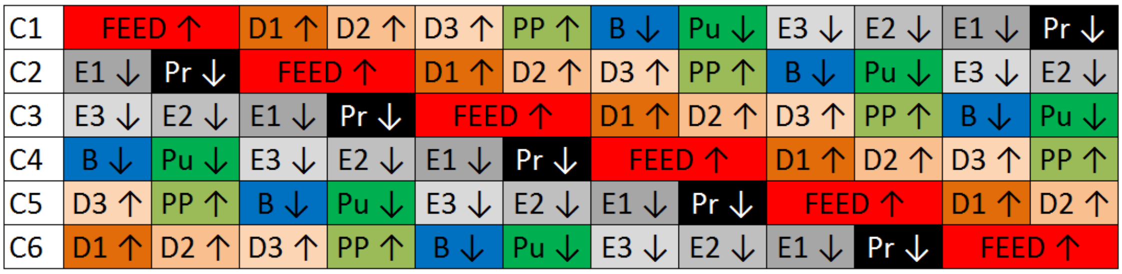


Figure 16. Estimated amount of CO_2 and CH_4 in the column at the end of feed step (a), end of first (b), second (c) and third (d) depressurizing pressure equalization steps.

Based on all the initial considerations, the initial cycle tested for this application was the one shown in Figure 17. In the initial cycle, no rinse step was used. The image of the PSA used for modelling of this cycle is shown in Figure 18. The performance of this unit has already been simulated and reported for the separation of a binary mixture 90% CH_4 - 10% CO_2 [87]. The maximum purity that this unit can deliver is around 40%, thus requiring a second PSA unit to improve the purity from 40% to around 90%. Between the two PSA units, a compressor should be placed in order to compress the streams exiting the blowdown and purge steps. A mass balance of the dual PSA unit performance is presented in Figure 19. The requirement of two compressors for internal recycles involving significant amount of gas imply that the energy consumption of this process is large and thus will not be viable for upgrading natural gas.



C1	FEED ↑		D1 ↑	D2 ↑	D3 ↑	PP ↑	B ↓	Pu ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓
C2	E1 ↓	Pr ↓	FEED ↑		D1 ↑	D2 ↑	D3 ↑	PP ↑	B ↓	Pu ↓	E3 ↓	E2 ↓
C3	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑		D1 ↑	D2 ↑	D3 ↑	PP ↑	B ↓	Pu ↓
C4	B ↓	Pu ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑		D1 ↑	D2 ↑	D3 ↑	PP ↑
C5	D3 ↑	PP ↑	B ↓	Pu ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑		D1 ↑	D2 ↑
C6	D1 ↑	D2 ↑	D3 ↑	PP ↑	B ↓	Pu ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑	

Figure 17. Six-column cycle comprising feed, three pressure equalization steps, blowdown and purge step using gas from a provide-purge step.

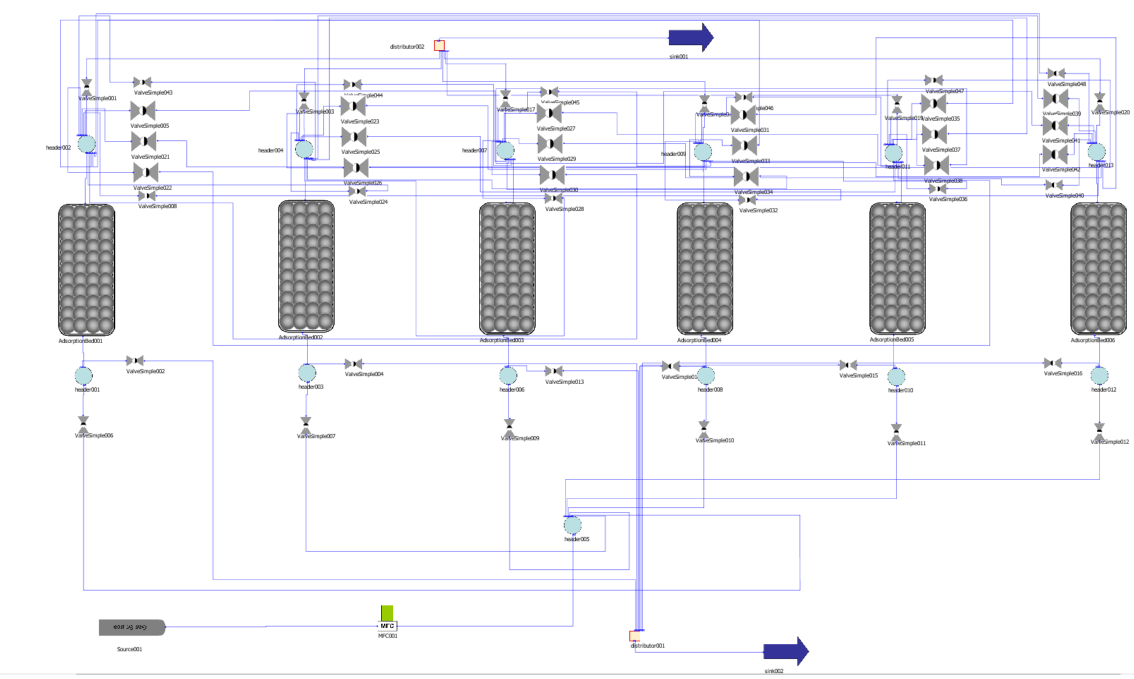


Figure 18. Scheme of the PSA unit used for modelling a 6-column cycle.

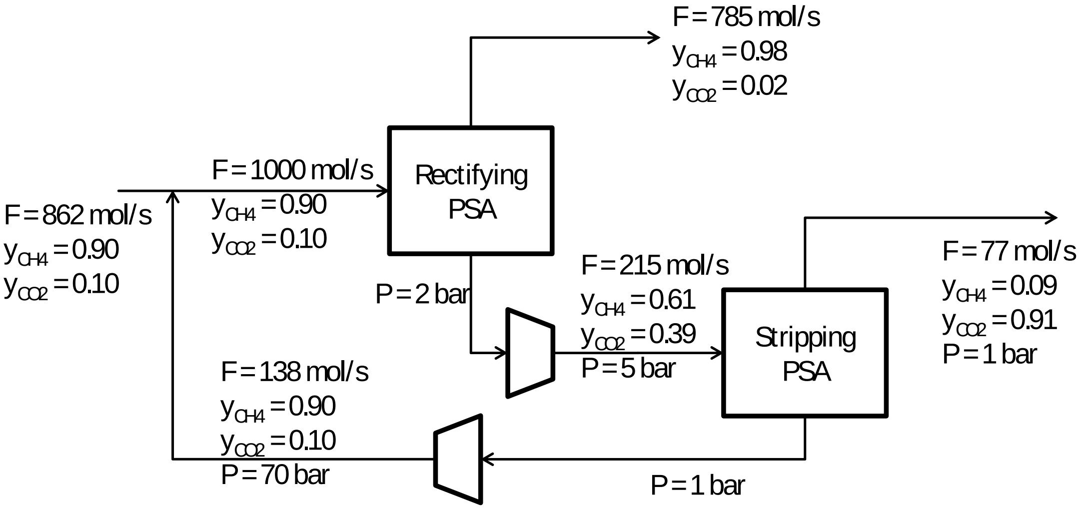
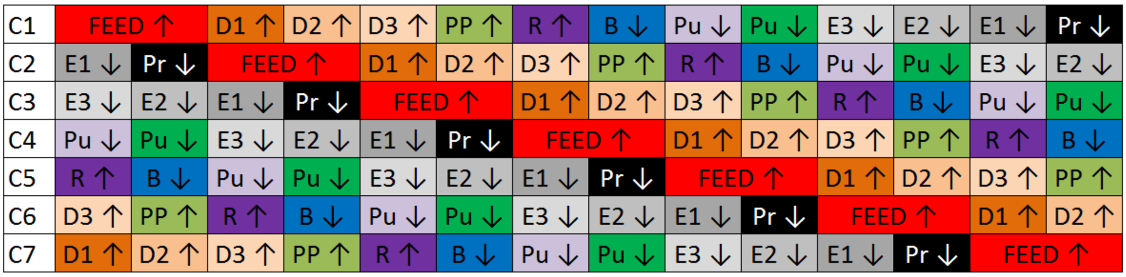


Figure 19. Mass balance of a dual PSA unit for upgrading of natural gas using the cycle shown in Figure 18.

In order to improve the purity of the CO_2-rich stream obtained in the first PSA stage (rectifying PSA), a rinse step was included in the cycle. The new cycle configuration is shown in Figure 20. In order to comply with the cycle requirements a new column has to be added. Note that in this cycle, the purge stream contains the gas that exits the columns from the "provide purge" and "rinse" steps and for this reason they are indicated in different colours. With this approach it was possible to increase and tailor the CO_2 purity since a good control of the location of the CO_2 concentration is possible. The rinse with a fraction of the CO_2-rich stream is recycled to the PSA at a pressure of around 9 bar so in principle, since the CO_2 stream is to be compressed to 110 bar in a multi-stage compressor, there is no need to include a new compressor in the unit, just accounting for this recycle in some of the compression stages.

Once a proper cycle has been established, its tailored design should be performed. The main weakness of the cycle shown in Figure 20 is that all the incoming stream is processed by a single column and thus the column diameter of the seven columns must be quite large. The size is a big issue because the "time on stream" of one column is only 1/7th of a cycle: desorption takes six times more than the time allocated to the adsorption step and that makes the size of the PSA extremely large.

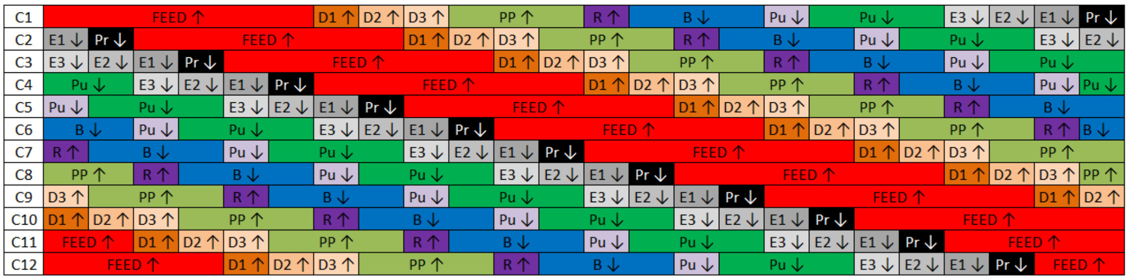


C1	FEED ↑		D1 ↑	D2 ↑	D3 ↑	PP ↑	R ↑	B ↓	Pu ↓	Pu ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓
C2	E1 ↓	Pr ↓	FEED ↑		D1 ↑	D2 ↑	D3 ↑	PP ↑	R ↑	B ↓	Pu ↓	Pu ↓	E3 ↓	E2 ↓
C3	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑		D1 ↑	D2 ↑	D3 ↑	PP ↑	R ↑	B ↓	Pu ↓	Pu ↓
C4	Pu ↓	Pu ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑		D1 ↑	D2 ↑	D3 ↑	PP ↑	R ↑	B ↓
C5	R ↑	B ↓	Pu ↓	Pu ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑		D1 ↑	D2 ↑	D3 ↑	PP ↑
C6	D3 ↑	PP ↑	R ↑	B ↓	Pu ↓	Pu ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑		D1 ↑	D2 ↑
C7	D1 ↑	D2 ↑	D3 ↑	PP ↑	R ↑	B ↓	Pu ↓	Pu ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑	

Figure 20. Seven-column cycle comprising feed, three pressure equalization steps, provide purge, rinse, blowdown and purge step using gas from a provide-purge step.

In order to tackle both of these problems, a multiple feed cycle was conceived. Multi-feed strategy is common practice in hydrogen purification applications [88-90] but they do not include the possibility of a rinse step, so the cycle presented in Figure 21 has not been presented before in literature. The cycle presented in Figure 21 has multiple advantages when compared to the ones previously shown:

1. Multiple feed allows the feed stream to be divided into three columns at all times. That means that the column diameter of the column can be much smaller and despite of having more columns, the amount of adsorbent is significantly lower. To keep the same feed velocity, the amount of adsorbent used in the 12-column cycle is 32% smaller than the 6-column cycle and is 42% smaller than in the case of the 7-column cycle.
2. The "time on stream" of the column is larger than in previous cases corresponding to 1/4th of the time. That also contributes to a smaller PSA unit.
3. Once that the flowrate exiting the blowdown step is varying exponentially with temperature, having two columns performing blowdown at the same time will reduce the flowrate variations of the CO_2-rich stream.
4. The system is flexible and purge and rinse scheduling can be changed to provide more flexibility to the unit. What is important is that the following relation is maintained: $t_{pp} + t_r = t_{cycle}/6$.

