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Membrane contactor for subsea natural gas dehydration: Model development and sensitivity study

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Abstract

A mathematical model of a membrane contactor using triethylene glycol (TEG) for dehydration of natural gas at subsea operation conditions has been developed. The goal for the membrane contactor is to dehydrate the natural gas to transport pipeline specifications, which are -19°C at 69barg. The membrane contactor model is based on a hollow fiber configuration with the gas in the shell side and the liquid absorbent inside the fiber. The shell side gas is modelled as one-dimensional on the assumption of turbulent flow, while the fiber/lumen side is modelled as two-dimensional flow due to the laminar flow. Orthogonal collocation is applied to solve the two-point boundary value problem. The developed model is validated against proprietary high pressure experimental data for dehydration of natural gas with TEG in a membrane contactor. The H₂O molar flow removed from the gas phase is predicted by the model with a mean absolute error range of 3 to 7% compared to the experimental results, based on two methods of calculation due to uncertainty in experimental basis. A sensitivity study was performed to evaluate the effect of membrane properties and operation conditions on the dehydration performance. The main findings are that preferred membrane properties from a separation performance point of view are thin membrane, small fiber diameter, long membrane module, high porosity and high permeability. But, the production of the membrane, stability and long term operation also need to be considered in the selection of membrane material and module parameters. For high pressure subsea operation it is found that the use of a dense layer on the top of the porous support could be favourable to prevent wetting of the membrane. It is found that a wetting of 1% already provides a significant drop in separation performance. For the operation conditions the main findings are that high pressure and low temperature are favourable for the separation. Increasing the gas and liquid flow gives increased flux over the membrane, but also results in increased pressure drop in the module. However, as the the membrane contactor will be placed in a system with regeneration of the solvent, the operation conditions should be optimized considering the whole system.

Keywords: Natural gas dehydration, Membrane contactor, Modelling, Triethylene glycol (TEG)

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1. Introduction

After a century of exploration, the petroleum industry is running out of easily accessible oil and gas reservoirs giving an increased interest for subsea processing. Subsea processing is considered as an enabling technology for development of fields with longer tie-back distance, in deeper water and in colder/harsher environments. In addition, subsea production can enable increased hydrocarbon production with greater energy efficiency and lower environmental footprint [1]. Natural gas dehydration is one of the main processing steps in natural gas treatment. Water present in the natural gas can cause severe transport problems such as hydrate formation, corrosion and errosion. The common used technology today is monoethylene glycol (MEG) injection to prevent hydrate formation from the reservoir to the topside facility, and further dehydration of the gas topside with triethylene glycol (TEG) in a conventional absorption tower. With the increased interested in subsea processing, alternative natural gas dehydration technologies are need. Several critical aspects need to be considered when designing a subsea processing systems such as: unmanned operation, low maintenance, easy accessibility, high modularity, limited moving parts and compacted units. Subsea dehydration systems are required in the vision of the oil and gas industry to realize the subsea factory. However, subsea dehydration has also several advantages such as no need for continuous injection of MEG, reduced complexity of downstream operation and enabling tie-in of new fields to existing platforms with gas processing limitations and direct export of the gas [2].

Membranes and membrane contactors have been suggested as potential technology for subsea natural gas treatment due to the high modularity, high flexibility and compact design [2]. Membrane contactor is a hybrid technology combining the advantages from membranes and absorption processes. Compared to conventional towers, membrane contactors have several advantages such as high and constant interface between the two phases, no direct contact of the two phases giving more flexibility to independent control the gas and liquid flow rates without problems such as flooding or foaming [3, 4]. Membrane contactors have been intensively studied over the last decade for different applications, especially for CO_2 capture. Accordingly, reported membrane contactor models are mainly devoted to CO_2 capture with chemical absorption [5–22], but also some with physical absorbents [23–25]. Dehydration of natural gas with TEG is a physical absorption process, and models for dehydration will be similar to physical CO_2 capture. To the best of our knowledge, only one study on natural gas dehydration with membrane contactors is reported [26, 27]. King et al. reported results from a pilot tests of a membrane contactor unit for dehydration of natural gas. The main purpose with the test was to provide dry natural gas which meets the pipeline specifications, test a specially coated membrane to prevent BTEX (Benzene, Toluene, Ethylenen benzene and Xylenes) emissions and to verify a simulation model for water absorption into TEG [26].

There are several different modelling strategies currently used for membrane contactors (CO_2 removal), namely one-dimensional (1D) models [5–9, 23, 28, 29], combined one-dimensional and two-dimensional (1D-2D) models [10–12, 30, 31] and two-dimensional (2D) models [8, 13–22, 24, 25]. In the 1D modelling strategy, both the liquid and gas phases are evaluated in one direction, the axial direction. Changes in radial direction due to diffusion in the liquid or gas phase are not included in these models. The total mass transfer resistance from the bulk gas phase to the bulk liquid phase is found based on a resistance in series approach with film theory for the boundary layers. Both convective flow in axial direction and diffusion in radial direction are considered for the liquid phase in the 1D-2D model approach. While for the gas phase, only convective flow in axial direction is considered. The introduction of a more rigorous differential mass balance for the liquid phase gives no need for a correlation to estimate the liquid mass transfer coefficient. This model approach is supported by the fact that the mass transfer resistance in the gas phase has almost negligible effect and the liquid phase normally has significant effect. Therefore, including a more detailed estimation of the concentration profile in the liquid phase may give a better description of the system [21]. The most complex strategy is the 2D model. In these models convection and diffusion contributions for both liquid and gas phases are included. Increased complexity of the model results in larger computational time, and hence the proper level for a given system needs to be found. Chabanon et al. [21] gives a critical comparative study of the different modelling strategies, concluding that all the models perform equally in terms of fitting to experimental results by adjusting the membrane mass transfer resistance. The required complexity of the model is therefore dependent on the system. If the liquid phase in the fiber has a concentration profile, using a 1D model can give wrong predictions as the driving forces can be over- or underestimated compared to the actual conditions.

