

Modelling of Natural Gas Sweetening and Dehydration prior to Liquefaction

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Abstract

The present work comprises the modelling of natural gas (NG) purification prior to liquefaction, more precisely its sweetening and dehydration.

Since NG exists in underground reservoirs it contains several impurities that must be removed in order to meet liquefied natural gas (LNG) specifications, since they can cause corrosion, plugging and others. In this way, the sweetening of NG using diethanol amine (DEA) was simulated in gPROMS[®], as well as its dehydration using in the first place a glycol solvent (absorption) and then molecular sieves (adsorption).

The first two processes are very similar and both use absorption columns with equilibrium stages to promote intimate contact between the solvent and the impurities. Then, both solvents are regenerated in distillation columns with trays. Regarding the dehydration of NG via adsorption, zeolite 5A was used, and some custom models were developed. In this case, the adsorption of water was simulated using an isothermal adsorption bed.

In the sweetening of NG, a sweet gas was obtained with CO₂ concentration of 1.3x10⁻⁴ mol. % and H₂S concentration of 5.2 mol. %, using DEA with a concentration of 35 wt. %, and at the expense of 7.3 GJ/ton acid gases absorbed.

In the simulation of NG dehydration with triethylene glycol (TEG), a dried gas was obtained with 41 ppmv of water, at the expense of 5.4 GJ/ton water absorbed and using a solvent with 99 wt. % concentration.

Finally, in the simulation of NG dehydration with zeolite a breakthrough time equal to 1336 minutes was obtained.

Keywords: gPROMS, LNG, sweetening, dehydration, absorption, adsorption

1. Introduction

NG is used primarily as a fuel and as a raw material in manufacturing. It is used in home furnaces, water heaters, and cooking stoves. As an industrial fuel it is used in brick, cement and ceramic-tile kilns, and for generating steam in water boilers. As a raw material in petrochemical manufacturing, NG is used to produce hydrogen, sulphur, carbon black, and ammonia, and as a secondary feedstock for manufacturing other chemicals, such as nitric acid and urea. Ethylene, an important petrochemical, is also produced from NG [1].

NG offers important environmental benefits when compared to other fossil fuels since its emissions of sulphur dioxide are negligible and the levels of nitrous oxide and carbon dioxide emissions are lower in up to 60%. This helps to reduce problems of acid rain, ozone layer, or greenhouse gases [1]. The reserves of conventional NG have grown by 36% over the past two decades and its production by 61%. Between 2010 and 2013, the proved NG reserves have grown by 3% and production by 15% [2].

In 2012, for the first time in many years, the growth in NG demand surpassed that of coal [2]. By 2025, NG is expected to have overtaken coal as the second most consumed fuel, after oil [3]. Despite the current economic difficulties, the global gas market is expected to reach 4 700 bcm by 2030. This growth is supported by an increase in gas production potential and expansion of international trade based on a growing number of liquefied natural gas (LNG) facilities and high pressure pipelines [2].

2. Background

NG exists in nature under pressure in rock reservoirs in the Earth's crust, either in conjunction with and dissolved in heavier hydrocarbons and water, or by itself. NG has been formed by the degradation of organic matter accumulated in the past millions of years [4].

The principal constituent of NG is methane. Others include paraffinic hydrocarbons such as ethane, propane, and butanes. Most of NGs contain nitrogen, as well as carbon dioxide, hydrogen sulphide, and water [1]. The composition of NG varies depending on where it is extracted. It is considered a "dry gas" when it is composed of almost pure methane. Otherwise, it is referred to as "wet gas" [4].

Due to its storage difficulties, gas needs to be transported immediately to its destination after production. Therefore, there are several options for transporting NG energy from oil and gas fields to the market [4].

Pipelines are a very convenient method of transport but are not flexible. If the pipeline has to be shut down, the production and receiving facilities often also have to be shut down because gas cannot be readily stored [4].

LNG technology has been proven to be effective since the mid-1970s. LNG is the liquid form of NG, i.e., gas cooled to approximately -162 °C with a 1/600 volume reduction. The costs of building a LNG plant have lowered since the mid-1980s due to improved thermodynamic efficiencies, making LNG a major gas export method around the world [4]. Since the production of LNG requires low temperatures, the allowable impurity concentrations in the gas to be liquefied are much tighter than that of a pipeline gas, as shown in Table 1.