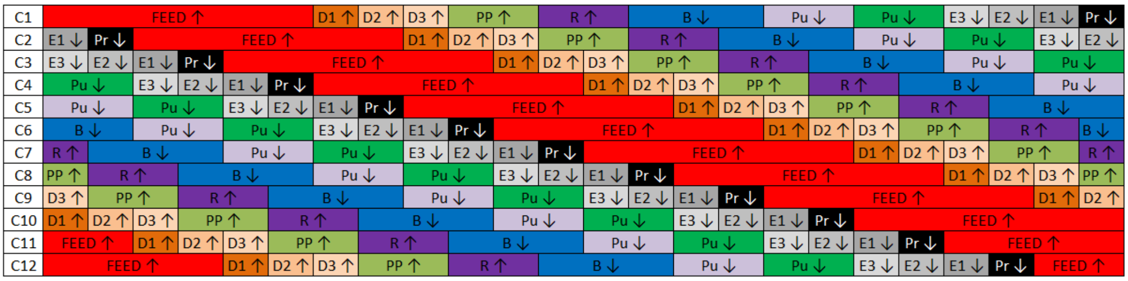


C1	FEED ↑						D1 ↑	D2 ↑	D3 ↑	PP ↑			R ↑	B ↓			Pu ↓	Pu ↓			E3 ↓	E2 ↓	E1 ↓	Pr ↓
C2	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	PP ↑			R ↑	B ↓			Pu ↓	Pu ↓			E3 ↓	E2 ↓
C3	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	PP ↑			R ↑	B ↓			Pu ↓	Pu ↓		
C4	Pu ↓		E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	PP ↑			R ↑	B ↓			Pu ↓	Pu ↓
C5	Pu ↓	Pu ↓			E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	PP ↑			R ↑	B ↓		
C6	B ↓		Pu ↓	Pu ↓			E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	PP ↑			R ↑	B ↓
C7	R ↑	B ↓			Pu ↓	Pu ↓			E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	PP ↑		
C8	PP ↑		R ↑	B ↓			Pu ↓	Pu ↓			E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	PP ↑
C9	D3 ↑	PP ↑			R ↑	B ↓			Pu ↓	Pu ↓			E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑
C10	D1 ↑	D2 ↑	D3 ↑	PP ↑			R ↑	B ↓			Pu ↓	Pu ↓			E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑					
C11	FEED ↑		D1 ↑	D2 ↑	D3 ↑	PP ↑			R ↑	B ↓			Pu ↓	Pu ↓			E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑			
C12	FEED ↑				D1 ↑	D2 ↑	D3 ↑	PP ↑			R ↑	B ↓			Pu ↓	Pu ↓			E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑	

Figure 21. Twelve-column cycle comprising multi-column feed, three pressure equalization steps, provide purge, rinse, blowdown and purge step using gas from a provide-purge step.

It should be noted however that when the configuration of the provide purge and rinse steps is changed, some physical changes might be required. For example in the cycle shown in Figure 22, the provide purge step and the purge steps are not matching directly from one column to the other so each column should have two valves for the purge step.

Using the cycle reported in Figure 21, the total number of valves per column is 10: feed (top and bottom), provide gas to pressurization, three depressurizations, provide purge, rinse (top and bottom) and blowdown (and purge). This means that the PSA will have at least 120 valves.



C1	FEED ↑						D1 ↑	D2 ↑	D3 ↑	PP ↑		R ↑		B ↓			Pu ↓		Pu ↓		E3 ↓	E2 ↓	E1 ↓	Pr ↓
C2	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	PP ↑		R ↑		B ↓			Pu ↓		Pu ↓		E3 ↓	E2 ↓
C3	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	PP ↑		R ↑		B ↓			Pu ↓		Pu ↓	
C4	Pu ↓		E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	PP ↑		R ↑		B ↓			Pu ↓	
C5	Pu ↓		Pu ↓		E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	PP ↑		R ↑		B ↓		
C6	B ↓		Pu ↓		Pu ↓		E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	PP ↑		R ↑		B ↓
C7	R ↑	B ↓			Pu ↓		Pu ↓		E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	PP ↑		R ↑
C8	PP ↑	R ↑		B ↓			Pu ↓		Pu ↓		E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑	D3 ↑	PP ↑
C9	D3 ↑	PP ↑		R ↑		B ↓			Pu ↓		Pu ↓		E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑						D1 ↑	D2 ↑
C10	D1 ↑	D2 ↑	D3 ↑	PP ↑		R ↑		B ↓			Pu ↓		Pu ↓		E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑					
C11	FEED ↑		D1 ↑	D2 ↑	D3 ↑	PP ↑		R ↑		B ↓			Pu ↓		Pu ↓		E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑			
C12	FEED ↑				D1 ↑	D2 ↑	D3 ↑	PP ↑		R ↑		B ↓			Pu ↓		Pu ↓		E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑	

Figure 22. Alternative twelve-column cycle comprising multi-column feed, three pressure equalization steps, provide purge, rinse, blowdown and purge step using gas from a provide-purge step.

The typical results of the cycle shown in Figure 21 for the separation of a stream comprising 88% CH_4 – 10% CO_2 and 2% C_2H_6 are described below. The pressure history of each of the columns in cycle 21 is shown in Figure 23. In a normal simulation, the cyclic steady state (CSS) was reached after 20-25 cycles. Despite of being a kinetic adsorbent where CSS is achieved after many cycles, in this case, only few cycles were necessary. The product composition at the end of the distributors at the top and bottom of the PSA unit is displayed in Figure 24. The oscillations in the composition are due to the flow variations in the system. In the final unit design, such oscillations are controlled with a tank and a valve with a PIC control unit.

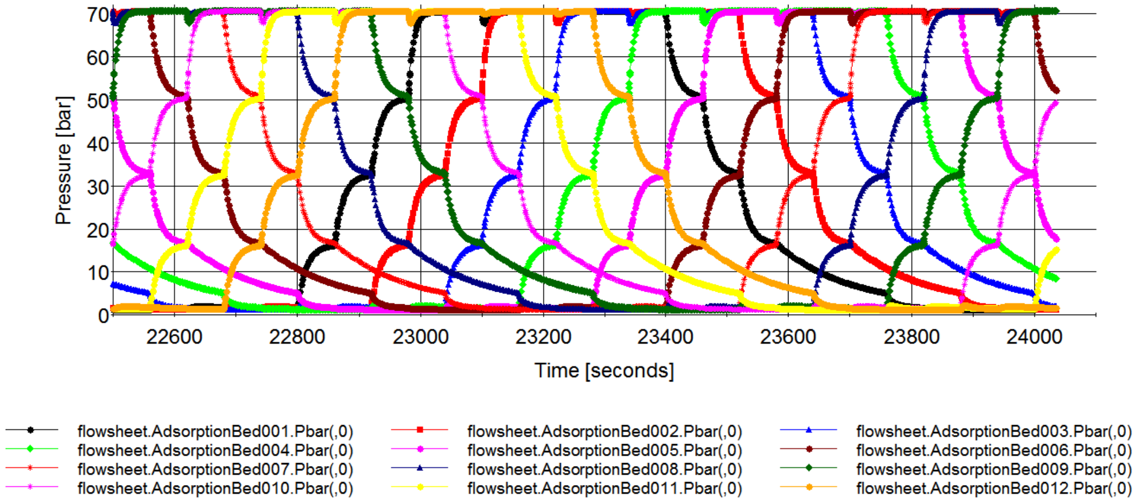


Figure 23. Pressure history at the exit of each column in a 12-column multi-feed PSA cycle.

The CO_2 product purity obtained with the cycle shown in Figure 21 is ~ 69%. It is also observed that the ethane is almost equally divided into both top and bottom products, with a significant fraction ending up in the CO_2-rich stream. This cycle has many variables that should be optimized in order to operate the PSA under optimal conditions for the specific feed composition. These variables comprise the flowrate of rinse and purge steps and the extent of the pressure equalizations. All these variables are controlled with the valve coefficients: i. e. if the valves allow the passage of a higher flowrate, the flowrate of the gas transferred from one column to the other will be larger. Several attempts to optimize such variables resulted in different performance, but the purity of CO_2 was nearly unchanged. This is due to the fact that ultimately, the gas being transferred in the provide purge and rinse steps end up with the CO_2-rich stream since they are collected from the bottom of the column. At the beginning of the provide purge, the column is at a total pressure of ~ 18 bar and it has a large content of methane. This means that the only way to control the CO_2 purity of the PSA unit will be to exclude the recycling of the stream exiting the rinse step to another column for its regeneration. This will have an impact in natural gas and CO_2 recovery and also, the concentration of C_{2+} in this stream is quite high, resulting in higher value of the loss. Alternative is to compress it and recycle it to the feed stream.

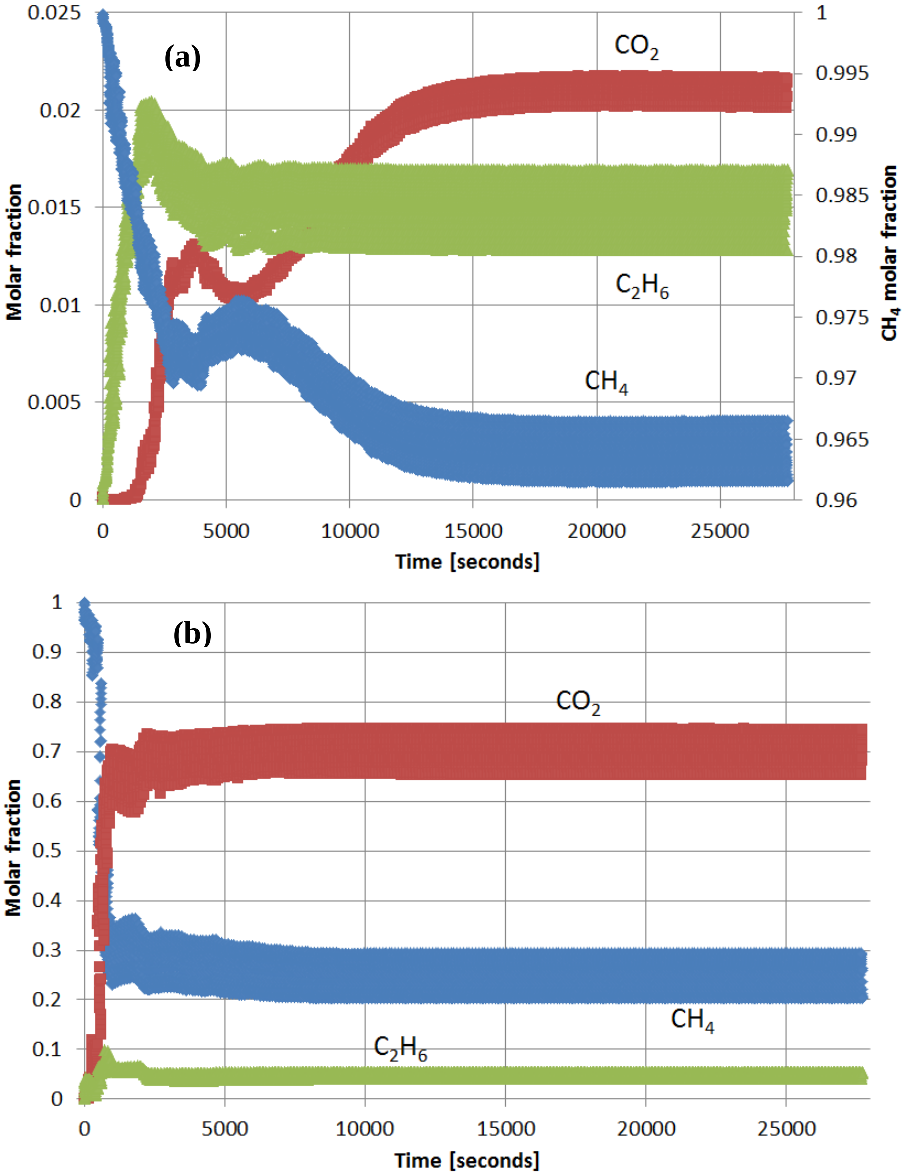
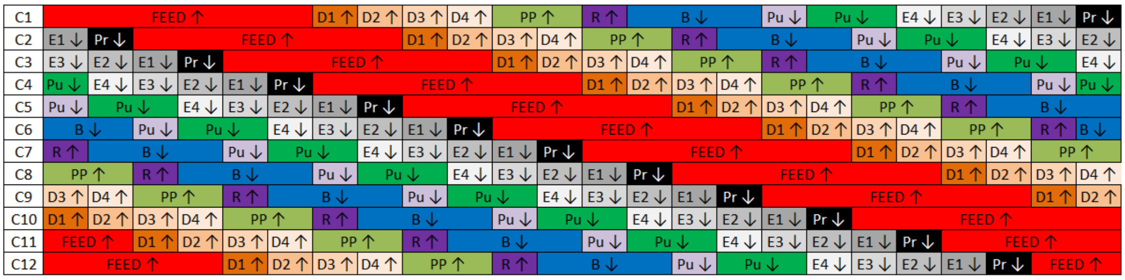


Figure 24. History of molar fraction in the top (a) and bottom (b) distributors of the PSA unit for cycle shown in Figure 22.

Another alternative is to further reduce the pressure before the provide purge step by adding another pressure equalization. This alternative will have an impact in the CO_2 purity without adding an extra compressor. The final cycle designed is thus presented in Figure 25. This cycle kept all the advantages of the other 12-column cycles but adding another pressure equalization and shortening the time for purge + rinse. The pressure history of a cycle under cyclic steady state is shown in Figure 26. As can be seen, the pressure at the beginning of the provide purge step is ~ 14 bar which has a great impact in the purity of the CO_2-rich stream, increasing its value to around 73%.