Membrane contactors are evaluated as possible candidates for subsea natural gas dehydration. However, to investigate the feasibility, models of the dehydration system are required to evaluate the performance. In the present work, a mathematical model of the membrane contactor is developed and a sensitivity analysis with regard to operation parameters is performed. The mathematical model developed is implemented into MATLAB and solved with the use of orthogonal collocation. The model is also implemented into Aspen HYSYS with the use of MATLAB Cape-Open. This is for use in process simulation and optimization of a subsea natural gas dehydration system.

2. Model Development

The membrane contactor model reported in this paper evaluates a cylindrical hollow fiber with the liquid flow inside the fiber, and the gas on the shell side. The liquid out/gas in configuration with liquid on the shell side and gas in the fiber would not be a good alternative for this application. The large natural gas flow requires a huge amount of fibers and module space, and hence a large liquid flow is needed. By having the liquid inside the fiber more of the liquid is exposed to the membrane surface, giving a more efficient absorption and less bulk liquid [32]. The model is based on a 1D-2D model strategy, with laminar flow in the liquid side and plug flow on the shell side, as illustrated in Figure 1. The assumption of plug flow implies no axial dispersion in the gas phase. This has been evaluated based on the Peclet number and axial diffusion is found to be neglected. The membrane in the process can be porous, or as illustrated in Figure 1, a dense layer can be used on the top of the porous support. Both cases are reported in the sensitivity study of this paper. The model is developed so the liquid can flow counter-current or co-current to the gas. However, counter-current flow is preferred to maximize the driving force, and hence only this configuration is considered in this paper.



Figure 1: Illustration model strategy used in this paper.

2.1. Assumptions

The following assumptions is used in the model development:

- 1. Steady state
- 2. Equal performance of each fiber
- 3. Plug flow for the gas phase
- 4. Laminar flow for the liquid phase
- 5. Equilibrium at gas-liquid interface
- 6. Gas diffusion in the membrane pores with no Knudsen diffusion

The mathematical model describing the membrane contactor can be developed by evaluating a short section of the membrane fiber, as illustrated in Figure 2.



Figure 2: Illustration of flow model for the membrane contactor.

2.2. Gas Phase - Shell Side

The axial flow model assumed for the gas phase is plug-flow. Base on this assumption the component mass balance equation for the gas phase is given by equation 1

$$\frac{\mathrm{d}n_{\mathrm{g},i}^{\mathrm{s}}}{\mathrm{d}z} = -J_{i}a \tag{1}$$

where $n_{g,i}^{s}$ is the convective molar flow of component *i* referred to the total cross sectional area of the membrane module [kmol/m²_ts], *z* is the axial length segment [m], J_i is the molar flux of component *i* from the gas phase through the membrane and into the liquid phase [kmol/m²_ms] and a is the packing density of membrane area per total volume of membrane module [m²_m/m³_t], equation 2.

$$a = \frac{A_{\rm m}}{V_{\rm mod}} = \frac{\pi n d_{\rm i} L}{\frac{\pi}{4} D^2 L} = \frac{4n d_{\rm i}}{D^2}$$

$$\tag{2}$$

where $A_{\rm m}$ is the membrane area $[{\rm m}_{\rm m}^2]$, $V_{\rm mod}$ is the module volume $[{\rm m}_{\rm t}^3]$, n is the number of membrane fibers, $d_{\rm i}$ is the inner diameter of the fibers [m], L is the length of the membrane module [m] and D is the diameter of the membrane module [m].

The energy balance is developed in the similar way and is given in equation 3 when heat loss to the surroundings are disregarded.

$$\frac{\mathrm{d}T_{\mathrm{g}}}{\mathrm{d}z} = \frac{-U_{\mathrm{tot}}a}{\sum (c_{\mathrm{p},i}n_{\mathrm{g},i}^{\mathrm{s}})} (T_{\mathrm{g}} - T_{\mathrm{l,mem}}) \tag{3}$$

 $T_{\rm g}$ is the temperature of the bulk gas phase [K], $T_{\rm l,mem}$ is the temperature of the liquid phase at the membrane surface [K], $U_{\rm tot}$ is the overall heat transfer resistance from the bulk gas to the liquid phase at the membrane surface [W/m_m^2K] and $c_{\rm p,i}$ is the molar heat capacity of component *i* in the gas phase [J/kmolK].