Table 1: Composition specifications for LNG plant and pipeline gas [1]

Impurity	Feed to LNG plant	Pipeline gas
H ₂ O	<0.1 ppmv	150 ppmv
H ₂ S	<4 ppmv	5.7-22.9 mg/Sm ³
CO ₂	<50 ppmv	3-4 mol %
N ₂	<1 mol %	3 mol %
C ₄ H ₁₀	<2 mol %	-
C ₅ ⁺	<0.1 mol %	-

The three basic reasons for processing raw NG are the following: purification (i.e., removal of materials that inhibit the use of the gas as a fuel), separation (i.e., splitting out of components that have greater value as petrochemical feedstocks, stand-alone fuels, or industrial gases), and liquefaction (i.e., increase of the energy density of the gas for storage or transportation, as stated before) [1]. A typical process operation for NG processing includes steps such as condensate and water removal, sweetening, dehydration, mercury removal, nitrogen rejection, natural gas liquids recovery and fractionation train.

2.1. Sweetening

NG often contains CO₂, H₂S, and other sulphur-containing species that require partial or complete removal since they can form acids in the presence of water. Therefore, these compounds are known as "acid gases" [4]. Depending on various factors, there are several available processes to remove them, being the most common ones solvent absorption (chemical, physical or hybrid), solid adsorption, and membrane separation [1].

Due to their availability and low cost, amines are the most widely used chemical solvents for NG sweetening. Amines are formed from ammonia (NH₃) by replacing one or more of the hydrogen atoms with a hydrocarbon group with OH groups attached to it. Amines remove acid gases in two steps: first the gas dissolves in the liquid (physical absorption) and then the dissolved gas reacts with the amine [1].

2.2. Dehydration

Since the gas leaving the sweetening unit is usually water saturated, almost all plants have a dehydration step. Also, most gas streams contain too much water to enter the cryogenic section of the plant [1]. Dehydration is therefore necessary to meet specifications, reduce corrosion, and to prevent hydrate formation. Gas hydrate formation is a major concern in NG industries, as it causes choking/plugging of pipelines [4]. In order to perform the required dehydration, the most common processes are absorption and adsorption.

Water levels in NG can be reduced to the 10 ppmv range with a physical absorption method in which the gas is contacted with a liquid that preferentially absorbs the water vapour. TEG is the most common liquid desiccant used in NG dehydration due to several reasons [1], [4].

Physical adsorption processes are also used for dehydrating NG streams. Two steps are involved in these processes: first, the component contacts the surface of the particles; after this, the adsorbate travels through the pathways inside the adsorbent. For LNG production, which has a tight water specification, adsorption processes are much more effective than absorption ones since water is much more strongly removed than any other components in the NG stream [1]. The most common commercial desiccants used in this application are silica gel, molecular sieves, and activated alumina. Molecular sieves are the most versatile desiccants because they can be manufactured for a specific pore size and they are capable of dehydration to less than 0.1 ppm water content [4].

3. Materials and Methods

For the development of the flowsheets, gPROMS[®], a process simulator software provided by Process Systems Enterprise Ltd. (PSE), was used. So, gPROMS[®] ModelBuilder and gPROMS[®] ProcessBuilder were used to build, validate, execute, and deploy steady-state and dynamic process models [5].

3.1. gPROMS[®] as Model Builder

A model developed in gPROMS[®] is defined as a set of quantities and mathematical equations that, when coupled with a set of specifications, describe the behaviour of a system. Thus, a model includes a set of equations, variables, and parameters. The value of the parameters is defined on the SET section of the model, whereas variables can either be calculated from equations or assigned on the ASSIGN section of the model. Each variable belongs to a variable type and has upper and lower bounds, and a default value. In the TOPOLOGY section of the model, the connections between objects are defined. These connections can be either written by code or by dragging and dropping objects from the Project Tree and connecting them [6]. Therefore, it is possible to build models in gPROMS[®] graphically in the TOPOLOGY tab of the model.

A component model is a set of equations that describes the physical and chemical behaviour of a unit. These models are usually taken from an existing library. In this manner, a flowsheet is a composite model, i.e., a model that contains other entities as sub-models, built up from component models that represent a process made up of connected unit operations. The required specifications are made using specification dialogs for each component model, which correspond to setting parameters and assigning variables [7].