With this cycle, the total mass balance of the PSA unit is shown in Figure 27. The operating conditions and the variables used to describe the 12-column PSA unit



C1	FEED ↑	D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑	R ↑	B ↓	Pu ↓	Pu ↓	E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	
C2	E1 ↓	Pr ↓	FEED ↑	D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑	R ↑	B ↓	Pu ↓	Pu ↓	E4 ↓	E3 ↓	E2 ↓	
C3	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑	D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑	R ↑	B ↓	Pu ↓	Pu ↓	E4 ↓	
C4	Pu ↓	E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑	D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑	R ↑	B ↓	Pu ↓	Pu ↓
C5	Pu ↓	Pu ↓	E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑	D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑	R ↑	B ↓	
C6	B ↓	Pu ↓	Pu ↓	E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑	D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑	R ↑	B ↓
C7	R ↑	B ↓	Pu ↓	Pu ↓	E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑	D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑	
C8	PP ↑	R ↑	B ↓	Pu ↓	Pu ↓	E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑	D1 ↑	D2 ↑	D3 ↑	D4 ↑	
C9	D3 ↑	D4 ↑	PP ↑	R ↑	B ↓	Pu ↓	Pu ↓	E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑	D1 ↑	D2 ↑	
C10	D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑	R ↑	B ↓	Pu ↓	Pu ↓	E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑	
C11	FEED ↑	D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑	R ↑	B ↓	Pu ↓	Pu ↓	E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑
C12	FEED ↑	D1 ↑	D2 ↑	D3 ↑	D4 ↑	PP ↑	R ↑	B ↓	Pu ↓	Pu ↓	E4 ↓	E3 ↓	E2 ↓	E1 ↓	Pr ↓	FEED ↑

Figure 25. Twelve-column cycle comprising multi-column feed, four pressure equalization steps, provide purge, rinse, blowdown and purge step using gas from a provide-purge step.

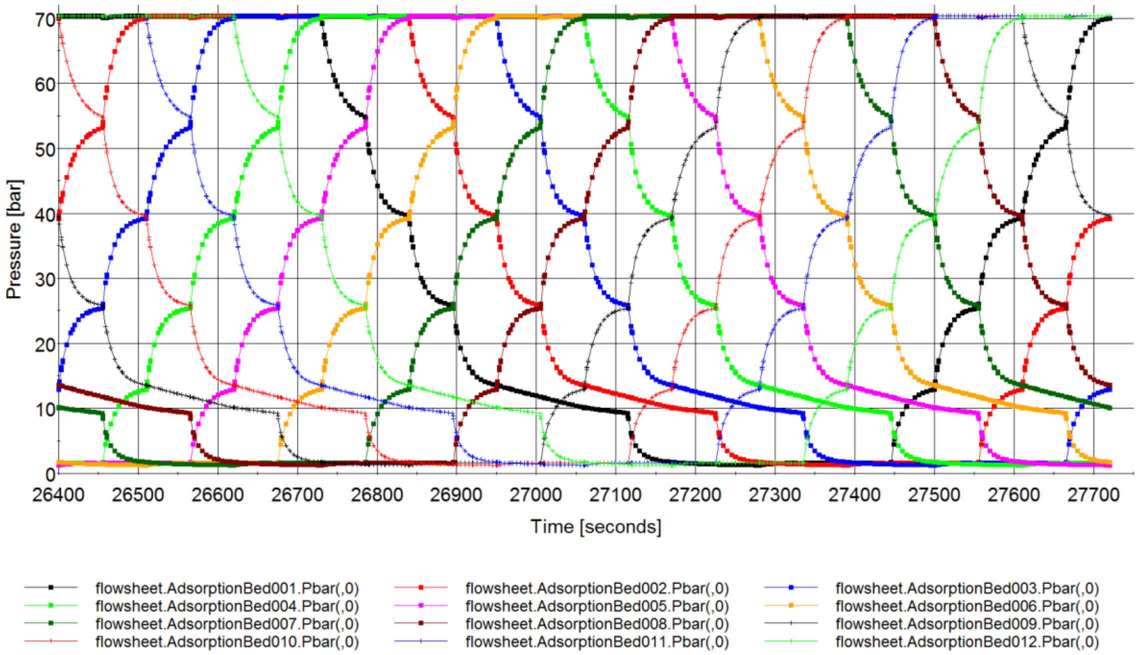


Figure 26. Pressure history at the exit of each column in a 12-column multi-feed PSA cycle with 4 pressure equalizations.

Adding extra pressure equalization steps will not solve the problem in a consistent way since the pressure equalizations will be less and less effective. The main solution to reduce the content of CH_4 (and C_2H_6) in the CO_2-rich product is to additionally remove an exit stream between the feed step and the blowdown step. This stream can be a side product for internal combustion if required or can be recycled to the feed step. Although the decision will depend on local plant needs, the position where this stream is removed will certainly contribute in changing the performance of the PSA unit.

In this case, the initial amount of methane available at higher pressures is removed from the column and recycled to the feed step. The decision of recycling the stream at higher pressure was only to reduce the overall power consumption of the system. The mass balance of the final PSA unit is shown in Figure 28. Adding the extra recycle of light gas, it was possible to increase the purity of CO_2 to almost 85%. Additionally, since the CO_2 concentration front moves further in the column, it is possible to recover more C_2H_6 with the light product.

In Figure 28, a "black-box" mass balance was presented in order to simplify the presentation of the results. The PSA unit design for NG upgrading will thus have the design shown in Figure 29. It is composed by twelve columns, three tanks and two compressors other than the compression train for the CO_2-rich stream that will be sent for EOR. Depending on the compression train used for EOR, it might be possible to eliminate one compressor by just increasing the capacity of the first compression stage to accommodate the internal recycle also.

The unit shown in Figure 29 is a first-of-a-kind and is still not optimized. The design of large PSA units is not an easy task, particularly when specifications are provided to both exiting streams. As it can be understood from the evolution of the cycle development, the main problem to achieve a high CO_2 purity is the large amount of paraffins in the gas phase of the column before the blowdown step. A significant portion of the cycle time is devoted to reduce the paraffin content by successive pressure equalizations. This indication means that if the PSA unit is thought to separate streams with higher CO_2 content than 10%, the problem might not be impossible to solve with this unit having the advantage of a higher partial pressure of CO_2 resulting thus in a higher loading.

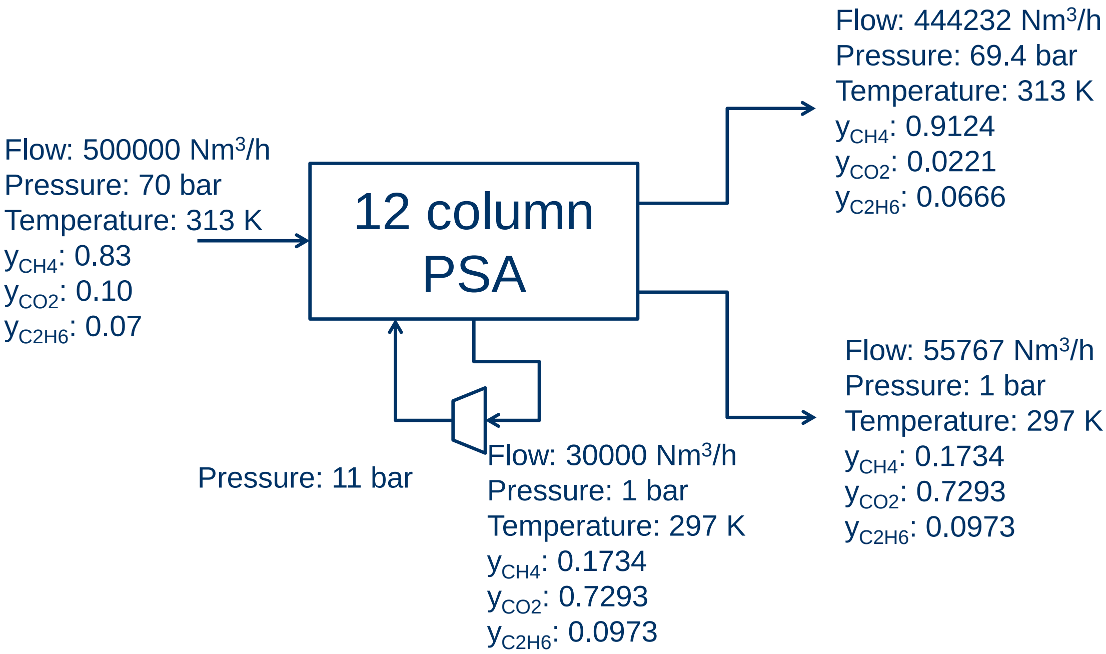


Figure 27. Mass balance of 12-column PSA unit to upgrade NG to pipeline specifications with integrated CO_2 capture.

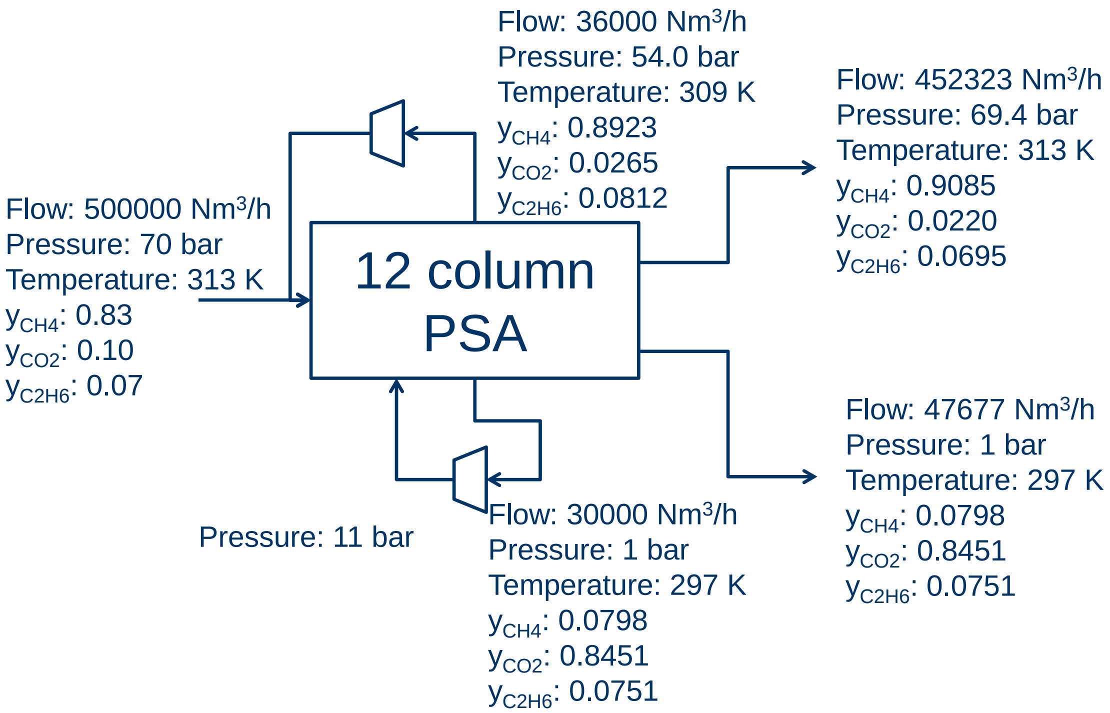


Figure 28. Mass balance of 12-column PSA unit to upgrade NG to pipeline specifications with integrated CO_2 capture.

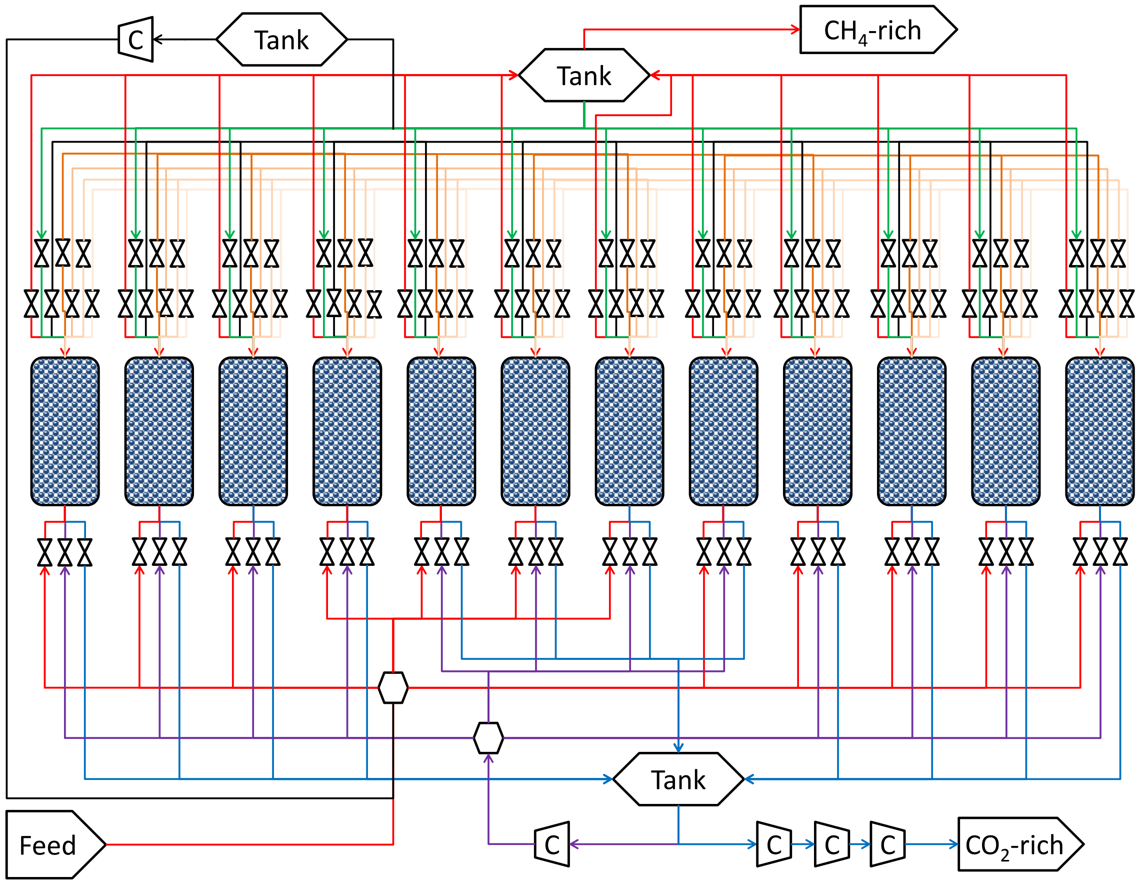


Figure 29. Diagram with the main components of the twelve-column PSA unit for natural gas upgrading including internal recycles and tanks.