The pressure difference over the membrane surface is an important factor to consider for porous membranes. If the pressure difference is over the critical liquid entry pressure of the membrane, this can lead to wetting of the membrane pores. Wetting of the membrane will drastically increase the mass transfer resistance and reduce the separation performance of the membrane contactor. The pressure drop in the gas phase over the membrane length is given by equation 4, with the friction factor given in equation 5 [33].

$$\frac{\mathrm{d}P_{\rm g}}{\mathrm{d}z} = -f_{D,\rm g}\frac{1}{2}\rho_{\rm g}v_{\rm g}^2\frac{1}{d_h}\frac{1}{1,000} \tag{4}$$

$$\frac{1}{\sqrt{f_{D,g}}} = -2\log\left(\frac{\epsilon_{RR}}{3.7} + \frac{2.51}{\operatorname{Re}_{g}\sqrt{f_{D,g}}}\right) \xrightarrow[\epsilon_{RR}=0]{\operatorname{smooth pipe}} \frac{1}{\sqrt{f_{D,g}}} = -2\log\left(\frac{2.51}{\operatorname{Re}_{g}\sqrt{f_{D,g}}}\right)$$
(5)

$$d_h = \frac{D^2 - nd_o^2}{(D + nd_o)} \tag{6}$$

 $P_{\rm g}$ is the total pressure of the gas phase [kPa], $f_{D,g}$ is the friction factor, $\rho_{\rm g}$ is the gas density [kg/m³], $v_{\rm g}$ is the gas velocity [m/s], $d_{\rm o}$ is the fiber outer diameter [m], d_h is the hydraulic diameter [m], ϵ_{RR} is the relative roughness and Re_g is the shell side Reynolds number.

2.3. Liquid Phase - Lumen Side

The liquid flow in the lumen side of the fibers is assumed to laminar based on the value of the Reynolds number in the fiber. The velocity in the z direction as function of radial position is given from equation 7 [34]. When using a parabolic velocity profile it is assumed that the velocity at the fiber walls is zero. This may not be the case in a membrane contactor where there is a radial flux at the membrane wall over the membrane. However, as this flow is small, it is assumed that the velocity profile will have a parabolic shape.

$$v_z = 2v_{z,\mathrm{av}} \left(1 - \left(\frac{r}{R_{\mathrm{i}}}\right)^2 \right) \tag{7}$$

where $v_{z,av}$ is the average liquid velocity [m/s], r is the position in radial direction [m] and R_i is the fibre inner radius [m]. The average liquid velocity is obtained by dividing the total flow rate by the flow cross sectional area.

The liquid inlet part of the module is covered by membrane fiber potting with a thickness of a few centimeters. In this part no mass transfer takes place, and it can be assumed that the velocity profile is fully developed in the active membrane region of the module. The entry length ($L_{\rm e}$) before fully developed velocity profile can be found from equation 8 [35].

$$\frac{L_{\rm e}}{d_{\rm i}} = 0.0575 {\rm Re} \tag{8}$$

The liquid flow in the membrane contactor can be counter-current or co-current. The developed model covers both cases and a parameter is used to select which flow configuration to use. In this paper only the counter-current flow conditions are reported. The equations for the liquid phase can simply be converted to the co-current flow configuration.

Instead of using a mass transfer coefficient for the liquid phase, which will be a lumped parameter, a two dimensional differential mass balance is derived. Based on a mass balance, including both the convective flow in the axial direction and the diffusion in radial direction, the changes in component i along the module length is given by equation 9.

$$\frac{\partial C_{\mathbf{l},i}}{\partial z} = \frac{-D_{\mathbf{l},i}}{v_z} \left(\frac{1}{r} \frac{\partial C_{\mathbf{l},i}}{\partial r} + \frac{\partial^2 C_{\mathbf{l},i}}{\partial^2 r} \right) \tag{9}$$

 $C_{l,i}$ is the molar concentration of component *i* in the liquid phase [kmol/m³], *r* is the radial length segment [m] and $D_{l,i}$ is the diffusivity of component *i* in TEG [m²/s].

The boundary conditions for equation 9 are as follow:

$$C_{l,i}(z=1) = C_{l,i,\text{feed}} \tag{10}$$

$$\frac{\mathrm{d}C_{\mathbf{l},i}}{\mathrm{d}r}|_{r=0} = 0 \tag{11}$$

$$\frac{\mathrm{d}C_{\mathrm{l},i}}{\mathrm{d}r}|_{r=R\mathrm{i}} = \frac{J_i}{D_{\mathrm{l},i}} \tag{12}$$

The differential equation describing the temperature changes in the liquid phase (equation 13) is developed from the energy balance, and includes conduction, energy flow due to convection and the heat of absorption. The heat by conduction in the z-direction is normally small compared to the convective heat flow and is therefore disregarded in the equation.

$$\frac{\partial T_{l}}{\partial z} = \frac{1}{\rho_{l}C_{p,l}v_{z}} \left[\lambda_{l} \left(\frac{\partial^{2}T_{l}}{\partial r^{2}} + \frac{1}{r} \frac{\partial T_{l}}{\partial r} \right) - \left(-\Delta H_{i,\text{abs}} * 1,000 \right) J_{i}a_{\text{L}} \right]$$
(13)

 $T_{\rm l}$ is the liquid temperature [K], $\rho_{\rm l}$ is the liquid phase density [kg/m³], $C_{p,l}$ is the heat capacity of the liquid phase [J/kgK], $\lambda_{\rm l}$ is the thermal conductivity of the liquid phase [W/mK], $(-\Delta H_{i,\rm abs})$ is the heat released due to absorption of component *i* into the liquid phase [J/mol] and $a_{\rm L}$ is the membrane area per volume liquid flow $[m_{\rm m}^2/m_{\rm l}^3]$.