3.2. Physical Properties Package

Most process models in gPROMS[®] make use of physical properties such as density, enthalpy, and fugacity, which are usually function of temperature, pressure, and composition [8]. Thus, the choice of the right model for the prediction of these properties is a key factor especially when using separation equipment.

In this way, Multiflash[™] (with Peng-Robinson (PR) equation of state) was used for the physical properties estimation of the dehydration of NG with glycol and molecular sieves, whereas gSAFT[®] was used in the sweetening flowsheet using amines.

3.2.1. Multiflash[™]

Multiflash[™] is an advanced software package that allows complex equilibrium calculations. The crucial thermodynamic property calculation performed in this package is the determination of phase equilibrium. This is based on the fundamental relationship that at equilibrium the fugacity of a component is equal in all phases.

Equations of state describe systems more accurately when binary interaction parameters (BIPs) have been derived from the regression of experimental vapour-liquid equilibrium (VLE) data. BIPs are adjustable factors used to alter the predictions from a model until these reproduce as closely as possible the experimental data. The closer the binary system is to ideality, the smaller the size of the BIP, which will be zero for ideal systems [9]. BIPs were therefore estimated from experimental VLE data for the dehydration of NG with glycol for a more accurate prediction, since most of the BIPs present in Multiflash[™] were equal to zero, which does not correspond to the reality. This was made by connecting Multiflash[™] to Microsoft Excel[®].

3.2.2. gSAFT®

The Statistical Associating Fluid Theory (SAFT) is an advanced molecular thermodynamic method that is able to predict thermodynamic properties of mixtures. This method is based on physically realistic models of molecules and their interactions with other molecules. The main advantage of SAFT is that it is predicted by a representation of the molecule that includes its shape, size, and specific interactions with other molecules within the mixture, which means that SAFT accounts for non-spherical molecules, attraction and repulsion between molecules, and strong directional interactions. Therefore, SAFT is capable of predicting properties beyond the range of conditions covered by experimental data. In this way, SAFT is a great tool for modelling the behaviour of systems with polar solvents, hydrogen bonded fluids, and polymers, considered complex materials [5].

gSAFT® Physical Properties Package, a PSE's product platform, is an efficient implementation of SAFT-Variable Range Square Well (SAFT-VR SW) and SAFT- γ Mie equations of state [7].

SAFT-VR SW is used in the simulation of the sweetening flowsheet. This equation of state is an extension of the original SAFT methodology, which deals with systems with variable polarities. With this equation, molecules are considered as associating chains of spherical segments with variable attractive interactions [7].

4. Modelling of Natural Gas Purification

4.1. Sweetening

A simulation was made for the sweetening of NG using a DEA solution as a solvent, in gPROMS® ProcessBuilder and taking into account data from Abdulrahman et al. [10]. The final assembled flowsheet is in Figure 1.

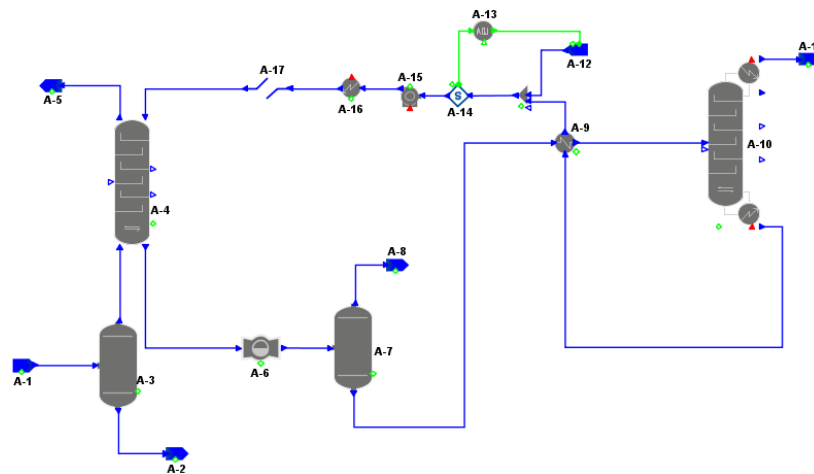


Figure 1: NG sweetening assembled flowsheet

The NG feed (A-1) entering the sweetening unit is at 38 °C and 35.5 bar, and at a flowrate of 120 stdm³/h, with the following composition:

