

# A PHYSICAL ABSORPTION PROCESS FOR THE CAPTURE OF CO<sub>2</sub> FROM CO<sub>2</sub>-RICH NATURAL GAS STREAMS

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## ABSTRACT

A new CO<sub>2</sub>/CH<sub>4</sub> gas separation process is presented in this paper. Capture of CO<sub>2</sub> from natural gas is carried out using an *n*-alkane solvent in a conventional physical absorption process. A methodology to find optimal process condition and solvent has been developed using an advanced equation of state (SAFT-VR), process modelling-optimisation software (gPROMS), and detailed process cost estimation. Natural gas feeds containing up to 70% mol/mol of CO<sub>2</sub> can be treated economically using this process.

**Keywords:** CO<sub>2</sub>, physical absorption, natural gas

## INTRODUCTION

The increasing importance of natural gas as a source of energy poses difficult gas separation design challenges, as the streams recovered from gas fields are at high pressures (typically about 10 MPa) and can contain a high proportion of CO<sub>2</sub> (up to 70%). In addition, as the implementation of the Kyoto protocol would require the capture of large quantities of CO<sub>2</sub>, its injection in depleted or near-depleted reservoirs for enhanced oil/gas recovery operations will become increasingly frequent. This is likely to result in natural gas streams which are even richer in CO<sub>2</sub>. Conventional separation techniques are usually restricted to low CO<sub>2</sub> content or low-pressure feeds, and consequently there is a pressing need for an alternative process that is appropriate for such a scenario.

## Separation techniques

The techniques used in the gas separation industry include adsorption on solid substrates, chemical absorption, gas permeation, and physical absorption [1]. Adsorption is economical for purification, typically reducing the CO<sub>2</sub> content from 3% down to 0.5 %. An adsorption process for a CO<sub>2</sub>-rich natural gas streams would require a very frequent regeneration of the solid bed. Chemical absorption has been used successfully for low-pressure gas streams containing between 3% and 25% of CO<sub>2</sub>, but the large solvent regeneration costs associated with the process hamper its application to higher CO<sub>2</sub> contents. The degree of absorption is limited by the fixed stoichiometry of the chemical reaction. As a consequence, the use of this process for CO<sub>2</sub>-rich gas streams will lead to high solvent circulation flowrates and high energy requirements. Gas permeation techniques are compact and flexible, and can be adapted easily to changes in CO<sub>2</sub> content. However, reliability is a concern because natural gas contaminants can lead to a deterioration in the performance of the membrane. Physical absorption can also be used successfully; the main advantage of such a process is that (unlike chemical absorption) physical solvents have no absorption limitation. The amount of CO<sub>2</sub> absorbed by the solvent is determined by the vapour-liquid equilibrium of the mixture, which is governed by the pressure and temperature. At high CO<sub>2</sub> partial pressure, the CO<sub>2</sub> loading capacity of the solvent is higher for a physical solvent than for a chemical solvent. Physical absorption processes are thus particularly appropriate for the treatment of CO<sub>2</sub>-rich gas streams.

## Solvents for physical absorption

Many solvents have been used for the absorption of CO<sub>2</sub> and H<sub>2</sub>S including, formulations of tributyl phosphate, polycarbonate, methylcyanoacetate, and *n*-formyl morpholine [2]. There are major

drawbacks with such solvents: they are not easily disposable (for offshore operations) and could be involved in side reactions with other natural gas constituents. A hydrocarbon solvent such as *n*-butane is more suitable as it does not react and can easily be handled in an oil and gas environment; *n*-butane has been used in the Ryan-Holmes cryogenic separation process [3]. The process has a satisfactory CO<sub>2</sub>/CH<sub>4</sub> separation factor, but operation at low temperatures is very energetically demanding. Like *n*-butane, other alkanes such as *n*-decane are known to absorb CO<sub>2</sub> preferentially to CH<sub>4</sub>: experimental findings indicate K-values [separation factor,  $K = (\text{CO}_2:\text{CH}_4)_{\text{liquid}} / (\text{CO}_2:\text{CH}_4)_{\text{gas}}$ ] ranging from 1.2 to 1.8 [4]. The use of higher alkanes or alkane blends may provide a promising route towards adapting the Ryan-Holmes process to the temperatures and pressures typical of gas fields. In addition, the alkane solvent presents the advantage to be cheap, easily available, and tuneable (mixture of alkanes).