The boundary conditions for equation 13 are given in equation 14 - 16.

$$T_{\rm l}(z=1) = T_{\rm l,feed} \tag{14}$$

$$\frac{\mathrm{d}T_1}{\mathrm{d}r}|_{r=0} = 0\tag{15}$$

$$\frac{\mathrm{d}T_{\mathrm{l}}}{\mathrm{d}r}|_{r=R\mathrm{i}} = -\frac{U}{\lambda_{\mathrm{l}}} \left(T_{\mathrm{l,mem}} - T_{\mathrm{g}}\right) \tag{16}$$

The pressure drop in the fiber follows the Darcy-Weisbach equation as given in equation 17.

$$\frac{\mathrm{d}P_{\mathrm{l}}}{\mathrm{d}z} = f_{D,\mathrm{l}} \frac{1}{2} \rho_{\mathrm{l}} v_{z,\mathrm{av}}^2 \frac{1}{d_{\mathrm{i}}} \frac{1}{1,000} \tag{17}$$

$$f_{D,1} = \frac{64}{\text{Re}_{l}} \tag{18}$$

where P_1 is the liquid phase pressure [kPa], $f_{D,1}$ is the friction factor and Re₁ is the fiber side Reynolds number.

2.4. Membrane Flux

The flux from the boundary gas to the liquid membrane surface can be found from the steady state condition and the local driving forces resulting in resistance in series. The liquid film layer is not included as a lumped factor as the liquid phase is described more accurately with the two dimensional model.

$$J_{i,g} = k_g (C_i^g - C_i^{g,mem}) = \frac{k_g}{R_g T_g} (P_{g,i} - P_i^{g,mem})$$
(19)

$$J_{i,\text{mem}} = k_{\text{mem}} (C_i^{\text{g,mem}} - C_i^{\text{l,mem}}) = \frac{k_{\text{mem}}}{R_{\text{g}} T_{\text{g}}} \left(P_i^{\text{g,mem}} - P_{\text{l},i}^{\text{VLE}} \right)$$
(20)

 $k_{\rm g}$ and $k_{\rm mem}$ are the gas and membrane mass transfer resistance coefficients [m/s] and $R_{\rm g}$ is the ideal gas constant [J/molK]. $C_i^{\rm g}$, $C_i^{\rm g,mem}$ and $C_i^{\rm l,mem}$ are the concentrations of component *i* [kmol/m³] in respectively gas bulk, gas-membrane interface and liquid-membrane interface, $P_{{\rm g},i}$ and $P_i^{\rm g,mem}$ are the partial pressures of component *i* [kPa] in the gas bulk and gas-membrane interface and $P_{{\rm l},i}^{\rm VLE}$ is the equilibrium partial pressure of component *i* [kPa] at the liquid-membrane interface.

Under the steady state assumption these two equations give the overall mass flux from the bulk gas to the membrane surface on the liquid side. The overall mass transfer is given by equation 21, where the transport area is based on the inner fiber area.

$$J_i = \frac{1}{R_{\rm g}T\left(\frac{R_{\rm i}}{k_{\rm g,i}R_{\rm o}} + \frac{1}{k_{\rm mem,i}}\right)} \left(P_{\rm g,i} - P_{\rm l,i}^{\rm VLE}\right)$$
(21)

The gas mass transfer coefficient $(k_{g,i})$ is found based on a correlations for turbulent flow given by equation 22 [13].

$$k_{\rm g,i} = 0.023 \operatorname{Re}_{\rm g}^{0.8} \operatorname{Sh}_{\rm g}^{\frac{2}{3}} \frac{D_{{\rm g},i}}{d_h}$$
 (22)

Sh_g is the Sherwood number for the gas on the shell side based on the hydraulic diameter (d_h) and $D_{g,i}$ is the diffusivity of component *i* in the gas phase $[m^2/s]$.

Three different cases of membrane resistance were tested including a porous membrane in dry state, wetted porous membrane with different percent of wetting and the use of a dense top-layer. All the different cases will lead to differences in the membrane mass transfer resistance. The membrane resistance for a dry porous membrane is given by the gas diffusivity through the pores, equation 23

$$\frac{1}{k_{\text{mem},i}} = \frac{R_{\text{i}} \ln(R_{\text{o}}/R_{\text{i}})}{\tilde{D}_{\text{g},i}}$$
(23)

$$\tilde{D}_{\mathrm{g},i} = D_{\mathrm{g},i} \frac{\epsilon_{\mathrm{P}}}{\tau_{\mathrm{P}}} \tag{24}$$

$$\tau_{\rm P} = \frac{\left(2 - \epsilon_{\rm P}\right)^2}{\epsilon_{\rm P}} \tag{25}$$

Where $\epsilon_{\rm P}$ is the porosity of the membrane and $\tau_{\rm P}$ is the tortuosity of the membrane which is calculated based on the membrane porosity by equation 25 [36].

Non-wetted mode is a frequently used assumption in modelling of membrane contactor. However, studies have shown that wetting of the membrane significantly increases the mass transfer resistance in the membrane [37–39]. For subsea operation at high pressure, wetting might by a challenge. Usually in modelling studies, when including membrane wetting, uniform wetting of all the pores is modelled. This is not completely true compared to what happens in reality. The wetting normally starts with the largest pores due to lower entrance pressure, and continue with the smaller one. The mass transfer resistance for a partially wetted porous membrane with uniform wetting of all pores is given in equation 26

$$\frac{1}{k_{\text{mem},i}} = \frac{R_{\text{i}} \ln(R_{\text{o}}/R_{\text{w}})}{\tilde{D}_{\text{g},i}} + \frac{R_{\text{i}} \ln(R_{\text{w}}/R_{\text{i}})}{\tilde{D}_{\text{l},i}}$$
(26)

$$\tilde{D}_{l,i} = D_{l,i} \frac{\epsilon_{\rm P}}{\tau_{\rm P}} \tag{27}$$

where $D_{l,i}$ is the diffusivity of component *i* in the liquid phase $[m^2/s]$ and R_w is the radius of the interface between dry and wetted membrane pores [m].

