13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland

CO$_2$ Capture in Natural Gas Production by Adsorption Processes

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Abstract

Natural gas (NG) is the fossil fuel with the lowest emissions of CO$_2$ per kilowatt of energy produced. 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.

In this study, we have evaluated the feasibility of using a Pressure Swing Adsorption (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. Our study has considered the effect of different PSA process operation modes. The PSA unit was designed to upgrade natural gas with a composition of 83% CH$_4$, 10% CO$_2$ and 7% C$_2$H$_6$ available at 70 bars at a temperature of 313 K and with an inlet flowrate of 500,000 Sm^3/h. The analysis also considered several process variables. An economic comparison of the price of capture has also been done. Our analysis indicated that the cost of CO$_2$ capture using PSA is around 40% higher than using amines dominated by poor performance in process recovery (NG lost with CO$_2$). Since this is the first study of its kind, there is a lot of room to improve process performance and that adsorption processes for this application should not only be limited to very low concentrations.

Keywords: Natural gas; adsorption; upgrading; CO$_2$ capture

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1. Introduction

Natural gas (NG) is the fossil fuel with lower emissions of CO_2 per kilowatt of energy produced. 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. 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.

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. 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. Problem definition

Natural gas is a mixture of hydrocarbons, primarily methane but also including 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 [2]. 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 PSA
Temperature [K]	313
Pressure [bar]	70
Flowrate [Nm^3/h]	500,000
y_{CH4}	0.8300
y_{C2H6}	0.070
y_{CO2}	0.1000

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. Amine scrubbing was used as a reference case to benchmark PSA technology.

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. The calculation of the Total Cost Requirement (TCR) is estimated based on a bottom up approach (BUA). Investment costs are updated according to the Chemical Engineering Plant Cost Index (CEPCI). The cost estimates are for 'n[th] 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 [3]. The estimate accuracy is expected to be +35/-15% (AACE Class 4).

3. Pressure Swing Adsorption process

The adsorbent selection is the main and initial task in the specification of a PSA unit. There are several criteria to specify an adsorbent. 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". Carbon molecular sieve is a readily available material that can be used for this purpose [4]. 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.

The PSA process was simulated using a mathematical model already available in literature [5]. The program is based on solving the equations of a fixed bed with oscillating boundary equations depending on the particular step of the PSA unit. The Benedict-Webb-Rubin equation of state was used to describe gas behaviour [6]. The multi-site Langmuir model 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 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 [7]. 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). From the several PSA cycles tested, the implementation of the program for a six-column PSA unit is shown in Figure 1.
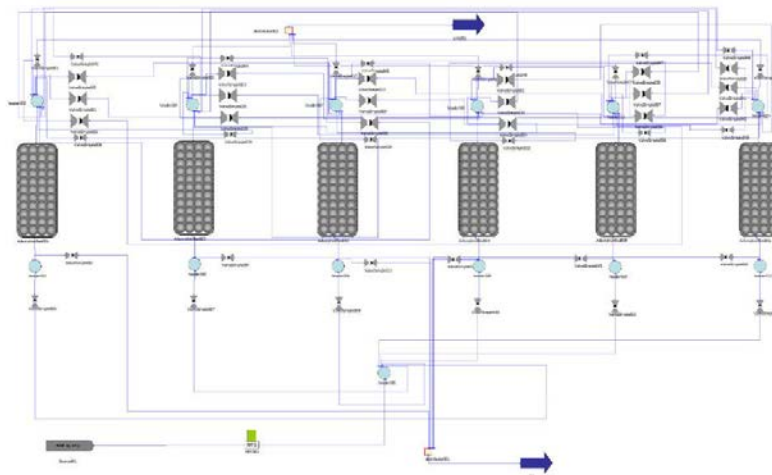

Figure 1. Scheme of the PSA unit used for modelling a 6-column cycle

4. Results and Discussion

Several cycles were tested in this study. In this report we will present the results obtained with one PSA unit composed of 12-columns in parallel and with four pressure equalization steps. Such large amount of pressure equalizations is necessary in order to reduce the pressure from 70 bar in the feed step to 1 bar in the CO_2 extraction or blowdown step.

The operation scheme of the columns in one cycle is given in Figure 2. In this scheme, three columns are in feed step all the time reducing the necessary diameter of a single column and also increasing the ratio of time in feed and time in regeneration.

Figure 2. 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.