Table 2: Composition of NG feed

Component	Molar composition (%)	Component	Molar composition (%)
H ₂ S	5.37	C ₃ H ₈	6.02
CO ₂	4.47	i-C ₄ H ₁₀	1.36
N ₂	0.11	n-C ₄ H ₁₀	2.44
H ₂ O	0.13	i-C ₅ H ₁₂	1.03
CH ₄	63.27	n-C ₅ H ₁₂	0.73
C ₂ H ₆	13.88	C ₆ H ₁₄	1.19

The gas goes through a knock out drum (A-3) in order to remove free liquids (A-2). The solvent is a DEA solution (35 wt. %), which enters at the top of the column at a volumetric rate of 400 m³/h and at 40 °C and 35.5 bar. The absorber has 20 equilibrium stages and the pressure is specified (35.5 bar).

The rich amine is directed to a valve (A-6) in order to reduce the pressure to 620 kPa and then to be flashed in a flash tank (A-7). The rich amine solution leaving the flash tank is heated to 95 °C with a pressure drop in the heat exchanger A-9 of 70 kPa.

The rich solvent needs to be regenerated before being recycled back to the absorber and this is done with a distillation column (**A-10**) at 1.9 bar and with a kettle reboiler and a partial condenser working at full reflux¹. This column has 23 equilibrium stages and the rich amine is fed in the 4th stage. The reflux ratio was assigned as equal to 1.5 mol/mol and the value of the boilup ratio (0.12 mol/mol) was defined in order to obtain the desired DEA concentration in the regenerated solvent stream.

The regenerated amine is cooled in the amine-amine heat exchanger (**A-9**) and a water make-up (**A-12**, at 25 °C) is added to the solvent solution. Finally, the lean solvent is pumped (**A-16**) and cooled again (**A-15**) before being recycled to the absorber.

4.1.1. Main Results

Table 3 presents the concentrations of acid gases in the sweet gas for gPROMS[®] simulation and the simulation results from Abdulrahman et al. [10].

Table 3: Comparison between results for sweet stream

	Abdulrahman et al. [10]	gPROMS [®]
CO ₂ in sweet gas (mol. %)	3.74x10 ⁻²	1.34x10 ⁻⁴
H ₂ S in sweet gas (mol. %)	3.42x10 ⁻⁴	5.24

As it can be seen, the sweet gas still has a high concentration of H₂S, which corresponds to a removal efficiency in the absorber quite low (4.8 wt. %). This is due to the fact that gSAFT[®] is not yet validated with data for H₂S, regarding its removal with amines.

The CO₂ content in the sweet gas is about 1.3 ppmv, far less than the 50 ppmv required for liquefaction. On the other hand, the minimum CO₂ concentration attainable with DEA is 50 ppmv [1]. However, a higher removal rate of CO₂ could be expected, because the absorption in the amine is competitive: since H₂S is not being absorbed as it should be in the DEA solution, there is no competitive absorption between the acid gases, which causes CO₂ to be almost completely removed from the NG feed.

The results for the regeneration column (**A-10**) are given in Table 4.

Table 4: Main simulation results for the regenerator (**A-10**)

	Top (acid gases, A-11)	Bottom (lean solvent)
Temperature (°C)	83.7	122.3
Pressure (bar)	1.9	1.9
Mass flowrate (kg/s)	3.4	111.2
Condenser heat duty (kW)	6134	
Reboiler heat duty (kW)	21451	
Mass composition (%)		
H ₂ S	3.3	0
CO ₂	82.3	0.2
H ₂ O	14.3	64.4
DEA	0	35.4

Since there are some water losses throughout the simulation, a water make-up is needed to guarantee a supply of 400 m³/h of DEA solution to the absorber and to avoid a build-up in DEA's concentration. The total water loss is around 0.516 kg/s, which corresponds to the water make-up (**A-12**) needed in the mixer.

4.2. Dehydration with Glycol

A flowsheet was assembled for the dehydration of NG using triethylene glycol (TEG) as a solvent. The flowsheet was simulated in gPROMS[®] ModelBuilder and it is presented in Figure 2, taking into account data from Ghati [11].

For the NG feed (**B-1**), a flow of 70 MMSCFD was chosen at 30 °C and 81.7 bar. The composition of the NG feed is shown in Table 5.