## METHODOLOGY

### Flowsheet

The proposed flowsheet, which is relatively conventional, is shown in Figure 1. A gas feed composed of CH<sub>4</sub> and CO<sub>2</sub> is expanded before entering the absorber. The gas mixture, travelling upwards, meets a solvent stream travelling downwards. The gas stream in contact with the solvent becomes leaner in CO<sub>2</sub>. The clean natural gas leaves through the top of the absorber, while the solvent charged in CO<sub>2</sub> leaves through the bottom of the absorber. The solvent passes through two flash units, where the pressure is progressively reduced. The vapour from the first flash unit is re-compressed and mixed with the natural gas feed. The vapour from the second flash unit, comprising mainly CO<sub>2</sub>, forms the CO<sub>2</sub> product stream, which can then be stored or used for enhanced recovery. The clean solvent leaving the second flash unit together with a make-up stream of fresh solvent is re-compressed and re-injected into the absorber.

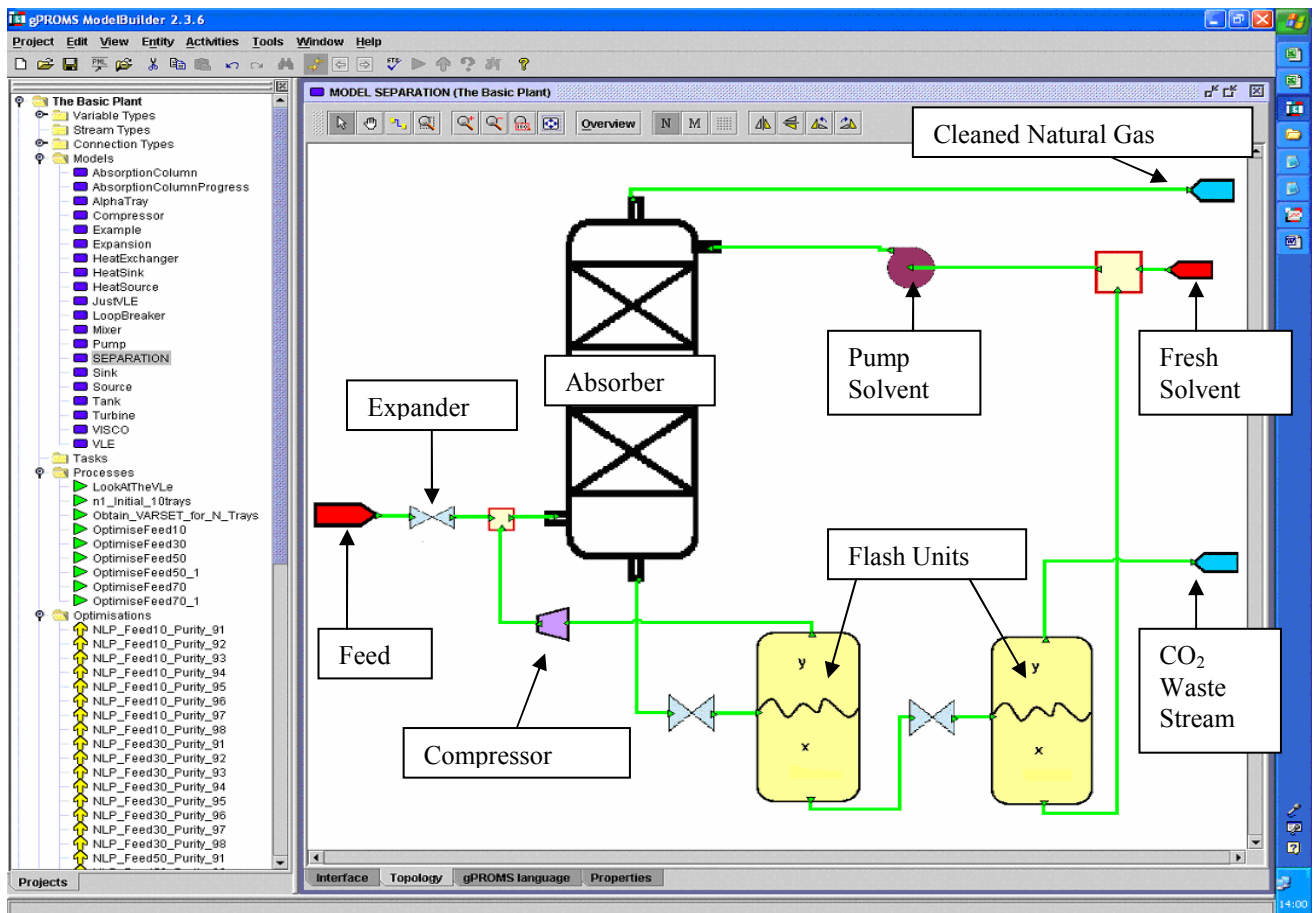


Figure 1: Separation process flowsheet in gPROMS.

## Process model

Steady-state mass and energy balances for all the units in the flowsheet are derived, and thermodynamic equilibrium is assumed in each. The model is able to identify whether one or two phases are