5.6 Cost estimation

The cost breakdown of equipment and direct cost of the adsorption based process are reported in Table 12. The evaluation show that the adsorption columns account for around 50% of the total direct cost, while the CO_2 conditioning section accounts for around 20% of the total direct cost while the internal compression and the buffer tanks account for the remaining part of the cost.

Table 12. Indicative equipment and direst costs breakdown of the adsorption based process

Unit	**Equipment cost [k€]**	**Direct cost [k€]**
Adsorber	17,700	27,400
Internal compression	5,200	8,200
Buffer tanks	3,100	6,800
CO_2 conditioning for transport (1st stage)	1,900	2,900
CO_2 conditioning for transport (2nd stage)	1,700	2,400
CO_2 conditioning for transport (3rd stage)	1,400	2,000
CO_2 pumping for transport	1,800	2,900
Total	**32,600**	**52,500**

Regarding the annual fixed operating cost, the labour cost including supervision and administration is evaluated to 700 k€/y based on the methodology presented previously while the maintenance, insurance, local taxes and fees correspond to 2,300 k€/y. This results in a total fixed operating cost of 3,000 k€/y.

Table 13 provides a summary of cost associated with utilities and sorbent consumption, the CO_2 stream transport and storage cost, as well as the loss of revenues due to the natural gas[5] present in the CO_2 stream. Indeed, compared to the solvent based case, the CO_2 stream in the adsorption case contain around 15.5 % of methane and ethane which are not produced as a NG product and therefore lead to a 1.6% decrease of the amount of natural gas which can be sold. The estimation shows that the loss of revenues due to the natural gas associated with the CO_2 stream account for more than 55% of the annual cost while the electricity consumption account and the CO_2 stream transport and storage accounts respectively for 23% and 20% of the cost.

Table 13. Cost of consumables the adsorption based process

	Annual consumption	**Annual cost [k€/y]**
Lost revenue from gas sales	2.76 [10^6GJ/y]	16,500
Electricity	88 [GWh/y]	7,000
Cooling water	1,150 [m^3/y]	0.5
Sorbent make up	89 [t/y]	600
CO_2 and Natural Gas transport and storage	80 [t/h]	6,000
Total variable operating cost consumption	-	30,100

Table 14 summarizes the results of the cost assessment of CO_2 removal from natural gas using an adsorption based concept with the case and boundary conditions presented

---

[55] This loss of revenues is here accounted as an additionnal cost compared to the solvent based case.

previously while Figure 30 presents the comparison of the adsorption based process with the reference solvent process. The evaluation shows that the natural gas losses in the CO_2 stream which represent 40% of the overall cost is a major part of the removal cost, while the investment, the electricity and the CO_2 transport and storage cost represent respectively 21, 17 and 16% of the cost.

The importance of the loss in natural gas revenue points out the potential of improving the process design and/or the sorbent selected in order to decrease the amount of natural gas present in the CO_2 stream which could therefore significantly decrease the natural gas sweetening cost. This impact of this potential improvement on the process cost will here be address through sensitivity analyses.

Table 14. Overall cost KPIs of the adsorption based process

	Cost
Discounted cost flow including transport and storage (k€)	432,500
Sweetening cost including transport and storage (€/kNm^3_{raw})	11.3
Sweetening cost including transport and storage (€/kNm^3_{sweet})	12.5
CO_2 removal cost including transport and storage (€/$t_{CO2,captured}$)	77
CO_2 removal cost without CO_2 conditioning, transport and storage (€/$t_{CO2,captured}$)	49
CO_2 avoided cost (€/$t_{CO2,avoided}$)	29

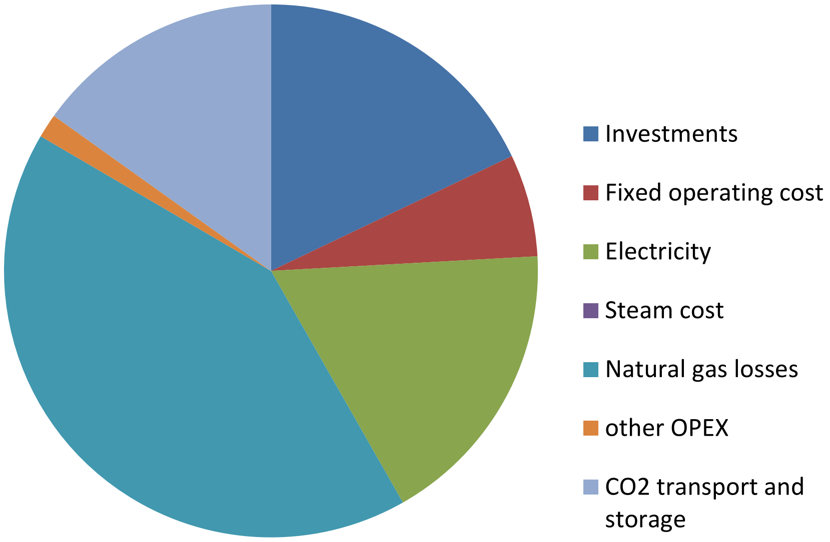


Figure 30. Break-down of the total discounted cost of the adsorption based process including CO_2 conditioning, transport and storage

As shown in Figure 31, the comparison of both processes shows that the adsorption based process lead to sweetening costs around 65% higher than the solvent based process for the reasons presented previously. In addition, the adsorption based process lead to CO_2 removal cost including transport and storage, CO_2 captured cost and CO_2

avoided cost respectively 50, 60 and 40% higher than with the reference CO_2 removal process.

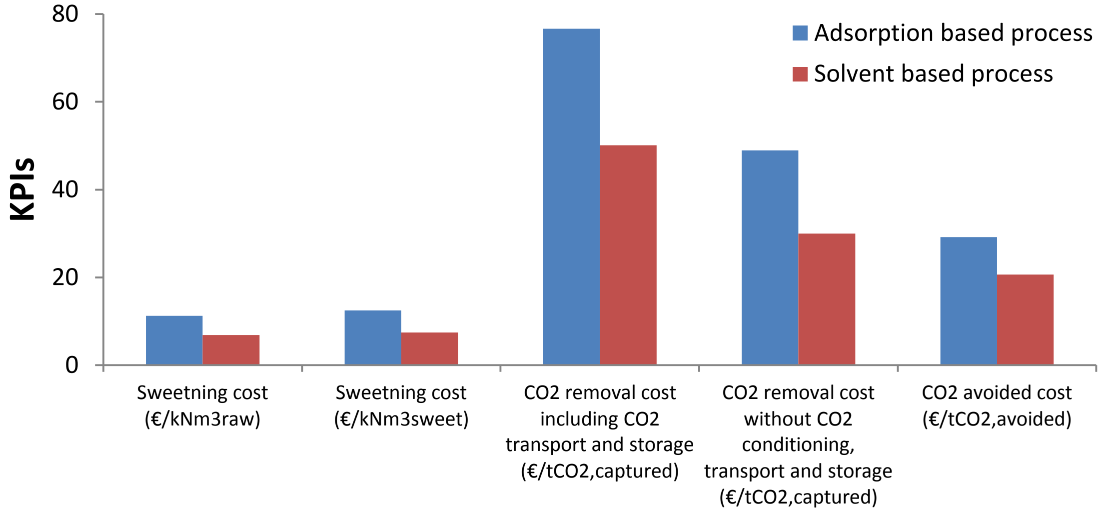


Figure 31. Comparison of both CO_2 removal technologies cost Key Performance Indicators (KPIs)

5.7 Sensitivity analysis

Sensitivity analyses are then performed in order to address and quantify the impact of a range of uncertainties and site specific characteristic issues on the cost performances of both the technology cost: investment cost, operating cost, discount rate, plant life, electricity cost, adsorbent cost, CO_2 transport and storage cost.

Figure 32 presents the results of the sensitivity analyses on the CO_2 removal cost including CO_2 conditioning, transport and storage. The assessment shows that the cost uncertainties which influence both technologies the most are gas price (due to the steam consumption in the solvent based process and the losses in the CO_2 stream in the adsorbent based process), variable OPEX and the transport and storage cost while the on-site steam availability is also an important factor for the cost of the solvent based process. More importantly, the sensitivity analyses show that the reduction of the amount of natural gas lost in the CO_2 stream represents major opportunity to reduce the CO_2 removal cost of the adsorbent based process. This reduction could be achieved for example by process or material improvement or by adding addition purification of the CO_2 stream after the considered adsorption process.

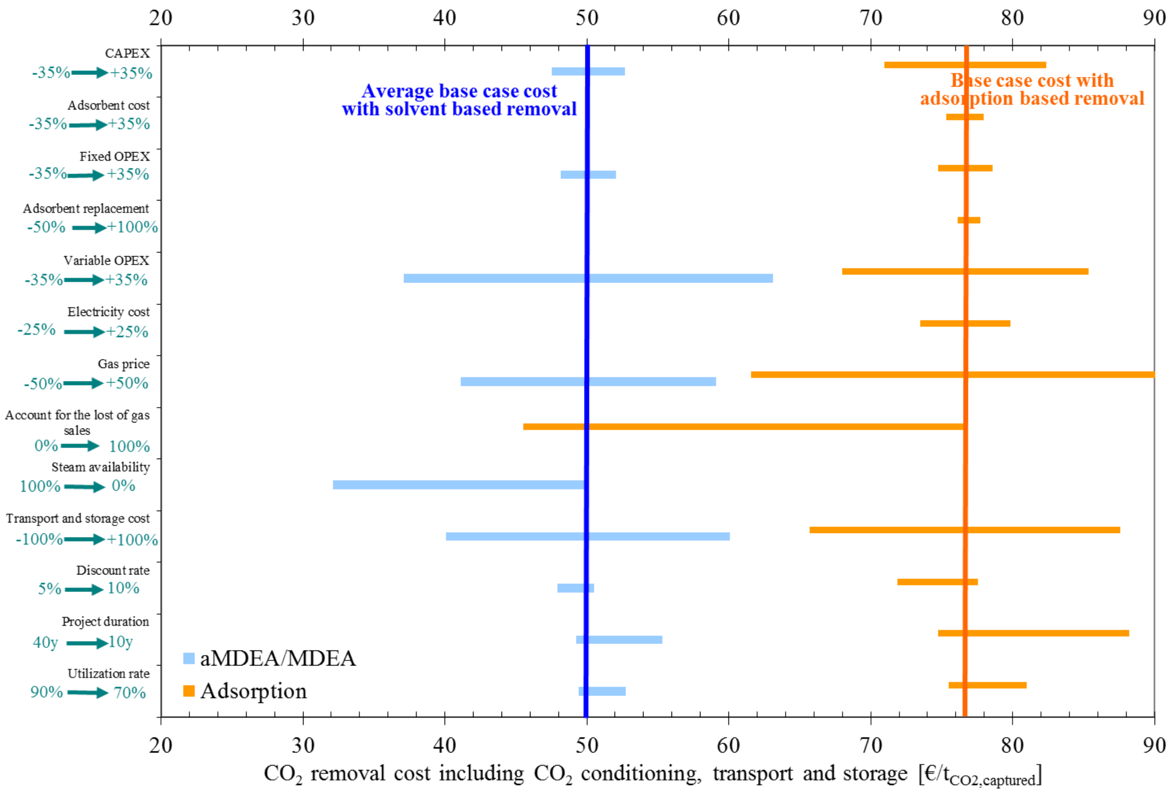


Figure 32. CO_2 removal cost including CO_2 conditioning, transport and storage

As discussed previously, the removal of CO_2 from the natural gas stream is required to meet the natural gas transport specification independently of this CO_2 removal being coupled with CCS or vented. Therefore only the cost of conditioning, transport and storing the CO_2 after removal shall be included in order to evaluate the decision to associate or not CCS with the CO_2 removal from natural gas [42]. Figure 33 present the influence of cost uncertainties on the CO_2 avoided cost.

The sensitivity analyses show that uncertainties and the CO_2 transport and storage cost, the electricity cost and the variable OPEX (through both previous parameters) are the parameters influencing the CO_2 avoided cost the most while other parameters have rather small to no effect on the CO_2 avoided cost.

In addition of the quantification on the cost uncertainties, the sensitivity analyses shows that CO_2 avoided cost associated with the adsorption based process will remain higher than with the solvent based process even considering the cost uncertainties. This is mainly due to higher electricity consumption in the CO_2 stream conditioning of adsorption based process as the CO_2 stream after removal is delivered at 1 bar instead of 1.9 bar in the solvent process and the increased CO_2 stream mass flow due to the present of 15% methane and ethane. Finally, the increased CO_2 mass flow also leads to higher CO_2 transport and storage cost.