Table 5: Composition of NG feed

Component	Molar composition (%)	Component	Molar composition (%)
CH ₄	97.00	C ₆ H ₁₄	0.03
C ₂ H ₆	1.03	C ₇ H ₁₆	0.11
C ₃ H ₈	0.31	C ₈ H ₁₈	0.05
i-C ₄ H ₁₀	0.07	C ₉ ⁺	0.02
n- C ₄ H ₁₀	0.09	H ₂ O	0.13
i-C ₅ H ₁₂	0.03	CO ₂	0.37
n-C ₅ H ₁₂	0.03	N ₂	0.72

¹ Top product liquid flowrate set to 0 kg/h.

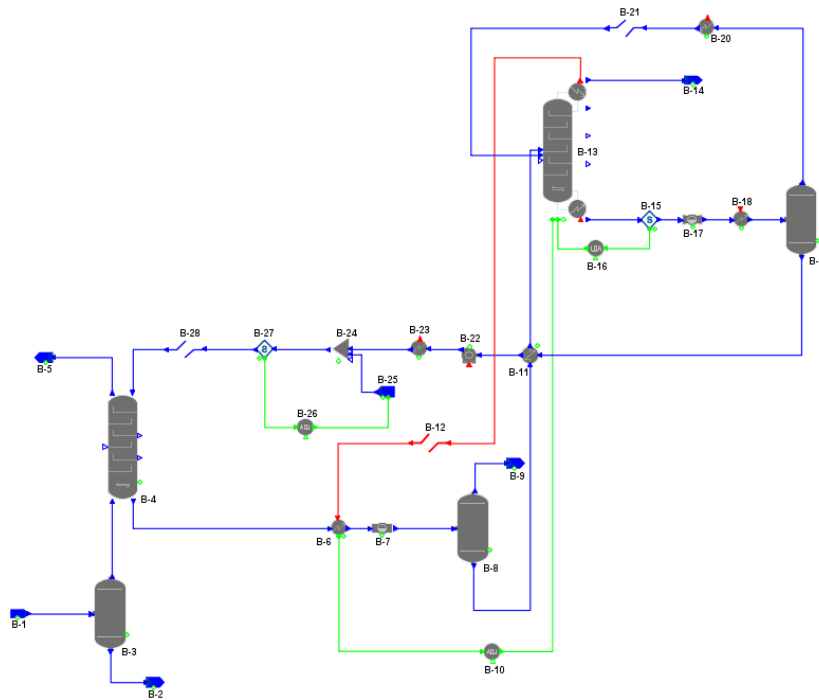


Figure 2: NG dehydration process flowsheet

The NG feed enters an inlet scrubber (**B-3**) in order to remove liquids (**B-2**). The absorber (**B-4**) has 3 equilibrium stages, operates at 81.7 bar, and works in counter current flow. The gas enters the column at 30 °C, while the solvent (TEG) is at 35 °C, with a glycol concentration of 99 wt. %. The glycol circulation rate entering the top of the absorber column should be around 1250 kg/h.

The rich glycol then flows to the regenerator's (**B-13**) condenser as the cooling fluid. In gPROMS®, it is not possible to connect the solvent stream directly to the condenser, so an alternative was arranged. The rich solvent enters a heater (**B-6**) that has an external energy connection (represented by the red line **B-12**), which indicates that the heat duty of the heater **B-6** is the same as the regenerator's condenser. Since the outlet temperature of the heater is not specified, an *adj_spec* model (**B-10**) is used to assign it. This model is used to achieve a target outlet temperature in the heater by changing the reflux ratio of the regeneration column.

After being heated, the rich solvent is flashed (**B-8**), due to a pressure reduction to 3.013 bar in a valve (**B-7**). After this, the rich solvent is heated again in the glycol-glycol heat exchanger (**B-11**) to 165 °C before entering the regeneration column. Finally, the rich solvent is regenerated in a distillation column (**B-13** with partial condenser (at full reflux) and kettle reboiler. This column has 5 equilibrium stages and the solvent enters at the 3rd stage. The column works at a pressure of 1.2 bar. The maximum allowable temperature in the reboiler is about 204 °C due to the possible decomposition of the solvent. In order to achieve this temperature, another *adj_spec* model (**B-16**) is used, adjusting the boilup ratio of the distillation column.