present in any of the units. Two-phase equilibrium is specified via the equality of pressures and chemical potentials of all components in the two phases. In the first instance, full efficiency is assumed for every equilibrium tray in the absorber. The process model requires the following physical properties: enthalpy, entropy, heat capacity, chemical potential, and pressure, which have to be calculated using an equation of state given the high-pressure conditions and non-ideality of the mixture. The SAFT-VR equation of state [5,6] has been chosen for its ability to represent phase behaviour accurately over a wide range of conditions, and to treat homologous series of mixtures, in a predictive way [7]. In addition, we are planning to compare our alkane solvent process with more conventional amine chemical absorption processes. SAFT-VR offers a unified platform for the description of association and the modelling of chemical reactions such as those involved in aqueous amine systems. The equation of state and conditions for phase equilibria are implemented in the gPROMS modelling software [8]; the SAFT-VR calculations are implemented in FORTRAN90 and accessed via a Foreign Object (FO) interface [9].

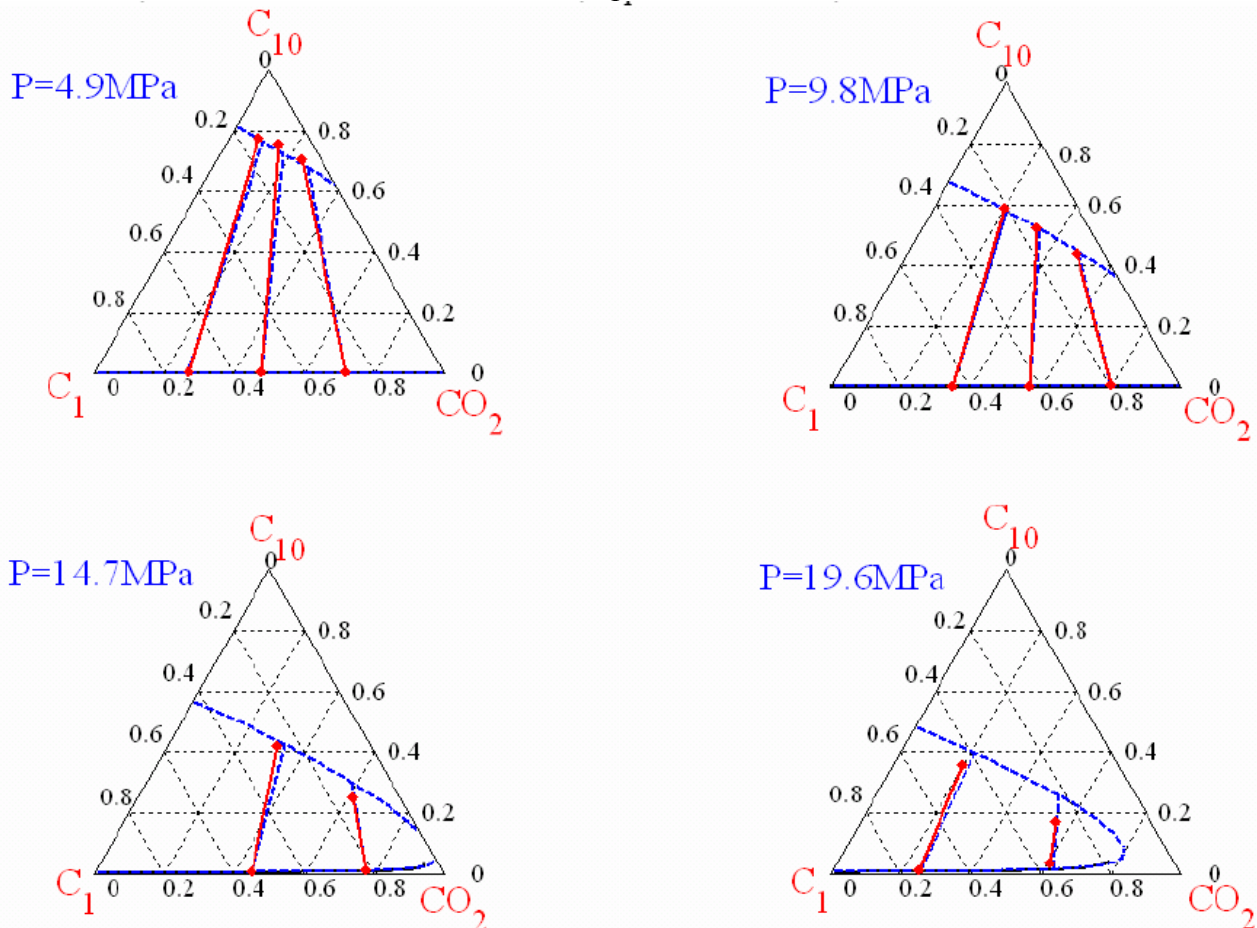
## SAFT-VR model for CO<sub>2</sub>/CH<sub>4</sub>/*n*-alkane mixtures