The third alternative is to use a composite membrane with a thin dense membrane layer on top of the porous support to prevent wetting. This dense layer will introduce an additional mass transfer resistance, and the

membrane mass transfer resistance will be as given in equation 28

$$\frac{1}{k_{\text{mem},i}} = \frac{R_{\text{i}} \ln(R_{\text{o}}/R_{\text{id}})}{\tilde{D}_{\text{g},i}} + \frac{R_{\text{i}} \ln(R_{\text{id}}/R_{\text{i}})}{P_{\text{mem}}R_{\text{g}}T_{\text{g}}}$$
(28)

where P_{mem} is the membrane permeability of the dense layer [kmol m/m^s s kPa] and R_{id} is the radius of the interface between the dense layer and the porous support [m].

The total heat transfer resistance can be found in a similar way as given for the mass transfer resistance. The total heat transfer resistance, U_{tot} [W/m²K], is hence given by equation 29

$$\frac{1}{U_{\rm tot}} = \frac{1}{h_{\rm g}} + \frac{1}{h_{\rm mem}} \tag{29}$$

where $h_{\rm g}$ is the gas phase boundary layer heat transfer resistance [W/m²K] and $h_{\rm mem}$ is the membrane heat transfer resistance [W/m²K].

The equation for the heat flux over the membrane, $Q [W/m_m^2]$, is given as follows

$$Q = \frac{1}{\frac{1}{h_{\rm g}} + \frac{1}{h_{\rm mem}}} (T_{\rm g} - T_{\rm l,mem})$$
(30)

In this equation, h_{mem} is further separated into several parts to include the gas phase of the membrane and the thermal conductivity of the membrane material. For the case of wetting or the use of a dense layer, this will also be included in this parameter in the similar way as for the mass transfer coefficient.

2.5. Physical Properties

The model reported comprises general equations valid for all components in the system. For dehydration of natural gas the main component for transport is H_2O . Based on this, only H_2O transport is evaluated and only H_2O equations are used in the model.

An overview over the most important physical properties used in the model is given in Table 1. The table includes the functional dependency for the properties and the literature source for the correlations.

Property	Symbol	Function dependence	Source
Diffusivity of H_2O in NG	$D_{\mathrm{g,H_2O}}$	$f(P_g, T_g)$	[40]
Diffusivity of H_2O in TEG	$D_{\rm l,H_2O}$	$f(T_1, x_{H_2O})$	[40]
Heat capacity of NG	$C_{p,g}$	$f(T_g)$	[40]
Heat capacity of TEG	$C_{p,l}$	$f(T_1, x_{H_2O})$	[41]
Thermal conductivity of TEG	λ_1	$f(T_1, x_{H_2O})$	[42]
Viscosity of NG	$\mu_{ m g}$	$f(T_1, \rho_g)$	[43]
Viscosity of TEG	μ_{l}	$f(T_1, x_{H_2O})$	[42]
Density of TEG	$ ho_{\mathrm{l}}$	$f(T_1, x_{H_0O})$	[42]

Table 1: Physical properties correlations

2.5.1. Vapor-Liquid Equilibrium (VLE) Model

To calculate the flux over the membrane contactor the driving force over the membrane is needed. A vapour-liquid-equilibrium (VLE) model for TEG-H₂O-CH₄ system at high pressure is required to get the H₂O equilibrium vapor pressure on the liquid side. To the best of our knowledge, little information is reported in the open literature about experiments or modelling of VLE for the TEG-H₂O-CH₄ system at high pressure. Therefore a VLE model for high pressure prediction of the vapor equilibrium pressure was developed. The VLE model reported by Parrish et al. [44] was used as basis. However, this model is developed based only on VLE data at low pressure. To adjust for high pressure operation, a new fugacity model for the vapor phase was developed. The fugacity coefficient model structure reported from Duan & Mao [45] was modified based on the local thermodynamic structure reported by Hillestad et al. [46], giving the new fugacity coefficient model in equation 31. The parameters in the new model (A_1 to A_6) were optimized based on reported high pressure H₂O-CH₄ VLE experimental results [47–51], giving an improved fit for high pressure operation. The values of the parameters, including a 95% confidence interval, are given in Table 3.

$$\ln \phi_{\rm H_2O} = A_1 + A_2 \ln (P_{\rm bar}) + A_3 \left[\ln (P_{\rm bar})\right]^2 + A_4 \ln (P_{\rm bar}) T + A_5 \frac{\ln (P_{\rm bar})}{T} + A_6 \frac{\left[\ln (P_{\rm bar})\right]^2}{T}$$
(31)

Parameter	Value	95% Conf.Interval	
		Low limit	Upper limit
A_1	-0.75728	-0.94107	-0.57349
A_2	1.00539	0.73275	1.27803
A_3	-0.01301	-0.03486	0.00884
A_4	-0.00101	-0.00137	-0.00064
A_5	-42.4133	-96.9484	12.1218
A_6	-29.9348	-38.9378	-20.9319

Table 2: Parameter values for the fugacity coefficient model from the fitting to high pressure CH_4 - H_2O vapor-liquid-equilibrium data, including a 95% confidence interval for the parameters.

The developed model was compared with the Duan & Mao model using other H_2O-CH_4 data sets [52–54]

and the new model fits better to these data, as illustrated in Figure 3a-3c. In addition, the use of the new correlation fits better with the experimental results from the one report on high pressure TEG-H₂O-CH₄ data [55, 56] (Figure 3d). However, there are still deviations between the experimental data and the model. To accurately measure small amounts of H₂O in CH₄ at high pressure can be difficult experimentally. Thus, there can be some errors in the experimental results, explaining part of the deviations between the experiments and the model. However, as there is no more reported experimental results for the system TEG-H₂O-CH₄ in the open literature, this hypothesis cannot be confirmed or rejected.