There is another stream being fed to the regeneration column: the vapour at the top of the vacuum drum (**B-19**) that acts like a stripping gas in the regenerator. This stream enters at the bottom of the column.

The water vapour is recovered at the top of the regenerator, while the lean solvent leaves at the bottom at 204 °C. The pressure of the lean solvent is reduced in a valve (**B-17**) to around 0.8 bar and reheated to 204 °C in a heater (**B-18**) before being fed to a vacuum drum (**B-19**). The vapour at the top is cooled to 165 °C and recycled back to the regenerator.

The liquid at the bottom of **B-19**, which has the desired concentration, is cooled in the glycol-glycol heat exchanger (**B-11**), pumped (**B-22**), and cooled again (**B-23**). Then, a solvent make-up (**B-25**) with the same composition as the lean solvent is added in a mixer (**B-24**).

4.2.1. Main Results

The water mass composition in the dry gas is around 44 ppm (41 ppmv), which corresponds to a removal of 94.2 wt. % of water in the absorber. The water content in the gas meets the specification for pipeline gas, but does not meet the required low water content for LNG plants. However, it is common practice in NG dehydration to use a glycol dehydration unit for bulk water removal followed by a unit with molecular sieves for final purification.

In Table 6 a comparison is made between the results from Ghati [11] and the ones from gPROMS® for the absorber.

Table 6: Comparison between the simulation results and the results from Ghati [11]

	Ghati [11]	gPROMS®	Deviation (%)
Dry gas temperature (°C)	30.73	30.66	0.4
Dry gas mass flowrate (kg/h)	58500	58528	0.05
Rich glycol temperature (°C)	30.55	30.50	0.2
Rich glycol mass flowrate (kg/h)	1299	1292	0.6
Absorption capacity (%)	98.2	94.2	4.1

The deviations are quite insignificant, except for the absorption capacity, which is higher in the simulation results from Ghati [11]. This is probably due to the physical properties package used by Ghati [11]: Aspen Hysys® includes a glycol package specially designed for TEG dehydration that uses Twu-Sim-Tassone equation of state [12], which could explain the difference in the absorption capacity.

For the regenerator (B-13), the main results are given in Table 7.

Table 7: Main simulation results for the regenerator (B-13)

	Top (B-14, water vapour)	Bottom (lean solvent)
Temperature (°C)	105	204
Mass flowrate (kg/h)	42	1266
Condenser heat duty (kW)	11.0	
Reboiler heat duty (kW)	62.6	
Reflux ratio (mol/mol)	0.41	
Boilup ratio (mol/mol)	0.24	
Mass composition (%)		
CH ₄	0.2	0
H ₂ O	99.0	1.6
CO ₂	0.8	0
TEG	0	98.4

A solvent make-up is needed since there are some minor losses of glycol throughout the process. The total glycol loss corresponds to 0.0018% of the flow of solvent entering the absorber. Hence, a make-up of 0.023 kg/h of glycol is needed.

4.3. Dehydration with Molecular Sieves

At last, a flowsheet was assembled for the dehydration of NG using molecular sieves, more precisely zeolite 5A, for which some custom models were developed. This process was simulated in gPROMS® ProcessBuilder and this is a dynamic simulation. Only the adsorption of water was simulated in gPROMS®.

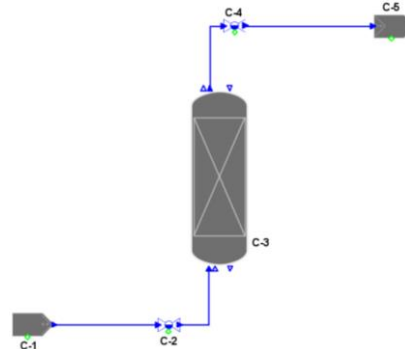


Figure 3: Adsorption scheme flowsheet

Some custom models from Gholami et al. [13] and Ruthven [14] were added to the existing gPROMS® adsorption models: models to obtain the axial dispersion coefficient and the adsorption isotherm were developed. Also, the model of the mass transfer rate was altered.

The axial dispersion coefficient is given by the equation below:

$$D_{axi} = \gamma_1 D_{mi} + \gamma_2 d_p u \quad (1)$$

where γ_2 is a constant usually equal to 0.5.