The pressure swing in the different columns in a cycle after achieving cyclic steady state (CSS) is shown in Figure 3. Note that when the blowdown step is about to start, the pressure of the columns is almost 9 bar, close to the 7 bar of CO_2 partial pressure in the feed step.
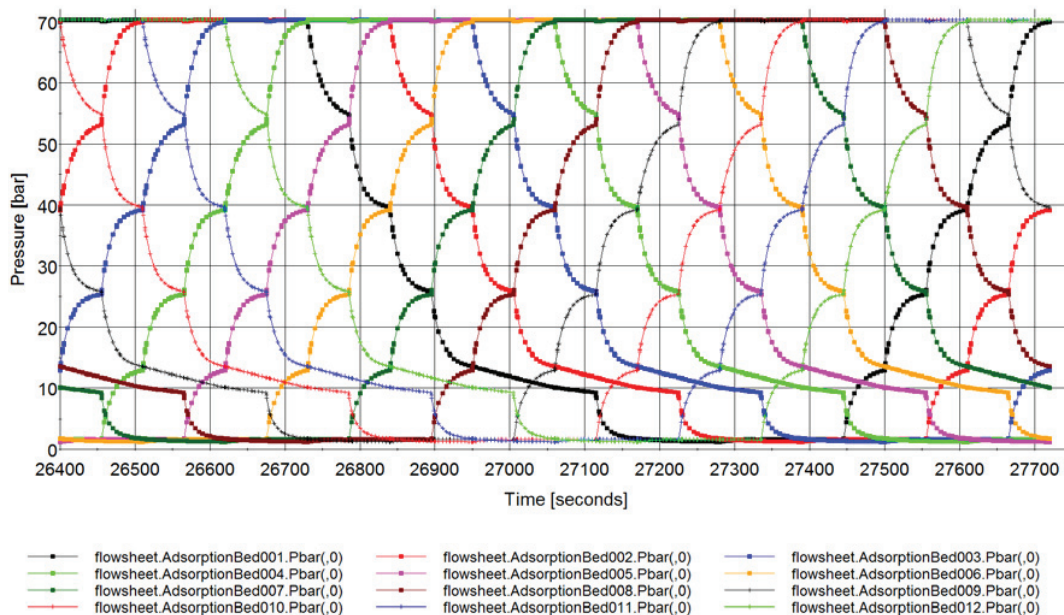
Figure 3. Pressure history at the exit of each column in a 12-column multi-feed PSA cycle with 4 pressure equalizations.

The overall mass balance resulting from this unit is shown in Figure 4. Such PSA unit 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.

Flow: 36000 Nm³/h
Pressure: 54.0 bar
Temperature: 309 K
y_{CH4}: 0.8923
y_{CO2}: 0.0265
y_{C2H6}: 0.0812

Flow: 452323 Nm³/h
Pressure: 69.4 bar
Temperature: 313 K
y_{CH4}: 0.9085
y_{CO2}: 0.0220
y_{C2H6}: 0.0695

Flow: 500000 Nm³/h
Pressure: 70 bar
Temperature: 313 K
y_{CH4}: 0.83
y_{CO2}: 0.10
y_{C2H6}: 0.07

12 column PSA

Flow: 47677 Nm³/h
Pressure: 1 bar
Temperature: 297 K
y_{CH4}: 0.0798
y_{CO2}: 0.8451
y_{C2H6}: 0.0751