Figure 3: Experimental data compared with the prediction of the equilibrium vapor pressure of H_2O from two different VLE models. The VLE models is based on the model reported by Parrish et al. [44] with the new developed fugacity coefficient model or the fugacity model reported from Duan & Mao [45] (A) Experimental H_2O-CH_4 data from Rigby & Prausnitz [52] (B) Experimental H_2O-CH_4 data from Yarrison et al. [53] (C) Experimental H_2O-CH_4 data from Chapoy et al. [54] (D) Experimental TEG-H₂O-CH₄ data from Ng et al. [55, 56].

3. Model Implementation

The two-point boundary condition problem is implemented into MATLAB, where orthogonal collocation was used to solve the problem. Orthogonal collocation is a subclass of the method of weighted residuals and solves two-boundary conditions problems simultaneously in both directions. For the shell side, with the gas flow, the model is one dimensional and is discretized in the axial direction. While, for the liquid phase, inside the fiber, the model is discretized in two dimensions, axial and radial.

In the implementation the parameters in the balance equations were scaled by introducing the following transformations giving dimensionless parameters.

$$\begin{split} \xi &= \frac{z}{L} \qquad \gamma = \frac{r}{R_{\rm i}} \qquad C^*_{\rm l,H_2O} = \frac{C_{\rm l,H_2O}}{C^{\rm ref}} \qquad n^{\rm s*}_{\rm g,H_2O} = \frac{n^{\rm s}_{\rm g,H_2O}}{n^{\rm s,ref}} \\ T^*_{\rm l} &= \frac{T_{\rm l}}{T^{\rm ref}} \qquad T^*_{\rm g} = \frac{T_{\rm g}}{T^{\rm ref}} \qquad P^*_{\rm l} = \frac{P_{\rm l}}{P^{\rm ref}} \qquad P^*_{\rm g} = \frac{P_{\rm g}}{P^{\rm ref}} \end{split}$$

Where C^{ref} [kmol/m³], n^{ref} [kmol/m²_ts], T^* ref [K] and P^{ref} [kPa] are chosen reference values for concentration, molar flow, temperature and pressure respectively.

In orthogonal collocation it is assumed that the spatial variation of the distributed variables can be approximated by Lagrange polynomials. This approximation are used to transform the differential equations to non-linear polynomial equations. The approximations for the differential and integral operators are given in equation 32 - 34 for the first order derivative, the second order derivative and the integral respectively.

$$\left(\frac{\mathrm{d}y}{\mathrm{d}\xi}\right)_{\xi_i} = \sum_j A_{i,j} y_j \tag{32}$$

$$\left(\frac{\mathrm{d}^2 y}{\mathrm{d}\xi^2}\right)_{\xi_i} = \sum_j B_{i,j} y_j \tag{33}$$

$$\int_{0}^{1} f\left(\xi\right) = \sum_{j} q_{j} f\left(\xi_{j}\right) \tag{34}$$

where $A_{i,j}$ is a matrix of first derivative weights, $B_{i,j}$ is a matrix of second derivative weights and q_j is the quadrature weights.

CC^O

The set of non-linear polynomial equations is solved in MATLAB with the f-solve routine. The residuals at the collocation points including the boundary conditions are to be zero.

$$\mathcal{L}y - g\left(y\right) = 0 \tag{35}$$

With the use of these approximations the residual equations to be implemented into MATLAB for the gas phase, including the boundary conditions, are given in equation 36-41.

$$0 = n_{g,H_2O(\xi=0)}^{s*} - n_{g,H_2O,feed}^{s*}$$
(36)

$$0 = T_{g(\xi=0)}^* - T_{g,\text{feed}}^*$$
(37)

$$0 = P_{g(\xi=0)}^* - P_{g,\text{feed}}^*$$
(38)

$$0 = \sum_{j} A_{z,i,j} n_{g,H_2O,j}^{s*} + J_{H_2O} a \frac{L}{n^{s,ref}}$$
(39)

$$0 = \sum_{j} A_{z,i,j} T_{g,j}^{*} + \frac{U_{\text{tot}} a L}{\sum \left(C_{p,i} n_{g,i}^{*} \right)} \left(T_{g}^{*} - T_{l,\text{mem}} \right)$$
(40)

$$0 = \sum_{j} A_{z,i,j} P_{g,j}^{*} + f_{D,g} \frac{1}{2} \rho_{g} v_{g}^{2} \frac{1}{d_{h}} \frac{L}{P^{\text{ref}}} \frac{1}{1,000}$$
(41)
where are given in equation 42-51.