The SAFT-VR equation of state allows a complete family of solvents to be considered in a seamless fashion. When treating systems which do not associate with the SAFT-VR approach, as is the case here, each component *i* is described by two molecular size parameters, the number of spherical segments in a molecule *m<sub>i</sub>*, and the hard-core diameter of the segment  $\sigma_{ii}$ , and two energy parameters, the strength  $\varepsilon_{ii}$  and range  $\lambda_{ii}$  of the dispersive interactions. Parameters for CO<sub>2</sub> and CH<sub>4</sub> have previously been refined to describe coexistence data as well as the critical temperature and pressure, as the region near the critical point of these two compounds is of interest here [10]. For the *n*-alkane solvent to be used in the process, a correlation that gives the SAFT-VR parameters as a function of the molecular weight of the *n*-alkane is used [7]. Standard combining rules can be used to model mixtures of different molecules [6]. This requires binary parameters to describe the interactions between species *i* and *j*. The following relations are used:  $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ ;  $\varepsilon_{ij} = (1 - k_{ij}^\varepsilon) \cdot \sqrt{\varepsilon_{ii} \cdot \varepsilon_{jj}}$ ;  $\lambda_{ij} = (\sigma_{ii} \cdot \lambda_{ii} + \sigma_{jj} \cdot \lambda_{jj}) / (\sigma_{ii} + \sigma_{jj})$ .  $k_{ij}^\varepsilon$  is an additional parameter, which captures the deviation of the unlike interaction energy from the geometric mean. In our work, this interaction parameter is estimated based on isothermal vapour-liquid equilibrium data over a wide range of temperatures and pressures for each of the three relevant binary mixtures. *n*-decane (*n*-C<sub>10</sub>H<sub>22</sub>) is used as a representative compound in the *n*-alkane series as large sets of experimental data are available. We select all the experimental data available in Detherm [11] at pressures below 10 MPa and temperatures below 477 K (this corresponds to the operating range of the process): namely, 312 points over 24 temperatures for CO<sub>2</sub>/CH<sub>4</sub> mixtures, 111 points for CH<sub>4</sub>/*n*-C<sub>10</sub>H<sub>22</sub> and 85 points for CO<sub>2</sub>/*n*-C<sub>10</sub>H<sub>22</sub>, both over 15 temperature values. Each  $k_{ij}^\varepsilon$  is estimated by using the maximum likelihood objective function for the mixture pressure and the vapour mole fraction, as a function of liquid mole fraction and temperature. A constant variance model was used. The binary interactions  $k_{ij}^\varepsilon$  for CO<sub>2</sub>/CH<sub>4</sub>, CH<sub>4</sub>/*n*-C<sub>10</sub>H<sub>22</sub> and CO<sub>2</sub>/*n*-C<sub>10</sub>H<sub>22</sub> were respectively 0.036798, -0.053006, and 0.089642, and resulted in an absolute average percentage error in the pressure of 2.1, 9.9, and 7.6%, and absolute average deviation in the vapour mole fraction of 0.0236, 0.0010, and 0.0027 mol/mol respectively. Since the *n*-alkanes belong to a homologous series, we assume that the interaction parameters between CH<sub>4</sub> (or CO<sub>2</sub>) and any *n*-alkane solvent are the same as those between CH<sub>4</sub> (or CO<sub>2</sub>) and *n*-decane. Furthermore, *n*-alkane *i*/*n*-alkane *j* interactions are described with  $k_{ij}^\varepsilon = 0$ .