Pressure: 11 bar

Flow: 30000 Nm³/h
Pressure: 1 bar
Temperature: 297 K
y_{CH4}: 0.0798
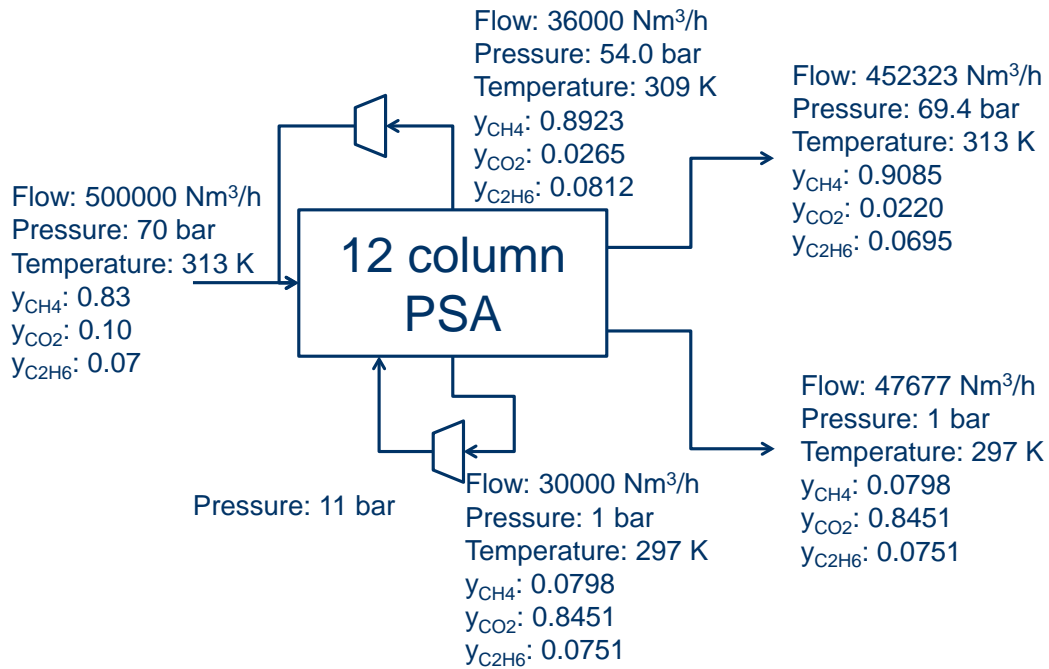y_{CO2}: 0.8451
y_{C2H6}: 0.0751

Figure 4. Mass balance of 12-column PSA unit to upgrade NG to pipeline specifications with integrated CO_2 capture.

Based on the process results, a cost estimation of the PSA unit has been made and compared with the cost estimation of an amine scrubbing process. The final results are shown in Figure 5. 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. 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.
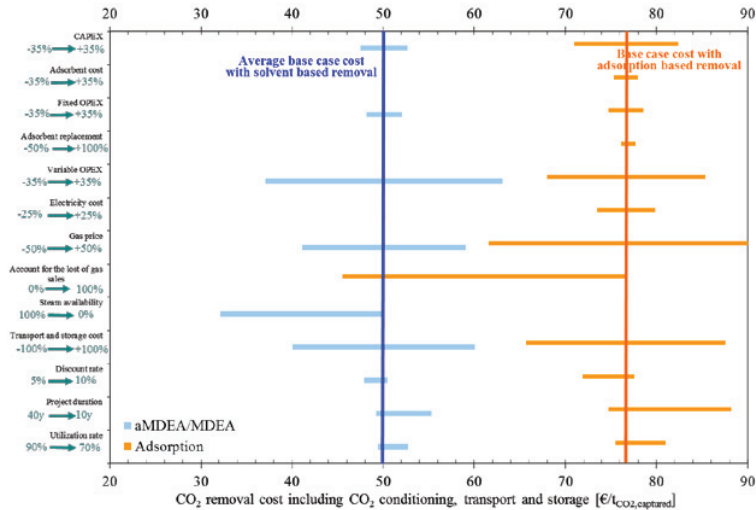
Figure 5. CO_2 removal cost including CO_2 conditioning, transport and storage

5. Conclusions

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$_{CO2,captured}$.

References

[1] IEA World Energy outlook 2012.
[2] 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. Nat. Gas Sci. Eng. 2014; 20:38-49.
[3] NETL, Quality guidelines for energy system studies: Cost estimation methodology for NETL assessments of power plant performance. DOE/NETL-2011/1455, 2011.
[4] Jayaraman A, Chiao AS, Padin J, Yang RT, Munson CL. Kinetic Separation of Methane/Carbon Dioxide by Molecular Sieve Carbons. Sep. Sci. and Tech. 2002; 37:2505-2528.
[5] Grande CA, Blom R, Möller A, Möllmer J. High-Pressure Separation of CH_4-CO_2 Using Activated Carbon. Chem. Eng. Sci. 2013; 89:10-20.
[6] Benedict M, Webb GB, Rubin LC. An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures I. Methane, Ethane, Propane and n-Butane. J. Chem. Phys. 1940; 8:334-345.
[7] Liu Z, Grande CA, Li P, Yu J, Rodrigues AE. Multi-bed Vacuum Pressure Swing Adsorption for Carbon Dioxide Capture from Flue Gases. Sep. Purif. Technol. 2011; 81:307-317.