The equations for the liquid phase are given in equation 42-51.

$$0 = C_{l,H_2O(\xi=1)}^* - C_{l,H_2O,\text{feed}}^*$$
(42)

$$0 = T_{l(\xi=1)}^{*} - T_{l,\text{feed}}^{*}$$

$$0 = P_{l(\xi=1)}^{*} - P_{l,\text{feed}}^{*}$$
(43)
(44)

$$0 = \sum_{j} A_{r(\gamma=0),1,j} C^*_{l,H_2O,j}$$
(45)

$$0 = \sum_{j} A_{r(\gamma=0),1,j} T_{1,j}^*$$
(46)

$$0 = \sum_{j} A_{r(\gamma=1),nr+2,j} C^*_{l,H_2O,j} - \frac{J_{H_2O}}{D_{l,H_2O}} \frac{R_i}{C^{ref}}$$
(47)

$$0 = \sum_{j} A_{r(\gamma=1),nr+2,j} T_{l,j}^* + \frac{U_{\text{tot}} R_i}{\lambda_l} \left(T_{l,\text{mem}}^* - T_g^* \right)$$
(48)

$$0 = \sum_{j} A_{z,i,j} C_{l,H_2O,j}^* + \frac{D_{l,H_2O}}{v_z} \left(\frac{1}{\gamma} \sum_{j} A_{r,i,j} C_{l,H_2O,j}^* + \sum_{j} B_{r,i,j} C_{l,H_2O,j}^* \right) \frac{L}{R_i^2}$$
(49)

$$0 = \sum_{j} A_{z,i,j} T_{l,j}^{*} - \frac{L}{\rho_{l} C_{p,l} v_{z}} \left[\frac{\lambda_{l}}{R_{l}^{2}} \left(\sum_{j} B_{r,i,j} T_{l,j} + \frac{1}{\gamma} \sum_{j} A_{r,i,j} T_{l,j} \right) - (-1,000 \Delta H_{H_{2}O,abs}) \frac{J_{H_{2}O} a_{L}}{T^{ref}} \right]$$
(50)
$$0 = \sum_{j} A_{i,j} P_{l,j}^{*} - f_{D,l} \frac{1}{2} \rho_{l} v_{z}^{2} \sum_{j} \frac{L}{1 + 1} \frac{1}{1 + 1}$$
(51)

$$0 = \sum_{j} A_{i,j} P_{1,j}^* - f_{D,1} \frac{1}{2} \rho_1 v_{z,av}^2 \frac{D}{d_i} \frac{1}{1,000}$$
(51)

The developed model consist of a set of sub-models for calculation of physical properties in addition to the flow models of the natural gas and TEG solution. The VLE model is the only part that has been optimized to experimental data, and there is no other parameters in the model to adjust to experimental data. The developed model was validated against proprietary high pressure experimental data for natural gas dehydration with TEG in a membrane contactor. The model was tested against about 20 runs with different flow rate, pressure, TEG purity and natural gas water content. The purity of the TEG solution ranged from 80 to 90 mol%TEG, the water content in the natural gas was 500-2,000 ppm, the total pressure 60-70 bar and operating temperatures 25-35°C. The membrane module used contained about 10,000 hollow PTFE fibers with length 1.8 m. The gas velocity was about 0.3 m/s and the liquid velocity less than 1 cm/s. The validation was preformed by evaluating the H_2O molar flow removed from the gas over the membrane. The results predicted from the model were compared with the experimental values. Due to uncertainty in the experimental basis, two calculation methods were used. For method one the model predicts the amount of water removed within an error from -11.2% to 2.9% with mean error of -3%. The second method predicts within -17.1% to -1.1% with a mean error of -7%.

4. Sensitivity Study

A sensitivity study for the membrane contactor was performed to evaluate the effect of different membrane and operating conditions on the performance of the separation. In the study, the parameters used for the operating conditions and membrane properties that were not investigated, were kept constant at the values given in Table 3, if nothing else is specified.

	0 1 1	T 7 1	TT
Parameter	Symbol	Value	Unit
Fiber inner diameter	d_{i}	600	$\mu { m m}$
Membrane length	L	1	m
Number of membrane fibers	n	9,200,000	
Membrane porosity	$\epsilon_{ m p}$	0.75	
Membrane thickness (porous)	$x_{ m p}$	50	$\mu { m m}$
Membrane thickness (dense)	x_{d}	1	$\mu { m m}$
Membrane permeability	$P_{\rm mem}$	3,000	Barrer
Packing density	a	1,500	$\mathrm{m}_m^2/\mathrm{m}_t^3$
Temperature	$T_{\rm g}$	30	$^{\circ}\mathrm{C}$
Pressure	$P_{\rm g}$	80	bar
Gas flow	$f_{ m NG}$	12.2374	$\rm kmol/s$
Mol fraction of H_2O in gas inlet	$x_{\mathrm{H_2O}}$	723	ppm
Temperature	T_1	30	$^{\circ}\mathrm{C}$
Pressure	P_{l}	80	bar
Liquid flow	f_{TEG}	0.0347	$\rm kmol/s$
TEG purity	$\mathrm{wt}\%_{\mathrm{TEG}}$	99.5	
Compressibility factor	Z	0.8407	
Correction factor for H_2O diffusivity in NG		0.851	

Table 3: Membrane and operation parameters used for sensitivity study

4.1. Heat Transfer Coefficient

A sensitivity analysis was performed to evaluate the effect of the heat transfer resistance in the model, where only the total heat transfer resistance value (U_{tot}) was changed. The result shown in Figure 4a indicates that the effect of heat transfer on the separation performance is negligible. The difference in outlet content of H₂O is below 1% when the total heat transfer coefficient is changed from zero to one hundred. The reason for the minor changes in separation performance is related how the liquid temperature is changes along the membrane module as illustrated in Figure 4b. The liquid temperatures will affect the equilibrium vapor pressure and hence the driving force of H₂O over the membrane in the membrane contactor.

Based on this evaluation, the value of the heat transfer coefficient is found to not effect the system. To avoid selection of a specific material and be able to evaluate the effect of different membrane properties independent of material, the heat transfer resistance value was set to zero in the following sensitivity studies.