## Separation Cost Estimation

Capital and operating costs are estimated using a detailed costing method. Each unit of the process is sized and its cost is evaluated. The sizing of the units is based on the characteristics of the flow passing

through the unit such as the flowrate, the pressure, the viscosity... etc. Correlations between the unit size and the unit purchased cost are available in the literature and provide reasonable purchased cost estimates [12, 13, 14, 15]. An installation factor is applied to the purchased cost of each unit in order to obtain the unit installed cost [16]. The total installation costs (or onsite cost) of the plant is a fraction of the total capital investments (TCI). Numerous other costs have to be accounted for, such as offsite direct costs (buildings, yard improvement, service facilities, non-process equipments), indirect costs (engineering and supervision, construction expenses, contractor's fees, and contingency), working capital, and start-up costs. A breakdown of such costs has been proposed by Douglas [15]. For this study, the TCI is taken to be 2.35 times the onsite cost. The operating costs are decomposed into direct and indirect operating costs. An estimate of these is based on the labour cost and utilities requirements for each unit, as well as the maintenance costs, supervisions costs, and taxes.



**Figure 2: A comparison of SAFT-VR predictions (dashed lines) and the experimental data (continuous lines) [4] for the vapour-liquid equilibria of the ternary  $\text{CO}_2/\text{CH}_4/n\text{-C}_{10}\text{H}_{22}$  at a temperature of 344.15K and pressures of 4.9, 9.8, 14.7, and 19.6 MPa.**

### Formulation of the design problem

The objective is to remove the  $\text{CO}_2$  from the natural gas so that the product is purified to some commercial specification, generally 97-98%. The cleaned natural gas is then sold, and the objective is thus to maximise the profit of the overall process. We quantify the profit as the income from the sales of natural gas over the life of the project minus the total separation cost (capital and operating). This problem is in fact equivalent to the minimisation of the sum of the losses of natural gas in the  $\text{CO}_2$  outlet (waste) stream, and of the total separation cost:

$$\text{Objective} = \text{Methane Losses in the } \text{CO}_2 \text{ stream} + \text{Total Separation Cost}$$

The minimisation of this cost function will give a maximal profit from the sales of the natural gas.

Several control variables can be tuned to get the optimal process for a given feed condition. The design variables are the pressures of the absorber (P0) and recycler (P1), the solvent recirculation flowrate (F), the number of carbon atoms of the *n*-alkane solvent (*n\_alkane*) and the number of theoretical plates in the absorber (*n\_trays*). Numerous constraints are required in order to obtain a realistic solution. Alkane-rich streams should be at a temperature 10K above the melting point to avoid solidification. The gas streams should have a temperature above 273.15K to avoid problems with rich-CO<sub>2</sub> streams. The size of the absorber should also be limited: the maximal height is taken as 50m and maximal cross section as 30m<sup>2</sup> (diameter 6.2 m). The number of carbon atoms of the *n*-alkane solvent has been chosen between 9 and 14 in order to avoid excessive volatility (low carbon number limit) or viscosity (high limit).