The constant γ_1 can be related to the bed voidage in the following manner:

$$\gamma_1 = 0.45 + 0.55 \epsilon_b \quad (2)$$

The equilibrium concentration of component i in the micropores is calculated using the extended dual site Langmuir isotherm for multi-component adsorption:

$$q_{ci}^* = q_{si1} \frac{\beta_{i1} p_i}{1 + \sum_{j=1}^n \beta_{j1} p_j} + q_{si2} \frac{\beta_{i2} p_i}{1 + \sum_{j=1}^n \beta_{j2} p_j} \quad (3)$$

The constants β_{ij} and q_{sij} are temperature dependent constants, obtained by:

$$\beta_{i1,2} = b_{0i,2} \exp\left(\frac{E_{i1,2}}{RT}\right) \quad (4)$$

$$q_{si1,2} = \frac{A_{i1,2}}{T} + A_{i1,2} \quad (5)$$

The linear driving force (LDF) model is used for the mass transfer rate through micropores volumes and it is given by the following equation:

$$\frac{\partial q_{ci}}{\partial t} = \frac{15D_{ci}}{R_c^2} (q_{ci}^* - q_{ci}) \quad (6)$$

The crystalline diffusivity is calculated using the following expression:

$$D_{ci} = D_{0i} \exp\left(-\frac{E_i}{RT}\right) \quad (7)$$

All the parameters presented in the above equations are provided by Gholami et al. [13].

The NG feed (**C-1**) enters the bottom of an adsorption bed at 295.5 K and 64.8 bar, with a molar flowrate of 23929 kmol/h. The composition of the gas stream is presented in Table 8.

Table 8: Molar composition of NG feed

Component	Molar composition (%)
H ₂ O	0.184
CO ₂	0.998
CH ₄	95.300
N ₂	3.518

The adsorption bed (**C-3**) has one layer of zeolite 5A and the bed and adsorbent properties specified in gPROMS[®] are presented in Table 9.

Table 9: Bed and adsorbent properties specified

Bed properties		Adsorbent particle properties	
Layer length (m)	5.5	Particle density (kg/m ³)	1812.5
Bed internal diameter (m)	3.5	Particle void (m ³ /m ³)	0.36
Bed void (m ³ /m ³)	0.34	Particle diameter (m)	0.0026
		Particle thermal conductivity (W/(m.K))	0.5
		Particle heat capacity (J/(kg.K))	1000

In what concerns heat transfer, an isothermal operation was considered for the sake of simplicity and time. In this manner, a bed temperature of 295.5 K was specified. Finally, a simplified momentum balance was chosen, as well as unidirectional flow mode and 80 discretisation points per layer.

4.3.1. Main Results

Table 10 presents the comparison between the breakthrough time obtained from gPROMS[®] and from Gholami et al. [13]. Breakthrough was considered to take place when the water concentration at the end of bed reached the maximum allowable concentration in LNG plants (0.1 ppmv).

Table 10: Comparison between breakthrough time for gPROMS[®] and Gholami et al. [13]

	Breakthrough time (min)
gPROMS [®]	1336
Gholami et al. [13]	610
Deviation (%)	119

As it can be seen, gPROMS[®] predicted breakthrough time is more than double than what it was expected. The breakthrough time depends on several factors, such as initial concentrations, flow rate, column length, temperature and adsorption capacities [15], [16]. All this data was provided by Gholami et al. [13] and used in gPROMS[®], so such a difference in the breakthrough time was not expected. The factor that has the greater impact in the breakthrough time is probably the adsorption isotherm parameters, so a further investigation of these parameters was made.

A comparison was made for the specific saturations capacities and the affinity parameters obtained from gPROMS[®] and Ohlin [17]. Ohlin [17] studied the removal of CO₂ and water from NG, using zeolite ZSM-5 (pore size of around 5 Å) using the dual-site Langmuir isotherm. It was observed that the values of the parameters are quite different, especially for water. This difference in the parameters is expected to have a great effect in the breakthrough time, as said before. Furthermore, an increase in the adsorption capacity (due to an increase in the parameters) of the more strongly removed component causes an increase in the

breakthrough time [15]. In fact, it seems that the parameters of the isotherm are over-estimated for water, which is the most strongly adsorbed component.

The mean interstitial velocity was also compared for both simulations, and it fits very well the results from Gholami et al. [13].