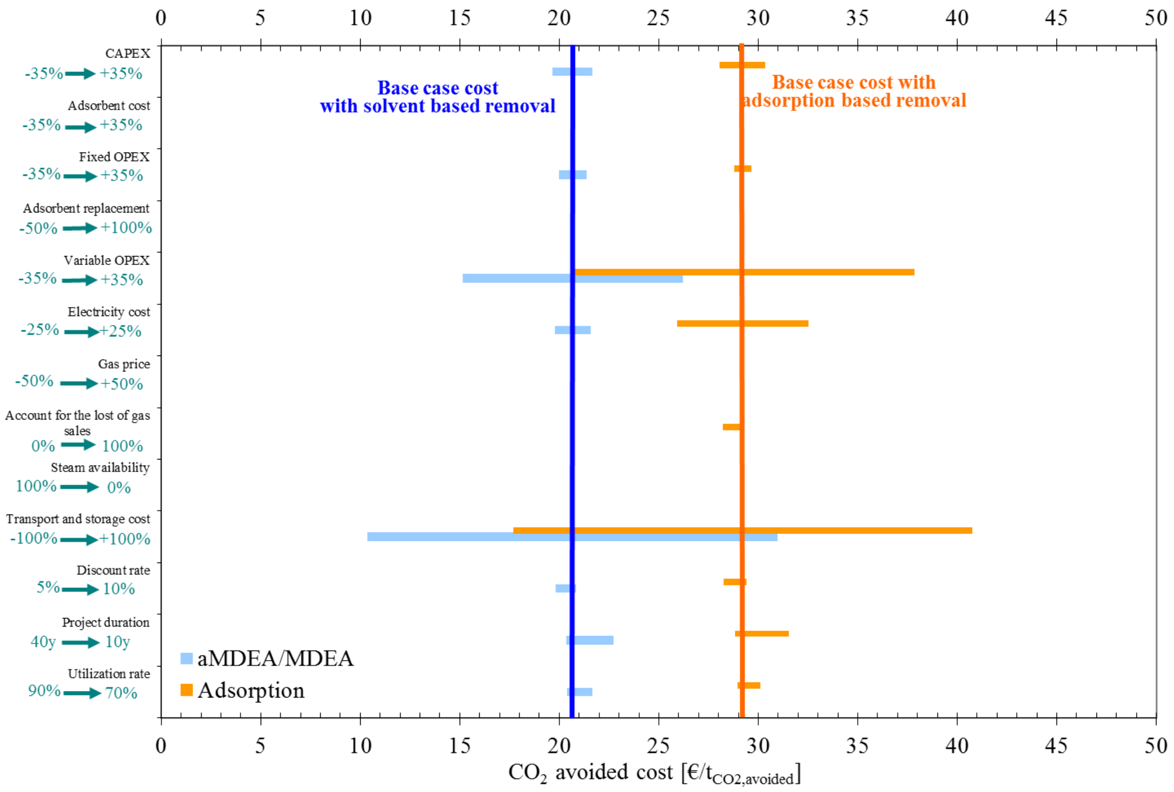


Figure 33. Sensitivity analyses on the CO₂ avoided cost

5.8 Process benchmarking

A summary of the technical and cost Key Performance Indicators of the solvent based process (reference) and the adsorption based process is presented in Table 15. The comparison shows that the solvent based process is more efficient from an energy point of view both in term of electricity and steam consumptions as well as in term of natural gas losses in the CO_2 stream. In addition, the adsorption process is expected to take significantly more places than the reference process as shows through the adsorption columns volume is 4.5 times bigger than the absorber and desorber volumes in the solvent based process.

Regarding cost, the solvent system is also more cost efficient in term of investments, variable operating costs and total discounted cost which is 40% lower than the cost of the adsorption based process while the fixed operating cost are lower as the adsorption process is more automatized and require lower labour costs. However as discussed previously, a major cost in the adsorption process is due to the natural gas losses in the CO_2 stream which decrease the amount of natural gas which can be sold and increase the cost associated with conditioning, transport and storage of the CO_2 stream. As shown by the sensitivity analyses, the sensitivity analyses shows that the reduction of the amount of natural gas lost in the CO_2 stream represents major opportunity to reduce the CO_2 removal cost of the adsorbent based process and lead to a process more cost efficient than the solvent based process. This reduction could be achieved for example by process or material improvement or by adding addition purification of the CO_2 stream after the considered adsorption process.

In term of cost related KPIS, the considered adsorption based process lead to less performant sweetening, CO_2 removal and CO_2 avoided costs due to its higher total discounted cost. Indeed, the comparison shows indeed that sweetening costs of the adsorption based process is around 65% higher than the solvent based process, while the

CO_2 removal cost including transport and storage, CO_2 captured cost and CO_2 avoided cost respectively 50, 60 and 40% higher than with the reference CO_2 removal process.

Finally, it is important to understand that the results of this benchmarking are specific to the case considered (natural gas flow, CO_2 content, natural gas composition) and that a different case might lead to different relative performance of both processes and therefore different conclusion. In addition, the results presented are also specific the adsorption process considered and that a different process (adsorbent, process configuration, the presence of a purification of the CO_2 stream) would lead to different performances of the adsorption process.

Table 15. Summary of technical and cost KPIs of both CO_2 removal technologies

	Solvent based process	**Adsorption based process**
Electricity consumption (MW)	7.72	11.76
Steam consumption (10^6 GJ/y)	1.02	0
Natural Gas losses (10^6 GJ/y)	0	2.76
Volume of main equipments (m^3)	290	1,293
CAPEX (M€)	38.9	91.6
Fixed OPEX (M€/y)	2.9	3.0
Variable OPEX (M€/y)	19.1	30.1
Total Discounted cost (M€)	265	432
Sweetning cost (€/kNm^3_{raw})	6.9	11.3
Sweetning cost (€/kNm^3_{sweet})	7.5	12.5
CO_2 removal cost including CO_2 transport and storage (€/$t_{CO2,captured}$)	50	77
CO_2 removal cost without CO_2 conditioning, transport and storage (€/$t_{CO2,captured}$)	30	49
CO_2 avoided cost (€/$t_{CO2,avoided}$)	21	29

6: Available kinetic adsorbents: data inventory

As mentioned in Section 5.2, kinetic adsorbents are able to minimize the adsorption of methane and higher molecular weight paraffins with molecular diameters larger than CO_2, even when present at higher pressures. The major benefit of these materials is their ability to adsorb CO_2 much faster than CH_4. A simple way to visualize this is by what is commonly called the "kinetic selectivity" [91]:

$$SEL_k = \frac{K_1}{K_2}\sqrt{\frac{D_1}{D_2}} \qquad [40]$$

The kinetic differences contribute to an increased selectivity. In the separation of CH_4-N_2 with kinetic materials it is also possible to invert the preferred adsorption towards CH_4 [64]. However, since the adsorbent in the PSA unit is in contact with the gas for long periods of time, the equilibrium selectivity (given by the adsorption constants) will have an important role. This behaviour is characterized by a very long time to be taken to reach cyclic steady state (CSS) when compared to equilibrium-based adsorbents.

Kinetic adsorbents are traditionally chosen for biogas upgrading. Biogas separation is basically a similar separation with similar gases (mostly CH_4, CO_2 and some inert gases) but performed at lower pressure levels, often requiring vacuum for regeneration [92]. Indeed, most of the literature mentioned below is related to adsorbents studied for this application.

In our study, the CMS material presents a reasonable good kinetic selectivity, but relatively poor equilibrium selectivity when compared with other materials. Activated carbons in general adsorb significant amounts of CH_4 at higher pressures. This means that using a material with similar kinetic effects but with higher equilibrium selectivity it will allow the PSA to have a better performance and possibly smaller footprint. Unfortunately, many of the materials were not tested at the pressure level considered in this study.

In this section, we will present some candidate materials that are not commercial but that were also reported as having kinetic limitations to CH_4 adsorption.

Zeolites are in the market for the past several years. When the cation of zeolite A is sodium, the pores of the zeolite are around 4Å while when the cation is potassium, the pores are around 3Å (and only gases like water or hydrogen can penetrate through them). Zeolite 4A is not a kinetic adsorbent for this mixture. Recently, a combination of Na and K cations was used [93]. It was reported that when zeolite 4A ($|Na_{12}|$-LTA) is modified to $|Na_{12-x}K_x|$-LTA such that $x \geq 1.8$, it is possible to significantly reduce the amount of methane adsorbed and thus transform it into a kinetic material. Unfortunately, the isotherms of CO_2 are still too steep requiring vacuum to desorb CO_2.

Eight-membered zeolites have a channel structure with 8-membered rings of tetrahedra defining the diffusion in the channels [94]. These zeolites are also substantially acid-free and have high Si:Al molar ratios (about 200). All silica zeolite deca-dodecasil 3R (DD3R) is one example of this kinetic selectivity [95, 96]. With equilibrium selecitivity around 2-3 favourable to CO_2, the kinetic selectivity goes to above 50 indicating the diffusional restrictions to adsorb methane. Chabazites, Si-CHA, rho (with different cations presenting a trap-door mechanism) and natural zeolites can also present kinetic effects [97-100]. The main problem of all these materials is that the isotherms of CO_2 are very steep requiring vacuum for significant regeneration. A possibility to overcome the high steepness of CO_2 isotherms is to change the Si:Al ratio as have already been demonstrated for LTA zeolites [101]. It was reported that for Si:Al > 3.5 it is possible to significantly reduce the high steepness while keeping a good CO_2 capacity.

Some materials of the titanosilicates family are other adsorbents that can perform this separation kinetically. ETS-4 (Engelhard titanosilicate) is commercially available and as mentioned before, several studies have reported its properties. Another titanosilicate material with interesting properties for this separation is UPRM-5 [102]. This material presents small pores with diameter that can be tailored with a proper activation procedure. However, adsorption equilibrium data has been reported only until 7 bars.

Metal-organic frameworks (MOFs) are a new class of material that has been extensively studied for CO_2 separation in general. These materials offer a great flexibility because they can combine the power of organic chemistry (to use different linkers) with inorganic chemistry (to be used as active metal sites for example). Many MOF materials present extraordinary specific surface areas and also high capacities towards CO_2 and some materials present a structural flexibility that allows them to have a higher capacity at higher pressures. However, very few MOF materials can be categorized as kinetic materials to perform this separation. $Cu(hfipbb)(H_2hfipbb)_{0.5}$[$H_2$hfipbb = 4,4'-(hexafluoro-isopropylidene)bis(benzoic acid) is one example of the very few materials that present a slight kinetic selectivity [103]. This material has unfortunately low adsorption capacity and also the kinetic selectivity is not very high. In MOF-508b with pores around 4Å, it is also possible to achieve a kinetic separation between CH_4 and CO_2 [104]. The crystal diffusivity of CO_2 is one order of magnitude higher than the diffusivity of CH_4. Single component data is presented up to 5 bars and isotherms are relatively linear which is very positive for PSA applications. Unfortunately, this material presents another common property of MOFs: a relatively low density. This means that even when the capacity for adsorbing gases is relatively good in terms of mass, the required adsorbent volume is high. Zeolitic imidazolate frameworks (ZIFs) are another type of materials that might perform a kinetic separation. Data on this has been presented for propane and propylene [105] and might be extended for separating CH_4-CO_2. According to molecular simulations, a kinetic separation is also possible with ZIF-9 [106].

The list of potential materials is indeed very large, but the amount of data at pressures higher than 10 bars is limited and higher than 30 bars is extremely limited. Additionally it should be mentioned that even when the adsorption data of single gases can be used to envision a PSA unit, it should be verified that the multicomponent adsorption equilibrium is well predicted.

7: Final remarks

7.1 Conclusions

This study is to the knowledge of the authors, the first report that designs a Pressure Swing Adsorption (PSA) process for the separation of CH_4 and CO_2 using a feed pressure of 70 bars and with high flowrates as in the natural gas industry. This report provides a short summary of the available technologies to perform this separation and uses amine scrubbing as a reference case of a mature technology to benchmark a PSA unit that was specifically designed for this report. We have additionally provided a small list of possible candidate materials that can be used for this application and result in improved unit performance.

The PSA unit was designed to upgrade natural gas with a composition of 83% CH_4, 10% CO_2 and 7% C_2H_6 available at a temperature of 313 K and an inlet flowrate of 500,000 Nm^3/h. Due to the lack of existing data at the pressure levels, unpublished adsorption equilibrium and kinetic data of carbon molecular sieve (CMS) available in SINTEF was used for designing the PSA unit. A PSA unit with 12 columns using a multi-feed principle (3 columns processing the feed gas at the same time) with 15 steps including a rinse of CO_2 was necessary to produce pipeline-quality natural gas and CO_2 purity with a purity of 84.5%. it has been observed that in order to minimize gas losses with the CO_2 stream, the number of pressure equalizations have to be significantly increased (a maximum of four was used in this study). A cost comparison between the existing amine scrubbing process and the designed PSA unit indicates that the cost of CO_2 removal (including transport and storage) is 77 €/$t_{CO2,captured}$ compared with 50 €/$t_{CO2,captured}$ obtained in the amine scrubbing process. The main contributor for the higher cost of the PSA unit is the amount of natural gas losses with the CO_2 stream. In the case that a PSA unit can significantly reduce the natural gas losses, costs can be reduced to around 46 €/$t_{CO2,captured}$.

7.2 Future recommendations

This study has reported the initial findings of using an adsorption process for removing CO_2 from natural gas at high pressures. Mostly due to lack of data, two important assumptions were done from the beginning. The gas is dry and there is no H_2S in the stream. In principle, using proper adsorbents, these gases can be removed from the stream using other adsorbents that should be located prior the material to separate CO_2. The decision whether water and H_2S are removed using layers in the same columns or in different pre-purification steps should result from a final economic study, although initial guess is that removing all components in the same vessels should be more economically feasible.