## RESULTS

### Prediction of the vapour-liquid equilibrium for CO<sub>2</sub>/CH<sub>4</sub>/*n*-C<sub>10</sub>H<sub>22</sub>

One key assumption of our thermodynamic model is that ternary phase behaviour can be captured solely by using the three binary interaction parameters. As for most equations of state the SAFT approach is a binary theory in which only separable pair interactions are assumed. To test this we compare the predicted tie-lines for mixtures of CO<sub>2</sub>, CH<sub>4</sub> and *n*-C<sub>10</sub>H<sub>22</sub> with experimental data [4] for four pressures. The description of the vapour-liquid equilibria of the ternary with the SAFT-VR thermodynamic model is in very good agreement with the data, even for pressures above 10 MPa, as shown in Figure 2.

### Process Optimisation & Cost Estimate

Our case-study corresponds to a natural gas feed composed of only CO<sub>2</sub> and CH<sub>4</sub>. The amount of CO<sub>2</sub> in the feed is increased successively: 10%, 30%, 50% and 70% (mol/mol). The feed temperature is taken as 301.4 K, the pressure as 7.961 MPa, and the gas flow rate is 68 MMSCFD (Million Standard Cubic Feet) (or 1000 mol/s); these values are taken for a separation in a typical gas process. The life time of the project is assumed to be 15 years, the sale price of natural gas is been taken to be 10 USD per million BTU (British Thermal Unit), and the interest rate is 5%pa. In this study, the number of equilibrium stages in the absorber is 10 as this is found not to be a critical parameter. The number of carbon atoms of the *n*-alkane solvent is taken as the top limit of 14 for this preliminary study. For the 4 feed compositions, it is possible to achieve a 97% purity for the clean natural gas. Details of the process economics, the control variables, and the absorber size are given in the table. The flexibility of our process to changes in the feed composition is particularly good as an increase in the CO<sub>2</sub> fraction in the feed does require large changes in the control variables and absorber dimensions.

**Table: Process economics, control variables and absorber dimensions for 4 feed compositions (costs are in MMUSD-2005, Million US dollar bases on 2005 figures)**

Amount of CO <sub>2</sub> in the Feed (mol/mol)	10%	30%	50%	70%
Natural Gas Sales	2400	1829	1314	793
Total Separation Cost	50	82	96	114
CH <sub>4</sub> losses in the CO <sub>2</sub> outlet	88	107	69	36
Total Operating Cost	27	42	50	61
Total Capital Investment	23	40	46	53
CH <sub>4</sub> recovery	96.5%	94.5%	95%	95.6%
CO <sub>2</sub> recovery	73.2%	93.2%	97.1%	98.7%
CO <sub>2</sub> stream purity	69.6%	87.9%	95.1%	98.1%
Absorber Pressure (MPa)	4.72	4.80	4.75	4.83
Recycling Tank Pressure (MPa)	1.56	1.99	1.94	1.93
Solvent Recirculation Flowrate (100mol/s)	6.4	8.6	10.4	12.7
Absorption Column Height (m)	30.1	30.0	30.1	30.0
Absorption Column Section (m <sup>2</sup> )	8.8	14.5	16.1	17.1

## CONCLUSION

We have developed a methodology to model a new physical absorption process for the capture of CO<sub>2</sub> from natural gas. Various conditions of pressure, temperature and composition occur in the plant, from atmospheric to high pressure – high temperature. The advantage of using advanced thermodynamics such as SAFT-VR is that the wide range of conditions is treated with a single model. A very good description of the phase behaviour is achieved over a wide range of pressures. A detailed analysis of the capital and operating cost is carried out. An optimal process is developed to cover a wide range of CO<sub>2</sub> concentration in the feed (from 10% up to 70%). In this study we have shown that the separation of CO<sub>2</sub> from natural gas with an ordinary *n*-alkane is not only possible solvent, but also economically viable. This new process can certainly compete with membrane processes in term of flexibility.

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