Table 11: Comparison of the results for mean interstitial velocity

	Mean interstitial velocity (m/s)
gPROMS®	0.71
Gholami et al. [13]	0.71
Deviation (%)	0.69

Also, the pressure drop in the adsorption bed was compared and the results are very similar.

Table 12: Comparison of the results for mean pressure drop

	Mean pressure drop (bar)
gPROMS®	1.81
Gholami et al. [13]	1.78
Deviation (%)	1.7

5. Conclusions

The composition of the NG extracted can vary largely depending on where it is extracted. In this manner, the adequate physical properties estimation is sometimes difficult to attain. On the other hand, this wide range in the composition causes the NG processing scheme to have a variety of different options, and their choice will depend on several factors.

In the construction of the flowsheet for NG sweetening, SAFT-VR SW equation of state was used in the form of a software recently developed (and still under development) at PSE, called gSAFT®. However, gSAFT® lacks validation for H₂S absorption in these solutions, and as said before, the physical properties estimation is of extreme importance in simulating NG treatment. In this manner, the results obtained from gPROMS® simulation do not fit the simulation results from the literature and the removal of H₂S is very low: the sweetened gas has 7.8 wt. % in H₂S (4.8 wt.% removal in the absorber) and only 1.3 ppmv in CO₂ (99.9 wt. % removal in the absorber), at the expense of around 21.5 MW of energy (7.3 GJ/ton acid gases absorbed).

One of the most important steps in the treatment of NG is its dehydration, since the water specification for LNG plants is extremely tight. This dehydration may be accomplished in two different ways: absorption or adsorption, which are by far the most common processes. These two methods were used since it is common in NG dehydration prior to liquefaction to first use the absorption method for bulk water removal, followed by adsorption for final purification.

First, a flowsheet for dehydration of NG using glycol was assembled and simulated. In the present work, an enhanced stripping process was used, since the use of a conventional atmospheric regenerator was not enough to achieve the desired glycol purity of 99 wt. % due to the temperature limitation in the reboiler. The dehydration flowsheet assembled in gPROMS®, which uses Peng-Robinson (PR) equation of state, fits well the simulation results from the literature, expect for a 4 % deviation in the absorption capacity that could be explained by the different physical properties packages. Therefore, a dried stream of NG is obtained with a water composition around 41 ppmv, with an energy consumption of 63 kW (5.4 GJ/ton water absorbed).

Finally, the adsorption of water from NG using molecular sieves was modelled and simulated. The simulation results from gPROMS® do not fit well the results from the literature: the predicted breakthrough time (1336 min) is almost double. This happens since gPROMS® predicts significantly higher adsorption capacities. The adsorption isotherm parameters obtained in gPROMS® were compared with typical values. In fact, gPROMS® values are in most cases much higher, which could explain the difference observed between breakthrough times.

Nomenclature

A_{ij}	Auxiliary adsorption equilibrium parameters (mol/kg or mol.K/kg)	q_{ci}^*	Equilibrium concentration of component i in the micropores (mol/kg)
b_{0j}	Pre-exponential factor on site j (kPa ⁻¹)	q_{sij}	Specific saturation capacity of component i on site j (mol/kg)
D_{0i}	Diffusional pre-exponential factor of component i (m ² /s)	R	Ideal gas constant (J/(mol.K))

D_{axi}	Axial dispersion coefficient of component i (m^2/s)	R_c	Sorbent crystal radius (m)
D_{ci}	Crystalline diffusivity of component i (m^2/s)	t	Time (s)
D_{ij}	Diffusivity coefficient (m^2/s)	T	Absolute temperature (K)
D_{mi}	Molecular diffusivity of component i (m^2/s)	u	Interstitial gas velocity (m/s)
d_p	Adsorbent particle diameter (m)	Y_i	Molar fraction of component i in the adsorbed phase (mol/mol)
E_i	Diffusional activation energy of component i (J/mol)	β_{ij}	Affinity parameter of gas i on site j (kPa^{-1})
E_{ij}	Adsorption energy of component i on site j (J/mol)	γ_1	Auxiliary parameter for axial dispersion
p_i	Partial pressure of component i (kPa)	γ_2	Auxiliary parameter for axial dispersion
q_{ci}	Mass of component i adsorbed into the micropore volume (mol/kg)	ε_b	Bed voidage (m^3/m^3)

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