The number of adsorbent materials where data is available at pressures about 70 bar is very limited. It will be highly desirable to extend the database of materials in order to have a possible selection of an ideal material. Measurements performed in powders will also constitute partial information provided that the pressure variations for this application are extreme. Ideally, shaped bodies (pellets, beads or monoliths) should be used and mechanical stability should also be a measured property together with the material density that is sometimes missing in the reports. This is particularly important for new materials like MOFs where the adsorbent density value can be very low. It is essential that either the material presents a kinetic selectivity towards methane or at least a very small adsorption towards this gas to avoid delayed steps and avoid massive temperature variations due to heat of adsorption / desorption. It is also very important to ensure that the isotherm of CO_2 is not very steep and that a significant partial regeneration is possible without utilization of vacuum.

Even having a good material, the major challenge in this work was the design of a PSA unit that can handle pressure variations from 70 to 1 bar producing both pipeline-quality natural gas and high-purity of CO_2 for EOR purposes. As was verified, the most important factor for the cost of gas cleaning is the gas losses with the CO_2. This is the main indicator that the PSA cycle is not yet optimized and that work is required, even considering the commercial and already available carbon molecular sieve adsorbents. To our knowledge, the 12-column multi-feed PSA cycle with four pressure equalization steps and light and heavy refluxes has never been reported in literature. A trade-off between a single PSA units and dual PSA units has also to be considered as an alternative [107, 108]. This can be a very good alternative for mixtures with a higher concentration of CO_2.

Commercially available materials in the shape of pellets and beads are normally used in PSA units. In this application where at least 4 pressure equalization steps are necessary, a large part of the cycle time is spent in moving gas from one column to the other with a relatively low velocity to avoid crushing the material. If honeycomb monoliths of the commercial materials available in pellets can be produced, it will be possible to reduce the total cycle time and with that reducing proportionally the size of the columns with a strong impact in the CAPEX of the unit. If a honeycomb monolith is used, it might be possible to reduce the cycle time up to 30% with a similar expected reduction in the column size.

As referred in several sources [18-21, 109-118], considering all these effects and optimizing a PSA unit for this application is indeed a work that requires a multi-task force and a significant interplay between engineers and material developers to achieve a common goal.

8: References

1. IEA World Energy outlook 2012.
2. Statoil webpage information. Available at: http://www.statoil.com/en/TechnologyInnovation/NewEnergy/Co2CaptureStorage/Pages/SleipnerVest.aspx
3. Shi, J-Q.; Imrie, C.; Sinayuc, C.; Durucan, S.; Korre, A.; Eiken, O. Snøhvit CO_2 Storage Project: Assessment of CO_2 Injection Performance through History Matching of the Injection Well Pressure over a 32-Months Period. *Energy Procedia*, **2013**, 37, 3267-3274.
4. Ringrose, P. S.; Mathieson, A. S.; Wright, I. W.; Selama, F.; Hansen, O.; Bissell, R.; Saoula, N.; Midgley, J. The In Salah CO2 Storage Project: Lessons Learned and Knowledge Transfer. *Energy Procedia*, **2013**, 37, 6226-6236.
5. Sridhar, S.; Smitha, B.; Aminabhavi, T. M. Separation of Carbon Dioxide from Natural Gas Mixtures through Polymeric Membranes – A Review. *Sep. Purif. Rev.*, **2007**, 36, 113-174.
6. Scholes, C. A.; Stevens, G. W.; Kentish, S.E. Membrane Gas Separation Applications in Natural Gas Processing. *Fuel*, **2012**, 96, 15-28.
7. Shekhawat, D.; Luebke, D. R.; Pennline, H. W. A Review of Carbon Dioxide Selective Membranes: A Topical Report, In: CO_2 selective membranes, Available from: http://www.osti.gov/bridge/product.biblio.jsp?osti_id=819990
8. White L. S.; Blinka, T. A.; Kloczewski, H. A.; Wang, I-F. Properties of a polyimide gas separation membrane in natural gas streams. *J. Membrane Sci.*, **1995**, 103, 73-82.
9. Baker, R. W.; Lokhandwala, K. Natural Gas Processing with Membranes: an Overview. *Ind. Eng. Chem. Res.*, **2008**, 47, 2109-2121.
10. Baker, R .W. Future Directions of Membrane Gas Separation Technology. *Ind. Eng. Chem. Res.*, **2002**, 41, 1393-1411.
11. CO_2 Removal from Natural Gas. MTR webpage. Available at: http://www.mtrinc.com/co2_removal.html.
12. Ryan, J. M.; Schaffert, F. W.; CO_2 Recovery by the Ryan/Holmes Process. *Chem. Eng. Prog.*, **1984**, 53-56.
13. Berstad, D.; Nekså, P.; Anantharaman, R. Low-temperature CO_2 Removal from Natural Gas. *Energy Procedia*, **2012**, 26, 41-48.
14. Baker, N. New Process Recovers NGLs from CO_2. *The American Oil & Gas Reporter*. February **2013**.
15. Appl, M.; Wagner, U.; Henrici, H. J.; Kuessnet, K.; Volkamer, F.; Ernst-Neust, N. *Removal of CO_2 and/or H_2S and/or COS from gases containing these constituents*. U.S. Patent 4,336,233, **1982**.
16. Kohl, A. L.; Nielsen, R. B. *Gas Purification*, fifth ed. Gulf Professional Publishing, Houston, **1997**.
17. Campbell JM & Co. *Gas conditioning and processing. Volume 4: Gas treating and sulfur recovery*. 4th edition. Campbell Petroleum Series, Norman, Oklahoma, **2006**.
18. Ruthven, D. M. *Priciples of adsorption and adsorption processes*, Wiley, New York, **1984**.
19. Yang, R. T. *Gas Separation by Adsorption Processes*. Butterworths, Boston, **1987**.

20. Suzuki, M. *Adsorption Engineering*. Elsevier, Tokio, **1990**.
21. Do, D. D. *Adsorption Analysis: Equilibria and Kinetics*. Imperial College Press. London, **1998**.
22. Ribeiro, A. M. P.; Sauer, T. Grande, C. A.; Moreira, R. F. P. M.; Rodrigues, A. E. Adsorption Equilibrium and Kinetics of Water Vapor on Different Adsorbents. *Ind. Eng. Chem. Res.*, **2008**, 47, 7019-7026.
23. Bar, N. K.; McDaniel, P. L.; Coe, C. G.; Seiffert, G.; Karger, J. Measurement of intracrystalline diffusion of nitrogen in zeolites NaX nad NaCaA using pulsed field gradient n.m.r. *Zeolites*, **1997**, 18, 71-74.
24. Grande, C. A.; Gigola, C. E.; Rodrigues, A. E. Propane – Propylene Binary Adsorption on Zeolite 4A. *Adsorption*, **2003**, 9, 321-329.
25. Shen, D.; Bülow, M.; Lemcoff, N. Mechanisms of Molecular Mobility of Oxygen and Nitrogen in Carbon Molecular Sieves. *Adsorption*, **2003**, *9*, 295-302.
26. Grande, C. A.; Rodrigues, A. E. Layered Vacuum Pressure-Swing Adsorption for Biogas Upgrading. *Ind. Eng. Chem. Res.*, **2007**, 46, 7844-7848.
27. Dolan, W. B.; Mitariten, M. J. *CO_2 Rejection from Natural Gas*. US Patent 2003/0047071, **2003**.
28. Wills, J., Shemaria, M., Mitariten, M.J., 2009. Production of Pipeline Quality Natural Gas with the Molecular Gate CO_2 Removal Process. Available in www.moleculargate.com.
29. Bauer, F.; Hulteberg, C.; Persson, T.; Tamm, D. *Biogas Upgrading – Review of Commercial Technologies*. SGC Report: **2013**:270. Available at: www.sgc.se
30. Kapoor, A.; Yang, R. T. Kinetic separation of methane-carbon dioxide mixture by adsorption on molecular sieve carbon. *Chem. Eng. Sci*., **1989**, 44, 1723-1733.
31. Baade, W.; Farnand, S.; Hutchison, R.; Welch, K. CO_2 Capture from SMRs: A Demonstration Project. Hydrocarbon Processing, Sept. **2012**, 63-68.
32. Van der Stel, J., Hattink, M.; Sert, D.; Borlée, J.; Hirsch, A.; Zagaria, M.; Eklund, N.; Pettersson, M.; Sundqvist, L.; Sköld, B.; Feilmayr, C.; Lin, R.; Feiterna, A.; Grant, M.; Ansseau, O.; Adam, J.; Kinnunen, K.; Simoes, J. P.; Küttner, W. Developments of the ULCOS Low CO_2 Blast Furnace Process at the LKAB Experimental BF in Luleå. Available at: https://www.lkab.com/Global/Documents/EBF%20publications/2011/2011%20Developments%20of%20the%20ULCOS%20Low%20CO2%20Blast%20Furnace%20Process%20at%20the%20LKAB%20Experimental%20BF%20in%20Lule%C3%A5.pdf, **2011**.
33. Willis, R. Carbon Dioxide Removal from Flue Gases Using Microporous Metal-Organic Frameworks. Final Technical Report. Department of Energy, United States. Project contract: DE-FC26-07NT43092. Available at: http://www.netl.doe.gov/research/coal/carbon-capture/post-combustion/mofs, **2010**.
34. Chaffee, A.L.; Knowles, G.P.; Liang, Z.; Zhany, J.; Xiao, P.; Webley, P.A. CO_2 capture by adsorption: Materials and process development. *Int J. Greenhouse Gas Control*, **2007**, 1, 11-18.

35. Schell, J.; Casas, N.; Blom, R.; Spjelkavik, A. I.; Andersen, A.; Cavka, J. H.; Mazzotti, M. MCM-41, MOF and UiO-67/MCM-41 adsorbents for pre-combustion CO_2 capture by PSA: adsorption equilibria. *Adsorption*, **2012**, 18, 213-227.
36. Millward, A.R.; Yaghi, O.M. Metal-organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature. *J. Am. Chem. Soc.*, **2005**. 127, 17998-17999.
37. Farruseng, D. *Metal-Organic Frameworks: Applications from Catalysis to Gas Storage*. John Wiley & Sons, **2011**.
38. Liu, Z.; Grande, C.A.; Li, P.; Yu, J.G.; Rodrigues, A.E. Adsorption and Desorption of Carbon Dioxide and Nitrogen on Zeolite 5A. *Sep. Sci. Technol.*, **2011**, 46, 434-451.
39. Watson, G.; May, E. F.; Graham, B. F.; Trebble, M. A.; Trengove, R. D.; Ida Chan, K. Equilibrium Adsorption Measurements of Pure Nitrogen, Carbon Dioxide and Methane on a Carbon Molecular Sieve at Cryogenic Temperatures and High Pressures. *J. Chem. Eng. Data*, **2009**, 54, 2701-2707.
40. Jensen, N. K.; Rufford, T. E.; Watson, G.; Zhang, D. K.; Ida Chan, K.; May, E. F. Screening Zeolites for Gas Separation Applications Involving Methane, Nitrogen and Carbon Dioxide. *J. Chem. Eng. Data*, **2012**, 57, 106-113.
41. Grande, C. A.; Blom, R.; Möller, A.; Möllmer, *J.* High-Pressure Separation of CH_4-CO_2 Using Activated Carbon. *Chem. Eng. Sci.*, **2013**, 89, 10-20.
42. Hafizovik Cavka, J.; Grande, C. A.; Mondino, G.; Blom, R. High-Pressure Adsorption of CO_2 and CH_4 in Zr-MOFs. *Ind. Eng. Chem. Res.*, **2014**, 53, 15500-15507.
43. Xebec Fast-Cycle PSA goes Off-Shore to Successfully Recover Stranded Gas. Available at: http://www.xebecinc.com/downloads.php
44. Roussanaly, S.; Anantharaman, R.; Lindqvist, K. Multi-criteria analyses of two solvent and one low-temperature concepts for acid gas removal from natural gas, J. Natural Gas Science and Engineering, 2014, 20, 38-49.
45. Chemical Engineering, Economic Indicators: Chemical Engineering Plant Cost Index (CEPCI), in, 2011.
46. XE Currency Data Feed, US Dollar/Euro: Monthly exchange rate, in, 2014.
47. NETL, Quality guidelines for energy system studies: Cost estimation methodology for NETL assessments of power plant performance. DOE/NETL-2011/1455, **2011**.
48. C.o. Mayors, Technical annex to the SEAP template instructions document: The emission factors, in, 2010.
49. Kohl, A. L.; Nielsen, R. B. *Gas Purification* (Fifth Edition), Gulf Professional Publishing, Houston, **1997**.
50. Cavenati, S.; Grande, C. A.; Rodrigues, A. E. Upgrade of Methane from Landfill Gas by Pressure Swing Adsorption. *Energy & Fuels*, **2005**, 19, 2545-2555.
51. Skarstrom, C. W. *Method and Apparatus for Fractionating Gas Mixtures by Adsorption*. US. Patent 2,944,627, **1960**.
52. Berlin, N. H. *Method for providing an oxygen-enriched environment*. U.S. Patent 3,280,536, **1966.**

53. Grande C. A. Advances in Pressure Swing Adsorption for Gas Separation", ISRN Chemical Engineering, **2012**. Available free of charge at: http://www.hindawi.com/isrn/chemeng/2012/982934/
54. Knaebel, K. S.; Reinhold, H. E. Landfill Gas: From Rubbish to Resource. *Adsorption* **2003**, 9, 87-94.
55. Yang, R. T.; Cen, P.L. Improved Pressure Swing Adsorption Processes for Gas Separation: By Heat Exchange between Adsorbers and By High Heat Capacity Inert Additives. *Ind. Eng. Chem. Process Des. Dev.*, **1986**, 25, 54-59.
56. Santos, M. P. S.; Grande, C. A.; Rodrigues, A. E. *Reducing Heat Effects in PSA processes for* CO_2 *removal*. Oral presentation in FOA-10, Awaji, May 23-28, **2010** (Japan).
57. Sundaram, N.; Yang, R. T. On the Pseudomultiplicity of Pressure Swing Adsorption Periodic States. *Ind. Eng. Chem. Res.*, **1998**, 37, 154-158.
58. Knaebel K. *A "How to" Guide for Adsorber Design*. Available free of charge at: http://adsorption.com/publications/adsorberdes2.pdf , **2004**.
59. Knaebel K. *Adsorbent selection*. Available free of charge at: http://www.adsorption.com/publications/AdsorbentSel1B.pdf .
60. Kuznicki, S. M.; Bell, V. A.; Petrovic, I.; Desai, B. T. Small-Pored Crystalline Titanium Molecular Sieve Zeolites and Their Use in Gas Separation Processes. International Patent, WO9932404 A1, 1999
61. Kuznicki, S. M.; Bell, V. A.; Nair, S.; Hillhouse, H. W.; Jacubinas, R. M.; Braunbarth, C. M.; Toby, B. H.; Tsapatsis, M. A titanosilicatemolecular sieve with adjustable pores for size-selective adsorption of molecules. *Nature*, **2001,** *412*, 720
62. Marathe, R. P.; Mantri, K.; Srinivasan, M. P.; Farooq, S. Effect of Ion Exchange and Dehydration Temperature on the Adsorption and Diffusion of Gases in ETS-4. *Ind. Eng. Chem. Res.* **2004**, *43*, 5281
63. Delgado, J. A.; Uguina, M. A.; Águeda, V. I.; Gracía-Sanz, A. Adsorption and Diffusion Parameters of Methane and Nitrogen on Microwave-Synthesized ETS-4. *Langmuir*, **2008**, *24*, 6107
64. Cavenati, S.; Grande, C. A.; Lopes, F. V. S.; Rodrigues, A. E. Adsorption of Small Molecules on Alkali-Earth Modified Titanosilicates. *Miroporous Mesoporous Mater*. **2009**, *121*, 114.
65. Jayaraman, A.; Chiao, A. S.; Padin, J.; Yang, R. T.; Munson, C. L. Kinetic Separation of Methane/Carbon Dioxide by Molecular Sieve Carbons. *Sep. Sci. and Tech.*, **2002**, 37, 2505-2528.
66. Benedict, M.; Webb, G. B.; Rubin, L. C. An Empirical Euqation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures I. Methane, Ethane, Propane and n-Butane. *J. Chem. Phys.*, **1940**, 8, 334-345.
67. Srinivasan, R.; Auvil, S. R.; Schork J. M. Mass transfer in carbon molecular sieves – an interpretation of Langmuir kinetics. *Chem. Eng. J.*, **1995**, 57, 137-144.
68. Qinglin, H.; Farooq, S.; Karimi, I. A. Identification of Transport Mechanism in Adsorbent Micropores from Column Dynamics. *Ind. Eng. Chem. Res.*, **2002**, 41, 1098-1106.

69. Sereno, C.; Rodrigues, A. E. Can Steady-State Momentum Equations Be Used in Modelling Pressurization of adsorption Beds? *Gas Sep. Purif.*, **1993**, 3, 167-174.
70. Da Silva, F. A.; Silva, J. A.; Rodrigues, A. E. A General Package for the Simulation of Cyclic Adsorption Processes. *Adsorption*, **1999**, 5, 229-244.
71. Grande, C. A.; Poplow, F.; Rodrigues, A. E. Vacuum Pressure Swing Adsorption to Produce Polymer-Grade Propylene. *Sep. Sci & Technology*, **2010**, 45, 1252-1259.
72. Lopes, F. V. S.; Grande, C. A.; Rodrigues, A. E. Fast-cycling VPSA for Hydrogen Purification. *FUEL*, **2012**, 93, 510-523.
73. Grande, C. A.; Blom, R.; Möller, A.; Möllmer, *J.* High-Pressure Separation of CH_4-CO_2 Using Activated Carbon. *Chem. Eng. Sci.*, **2013**, 89, 10-20.
74. Bird, R.B.; Stewart, W.E.; Lightfoot, E.N. *Transport Phenomena* (2nd edition), Wiley International, Singapore, **2002**.
75. Wakao, N.; Funazkri, T. Effect of Fluid Dispersion Coefficients on Particle-te-Fluid Mass Transfer Coefficients in Packed Beds. *Chem. Eng. Sci.*, **1978**, 33, 1375-1384.
76. Da Silva, F. A. *Cyclic Adsorption Processes: Application to Propane / Propylene Separation*. Ph.D. Dissertation, University of Porto, Portugal, **1999**.
77. Wasch, A. P. D.; Froment, G. F. Heat Transfer in Packed Beds. *Chem. Eng. Sci.*, **1972**, 27, 567-576.
78. Incropera, F. P.; Witt, D. P. D. *Fundamentals of Heat and Mass Transfer*, 4ºdition, John Wiley & Sons, New York, **1996**.
79. Nitta, T.; Shigetomi, T.; Kuro-Oka, M.; Katayama, T. An adsorption isotherm of multi-site occupancy model for homogeneous surface. *J. Chem. Eng. Japan*, **1984**, 17, 39-45.
80. Lee, C-H.; Yang, J.; Ahn, J. Effects of Carbon-to-Zeolite Ratio on Layered Bed H_2 PSA for Coke Oven Gas. *AIChE J.*, **1999**, 45, 535-545.
81. Luberti, M.; Friedrich, D.; Brandani, S.; Ahn, J. Design of a H_2 PSA for Cogenreation of Ultrapure Hydrogen and Power at an Advanced Integrated Gasification Combined Cycle with Pre-Combustion Capture. *Adsorption*, **2014**, 20, 511-524.
82. Nikolic, D.; Giovanoglou, A.; Georgiadis, M. C.; Kikkinides, E. S. Generic Modeling Framework for Gas Separations Using Multibed Pressure Swing Adsorption Processes, *Ind. Eng. Chem. Res*. **2008**, *47*, 3156-3169.
83. Nikolic, D.; Kikkinides, E. S.; Georgiadis, M. C. Optimization of Multibed Pressure Swing Adsorption Processes, *Ind. Eng. Chem. Res*. **2009,** *48*, 5388-5398.
84. Liu, Z.; Grande, C. A.; Li, P.; Yu, J.; Rodrigues, A. E. Multi-bed Vacuum Pressure Swing Adsorption for Carbon Dioxide Capture from Flue Gases. *Sep. Purif. Technol.*, **2011**, 81, 307-317.
85. Ko, D.; Siriwardane, R.; Biegler, L. T. Optimization of Pressure Swing Adsorption Process Using Zeolite 13X for CO_2 Sequestration. *Ind. Eng. Chem. Res.*, **2003**, *42*, 339-348.
86. Mehrotra, A. Ebner, A. D.; Ritter, J. A. Simplified Graphical Approach for Complex PSA Cycle Scheduling. *Adsorption*, **2011**, 17, 337-345.
87. Grande, C. A.; Blom, R. Utilization of Dual-PSA Technology for Natural Gas Upgrading and Integrated CO_2 Capture. *Energy Procedia*, **2012**, 26, 2-14.

88. Stöcker, J.; Whysall, M.; Miller, G. Q. *30 Years of PSA Technology for Hydrogen Purification*, UOP LLC, Des Plaines, Illinois, **1998**.
89. Xu, J.; Rarig, D. L.; Cook, T. A.; Hsu, K.-K.; Schoonover, M.; Agrawal, R. *Pressure Swing Adsorption Process with Reduced Pressure Equalization Time*, U. S. Patent 6,565,628, **2003**.
90. Baksh, M. S. A.; Simo, M. *Ten Bed Pressure Swing Adsorption Process Operating in Normal and Turndown Modes*. U. S. Patent 8,435,328, **2011**.
91. Habgood, H. W. The Kinetics of Molecular Sieve Action. Sorption of Nitrogen-Methane Mixtures by Linde Molecular Sieve 4A. *Can. J.Chem.*, **1958**, 36, 1384-1397.
92. Grande, C. A. *Biogas Upgrading by Pressure Swing Adsorption*. In Biofuel. Editor: Bernardes, M. A. d.S. Intech, Luxemburg, **2011.**
93. Bacsik, Z.; Cheung, O.; Vasiliev, P.; Hedin, N. Selective Separation of CO_2 and CH_4 for Biogas Upgrading on Zeolite NaKA and SAPO-56. App. Energy, 2016, 162, 613-621.
94. Olson, D.H. *Light Hydrocarbon Separation Using 8-Member Ring Zeolites*. U.S. Patent 6,488,741, **2002**.
95. Himeno, S. Tomita, T.; Suzuki, K.; Nakayama, K.; Yajima, K.; Yoshida, S. Synthesis and Permeation Properties of a DDR-Type Zeolite Membrane for Separation of CO_2-CH_4 Gaseous Mixture. *Ind. Eng. Chem. Res.*, **2007**, 46, 6989-6997.
96. Krishna, R.; van Baten, J. M. Influence of Segregated Adsorption on Mixture Diffusion in DDR Zeolite. *Chem. Phys. Letters*, **2007**, 446, 344-349.
97. Hernández-Huesca, R.; Diaz, L.; Aguilar-Armenta, G. Adsorption Equilibria of CO_2, CH_4 and N_2 in Natural Zeolites. *Sep. Purif. Technol.*, **1999**, 15, 163-173.
98. Jensen, N. K.; Rufford, T. E.; Watson, G.; Zhang, D. K.; Ida Chan, K.; May, E. F. Screening Zeolites for Gas Separation Applications Involving Methane, Nitrogen and Carbon Dioxide. *J. Chem. Eng. Data.*, **2012**, 57, 106-113.
99. Lozinska, M. M.; Mowat, J. P. S.; Wright, P. A.; Thompson, S. P.; Jorda, J. L.; Palomino, M.; Valencia, S.; Rey, F. Cation Gating and Relocation During the Highly Selective "Trapdoor" Adsorption of CO_2 on Univalent Cations Forms of Zeolite Rho. *Chem. Mater.*, **2014**, 26, 2052-2061.
100. Maghsoudi, H.; Soltanieh, M.; Bozorgzadeh, H.; Mohamadalizadeh, A. Adsorption Isotherms and Ideal Selectivities of Hydrogen Sulphide and Carbon Dioxide over Methane for the Si-CHA Zeolite: Comparison of Carbon Dioxide and Methane Adsorption with the All-Silica DD3R Zeolite. *Adsorption*, **2013**, 19, 1045-1053.
101. Palomino, M.; Corma, A.; Rey, F.; Valencia, S. New Insights of CO_2-Methane Separation Using LTA Zeolites with Different Si/Al Ratios and a First Comparison with MOFs. *Langmuir*, **2010**, 26, 1910-1917.
102. Yu, M.; Primera-Pedrozo, J. N.; Marcano-González, M. E.; Hernández-Maldonado, A. J. Selective Adsorption of N_2 over CH_4 in Flexible Sr^{2+}- and Ba^{2+}-UPRM-5 Titanium Silicates: Effect of Activation Temperature. *Chem. Eng. J.* **2014**, *252*, 311-319.

103. Bao, Z.; Alnemrat, S.; Yu, L.; Vasiliev, I.; Ren, Q.; Lu, X.; Deng, S. Kinetic Separation of Carbon Dioxide and Methane on a Copper Metal–Organic Framework. *J. Colloid Interface Sci.* **2011**, *357*, 504.

104. Bárcia, P. S.; Bastin, L.; Hurtado, E. J.; Silva, J. A. C.; Rodrigues, A. E.; Chen, B. Single and Multicomponent Sorption of CO_2, CH_4 and N_2 in a Microporous Metal-Organic Framework *Sep. Sci. Technol.* **2008**, *43*, 3494-3521.

105. Li, K.; Olson, D. H.; Seidel, J.; Emge, T. J.; Gong, H.; Zeng, H.; Li, J. Zeolitic Imidazolate Frameworks for Kinetic Separation of Propane and Propylene. *J. Am. Chem. Soc.*, **2009**, 131, 10368-10369.

106. Battisti, A.; Taioli, S.; Garberoglio, G. Zeolitic Imidazolate Frameworks for Separation of Binary Mixtures of CO_2, CH_4, N_2 and H_2: A computer Simulation Investigation. *Microp. Mesop. Mater.* **2011**, *143*, 46-53.

107. Grande, C. A.; Blom, R. Dual Pressure Swing Adsorption Units for Gas Separation and Purification. *Ind. Eng. Chem. Res.*, **2012**, 51, 8695-8699.

108. Chen, Y.; Kapoor, A.; Ramachandran, R. Two stage pressure swing adsorption process. U.S. Patent 5,993,517, **1999**.

109. Tagliabue, M.; Farrusseng, D.; Valencia, S.; Aguado, S.; Ravon, U.; Rizzo, C.; Corma, A.; Mirodatos, C. Natural gas treating by selective adsorption: Material science and chemical engineering interplay. *Chem. Eng. J.*, **2009**, 155, 553-566.

110. Ruthven, D. M. Past Progress and Future Challenges in Adsorption Research. *Ind. Eng. Chem. Res.*, **2000**, 39, 2127-2131.

111. Wankat, P. C. *Large-Scale Adsorption and Chromatography*. CRC Press, Boca Raton, **1986**.

112. Kärger, J.; Ruthven, D. M. *Diffusion in Zeolites and Other Microporous Solids*, Wiley, London, **1992**.

113. Humphrey, J. L.; Keller, G. E. II. *Separation Process Technology*, McGraw-Hill, New York, **1997**.

114. Thomas, J. W.; Crittenden, B. D. *Adsorption Technology and Design*. Elsevier, Boston, **1998**.

115. Keller, J.; Staudt, R.. *Gas Adsorption Equilibria: Experimental Methods and Adsorption Isotherms*. Springer, Boston, **2005**.

116. Wankat, P. C. *Separation Process Engineering*. Second Edition. Prentice Hall, London, **2007**.

117. Waldron, W. E.; Sircar, S. Parametric Study of a Pressure Swing Adsorption Process. *Adsorption*, **2000**, 6, 179-188.

118. Sircar, S. Pressure Swing Adsorption. *Ind. Eng. Chem. Res.*, **2002**, 41, 1389-1392.

Appendix A. Summary of economic parameters

Parameter	Assumption	Reference
Plant location	Netherlands	[A]
Total Plant Cost (TPC)		
Indirect cost [% plant cost]	14	[A]
Project contingency [% plant cost]	10	[A]
Total Capital Requirement (TCR)		
Owners costs and fees [% of TPC]	7	IEA Methodology
Interest during construction	From expenditure schedule and discount rate	
Spare parts [% of TPC]	0.5	IEA Methodology
Construction time and expenditure schedule		
Construction time [years]	3	[A]
Capital expenditure schedule [% of TPC, years 1-3]	20/45/35	[A]
Start-up costs		
Maintenance and operating and support labour costs	3 month	IEA Methodology
Maintenance materials	1 month	IEA Methodology
Chemicals, consumables and waste disposal costs	1 month	IEA Methodology
Fuel cost [% of full load]	25% of 1 month	IEA Methodology
Modifications [% of TPC]	2	IEA Methodology
Working capital		
Chemicals and consumables [days at full load]	30	IEA Methodology
Decommissioning cost	0	-
Capacity factor		
All except year 1 [%]	85	[A]
Year 1 [%]	60	[A]
Discount rate		
Plant construction and operation [%]	8	[B]
Operating life		
Base case [years]	25	[B]
Fuel prices		
Electricity cost [€/MWh]	80	[B]
Natural gas [€/GJ]	6	IEA Methodology
Labour, Maintenance, Insurance and taxes		
Maintenance costs [% of TPC/y – Sorbent concept]	2.2	IEA Methodology
Operating labour cost [€k/person-year]	60	[B]
Number of operating shifts	5	[B]
Administrative/support labour [% of operating labour]	30	[B]
Administrative/support labour [% of maintenance cost]	12	IEA Methodology
Insurance cost [% of TPC]	0.5	[B]
Local taxes and fees[% of TPC]	0.5	[B]
Material and utilities cost		
Carbon molecular sieve [€/t]	6,500	Vendor contacts
Raw process water [€/m^3]	0.2	[B]
MDEA [€/kg]	43	[B]
Piperazine [€/kg]	58	[B]
Sea cooling water [€/m^3]	0.39	[A]
CO_2 transport and storage [€/$t_{CO2,stored}$]	10	IEA Methodology
CO_2 emission cost [€/$t_{CO2,emitted}$]	0	-
Emission factor of fuel consumption		

Electricity (Netherlands) [kg_{CO2}/MWh]	0.435	[C]
Steam (produced from natural gas) [kg_{CO2}/MWh]	0.236	[C]

References:

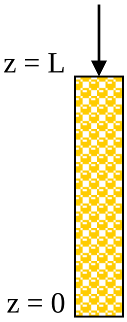
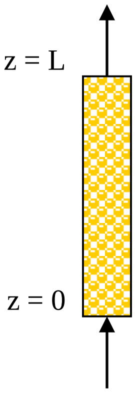
A - C.o. Mayors, Technical annex to the SEAP template instructions document: The emission factors, in, 2010.

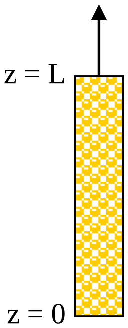
B - S. Roussanaly, R. Anantharaman, K. Lindqvist, Multi-criteria analyses of two solvent and one low-temperature concepts for acid gas removal from natural gas, Journal of Natural Gas Science and Engineering, 2014, 20, 38-49.

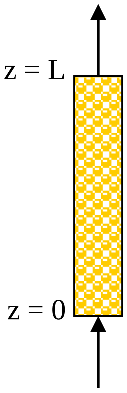
D - A.L. Kohl, R.B. Nielsen, Gas Purification (Fifth Edition), Gulf Professional Publishing, Houston, 1997.

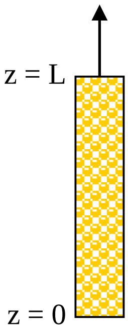
Appendix B. Boundary condition equations for PSA model

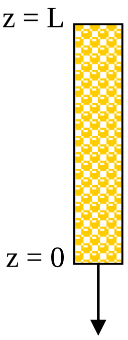
The boundary equations that were used in the mathematical model to describe the column behaviour are listed here, separated by their respective step within the PSA cycle.

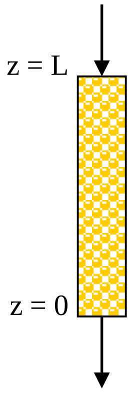
Pressurization with upgraded natural gas  	Momentum balance: $u_i\vert_{z=0}=0$ $P(z=L)=P_{inlet}$ Mass balance: $\left.\frac{\partial y_i}{\partial z}\right\vert_{z=0}=0$ $-\frac{\varepsilon D_{ax}}{u_i}\left.\frac{\partial y_i}{\partial z}\right\vert_{z=L}+y_i\vert_{z=L}-y_i\vert_{z=L}=0$ Energy balance: $\left.\frac{\partial T_g}{\partial z}\right\vert_{z=0}=0$ $\lambda\left.\frac{\partial T_g}{\partial z}\right\vert_{z=L}+u_iC_t\tilde{C}_pT_g\vert_{z=L}-u_iC_t\tilde{C}_pT_g\vert_{z=L}=0$
Feed step  	Momentum balance: $u_i\vert_{z=0}=u_{feed}$ $P(L)=P_{exit}$ Mass balance: $-\frac{\varepsilon_c D_{ax}}{u_i}\left.\frac{\partial y_i}{\partial z}\right\vert_{z=0}+y_i\vert_{z=0}-y_i\vert_{z=0}=0$ $\left.\frac{\partial y_i}{\partial z}\right\vert_{z=L}=0$ Energy balance: $-\lambda\left.\frac{\partial T_g}{\partial z}\right\vert_{z=0}+u_iC_t\tilde{C}_pT_g\vert_{z=0}-u_iC_t\tilde{C}_pT_g\vert_{z=0}=0$ $\left.\frac{\partial T_g}{\partial z}\right\vert_{z=L}=0$

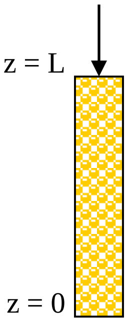
Co-current depressurizations  	Momentum balance : $u_i \vert_{z=0} = u_{feed}$ $P(z=L) = P_{\text{inter}}$ Mass balance: $\left.\frac{\partial y_i}{\partial z}\right\vert_{z=0} = 0$ $\left.\frac{\partial y_i}{\partial z}\right\vert_{z=L} = 0$ Energy balance: $\left.\frac{\partial T_g}{\partial z}\right\vert_{z=0} = 0$ $\left.\frac{\partial T_g}{\partial z}\right\vert_{z=L} = 0$

Rinse with CO_2-rich stream  	Momentum balance: $u_i(0) \vert_{z=0} = u_{rinse}$ $P(L) = P_{\text{inter}}$ Mass balance: $-\frac{\varepsilon_c D_{ax}}{u_i} \left.\frac{\partial y_i}{\partial z}\right\vert_{z=0} + y_i\vert_{z=0} - y_i\vert_{z=0} = 0$ $\left.\frac{\partial y_i}{\partial z}\right\vert_{z=L} = 0$ Energy balance: $-\lambda \left.\frac{\partial T_g}{\partial z}\right\vert_{z=0} + u_i C_t \tilde{C}_p T_g\vert_{z=0} - u_i C_t \tilde{C}_p T_g\vert_{z=0} = 0$ $\left.\frac{\partial T_g}{\partial z}\right\vert_{z=L} = 0$

Provide purge step 	Momentum balance : $u_i\big\|_{z=0} = u_{feed}$ $P(z=L) = P_{\text{inter}}$ Mass balance: $\left.\frac{\partial y_i}{\partial z}\right\|_{z=0} = 0$ $\left.\frac{\partial y_i}{\partial z}\right\|_{z=L} = 0$ Energy balance: $\left.\frac{\partial T_g}{\partial z}\right\|_{z=0} = 0$ $\left.\frac{\partial T_g}{\partial z}\right\|_{z=L} = 0$

Counter-current blowdown 	Momentum balance: $P(z=0) = P_{low}$ $u_i\big\|_{z=L} = u_{feed}$ Mass balance: $\left.\frac{\partial y_i}{\partial z}\right\|_{z=0} = 0$ $\left.\frac{\partial y_i}{\partial z}\right\|_{z=L} = 0$ Energy balance: $\left.\frac{\partial T_g}{\partial z}\right\|_{z=0} = 0$ $\left.\frac{\partial T_g}{\partial z}\right\|_{z=L} = 0$

Counter-current purge (gas coming from provide purge step)  	Momentum balance: $P(0) = P_{low}$ $u_i \big\rvert_{z=L} = u_{purge}$ Mass balance: $\frac{\partial y_i}{\partial z}\bigg\rvert_{z=0} = 0$ $-\frac{\varepsilon_c D_{ax}}{u_i}\frac{\partial y_i}{\partial z}\bigg\rvert_{z=L} + y_i\big\rvert_{z=L} - y_i\big\rvert_{z=L} = 0$ Energy balance: $\frac{\partial T_g}{\partial z}\bigg\rvert_{z=L} = 0$ $\lambda\frac{\partial T_g}{\partial z}\bigg\rvert_{z=0} + u_i C_t \tilde{C}_p T_g\big\rvert_{z=0} - u_i C_t \tilde{C}_p T_g\big\rvert_{z=0} = 0$

Pressure equalization steps and pressurization  	Momentum balance: $u_i \big\rvert_{z=0} = 0$ $P(z = L) = P_{\mathrm{inter}}$ Mass balance: $\frac{\partial y_i}{\partial z}\bigg\rvert_{z=0} = 0$ $-\frac{\varepsilon D_{ax}}{u_i}\frac{\partial y_i}{\partial z}\bigg\rvert_{z=L} + y_i\big\rvert_{z=L} - y_i\big\rvert_{z=L} = 0$ Energy balance: $\frac{\partial T_g}{\partial z}\bigg\rvert_{z=0} = 0$ $\lambda\frac{\partial T_g}{\partial z}\bigg\rvert_{z=L} + u_i C_t \tilde{C}_p T_g\big\rvert_{z=L} - u_i C_t \tilde{C}_p T_g\big\rvert_{z=L} = 0$

Appendix C. Equations of ancillary components of the PSA

Valves:

$F_{in} = F_{out}$, $T_{in} = T_{out}$, $y_{in} = y_{out}$

If $P_{in}^{info} > P_{out}^{info}$ then $y_{in}^{info} = y_{in}$, $T_{in}^{info} = T_{in}$ Else $y_{out}^{info} = y_{out}$, $T_{out}^{info} = T_{out}$

$$\tau \frac{\partial V_{sp}^{act}}{\partial t} = V_{sp} - V_{sp}^{act}$$

When the flow is reversible,

$$F_{in} = C_v * V_{sp}^{act} * (P_{in}^{info} - P_{out}^{info})$$

and when the flow is irreversible,

If $P_{in}^{info} > P_{out}^{info}$ then $F_{in} = C_v * V_{sp}^{act} * (P_{in}^{info} - P_{out}^{info})$ Else $F_{out} = 0$

Column header (top and bottom) and tanks:

$P_{in}^{info}(i) = P = P_{out}^{info}(j)$, $y_{in}^{info}(i) = y = y_{out}^{info}(j)$, $T_{in}^{info}(i) = T = T_{out}^{info}(j)$

$$\frac{\partial m}{\partial t} = \sum F_{in} - \sum F_{out}, \quad \frac{\partial (mC_pT)}{\partial t} = \sum F_{in} C_p T - \sum F_{out} C_p T, \quad \frac{\partial (my)}{\partial t} = \sum F_{in} y - \sum F_{out} y$$

where *i* is the number of inlets and *j* is the number of outlets

SINTEF

Technology for a better society

www.sintef.no

IEA Greenhouse Gas R&D Programme

Pure Offices, Cheltenham Office Park, Hatherley Lane,
Cheltenham, Glos. GL51 6SH, UK

Tel: +44 1242 802911
mail@ieaghg.org
www.ieaghg.org