Figure 4: The effect of increasing the overall heat transfer resistance (U_{tot}) on the separation performance. (a) H₂O outlet content as a function of U_{tot} . (b) Liquid temperature profile along the membrane module at the membrane-liquid interface as a function of U_{tot} .

4.2. Membrane Wetting versus Composite Membrane

One challenge with the use of a porous membrane in a membrane contactor is the wetting of the porous material. Wetting of the membrane will result in increased mass transfer resistance of the membrane and hence reduced separation performance. Investigations of the effect of wetting of the porous membrane in a membrane contactor have been performed and reported both through modelling [37, 38] and with experiments [39]. Common findings from all these studies are that wetting of the membrane significantly increases the mass transfer resistance of the membrane.

The effect of wetting was also tested for the developed model with TEG as solvent. The mass transfer resistance equation for the membrane used to study the wetting effect of the membrane pores is equation 26. The wetting is assumed to be equal for all pores, which gives a thickness of the membrane where the pores are wetted. In this study the only parameter changed was the percent of membrane thickness that is wetted. Figure 5a shows that even with wetting of 1% of the membrane thickness, the separation performance is reduced drastically. When the wetting is 50%, less than 1% of the H_2O in the gas is removed.

To eliminate the membrane wetting and keep the mass transfer resistance low, the use of a thin nonporous/dense and highly permeable (for wanted component) membrane might be a possibility [39]. This was confirmed with a experimental study by Chabanon et al. [57]. Long term performance for CO_2 absorption in MEA was evaluated, with emphasis on effects of membrane wetting. Based on this, the use of a composite membrane with a dense top layer could also be an alternative in a membrane contactor with TEG for dehydration of natural gas. However, a dense layer will also add extra mass transfer resistance and hence a comparison of the dense layer and wetting is done. As illustrated in figure 5b, the introduction of a dense layer reduced the separation performance, but to a lower degree than wetting. In this study the mass transfer resistance equation used for the membrane is equation 28.

Figure 5c compares the two scenarios. As can be seen, the performance of a porous membrane with 1% wetting is similar to a dense layer with a permeability of 100 Barrer. From this evaluation it can be found that the introduction of a dense layer is favourable for preventing wetting as it has better performance than a high degree of wetting. The mass transfer coefficient for the membrane under the different conditions evaluated such as dry, wetted and with a composite membrane is given in Figure 5d. The mass transfer coefficient is significantly reduced and hence the mass transfer resistance increased when wetting occur. When 1 μ m dense layer with a permeability of 100 Barrer is introduced the main mass transfer resistance is located in the dense layer. However, when the permeability of the dense layer is increased the porous support and the gas phase has a larger contribution to the mass transfer resistance and the dense layer is not the dominating mass transfer resistance.



Figure 5: The effect on separation performance is evaluated and compared with the use of a porous membrane or a composite membrane in the membrane contactor. (a) The effect of pore wetting when a porous membrane is used with different degree of wetting. (b) The effect of composite membrane with a dens membrane layer with different permeabilities. (c) Comparison of the pore wetting with the additional mass transfer resistance from the dens top-layer which prevent the wetting in a composite membrane. (d) The mass transfer coefficient value for the membrane under the different conditions: dry, wetted and composite membrane

4.3. Membrane Thickness

From the above investigation it seems favourable to use a composite membrane for subsea operation. Therefore a composite membrane was considered in the following sensitivity study. Evaluation was done to investigate the effect of the porous support thickness and the thickness of the dense layer. It is obvious that the mass transfer resistance will decrease with reduced thickness of both layers, which is favourable for the separation performance. The results given in Figure 6a, where the dense layer thickness is 1 μ m, indicate that the effect of the porous support is dependent on the permeability of the dense layer. With low permeability the dense layer gives a large resistance and hence the porous support thickness does not affect the separation significantly. Some more effect is seen when the permeability of the dense layer is

increased. It could also be mentioned that when changing the thickness of the membrane the gas cross section is somewhat reduced, due to the constant packing density. This gives a small increase in gas velocity when the porous layer thickness is increased.

Figure 6: Illustration of how the membrane thickness of both the porous and the dense top layer effect the separation performance with different permeabilities of the dense layer: 100, 3,000 and 10,000 Barrer, and a fiber inner diameter of 600 μ m. (a) The effect of changing the porous layer thickness from 50 to 150 μ m with a dense layer of 1 μ m. (b) The effect of changing the dense layer from 1 to 10 μ m with a porous layer of 50 μ m.

The effect of the thickness of the dense layer is also evaluated. As can be seen from the results in Figure 6b, the effect of the dense layer thickness is more important as the permeability is decreased. The 100 Barrer line is not changing much after 5 μ m, as the driving force is reduced and the inlet is almost equal to the outlet H₂O content.

As a conclusion from the study of the membrane thickness, it can be stated that from a separation point of view it is favourable to reduce the thickness. However, the membrane stability and processability of a thin membrane will be a limiting factor.

4.4. Porosity

The effect of changing the porosity in the porous membrane was investigated for two different cases. The first one where wetting may occur and the second case where a composite membrane is used and the dense layer prevents wetting. The investigation shows that increased porosity is favourable for the separation when the membrane pores are non-wetted (Figure 7a). This is obvious from equation 23, as higher porosity will reduce the mass transfer resistance in the membrane phase and increase the diffusivity through the membrane. This study was done to evaluate the trend. However, a porosity of 0.9 might be unrealistic due to fabrication difficulties and the reduction in membrane mechanical strength with increased porosity.

As previously mentioned, wetting may be a problem for high pressure subsea operation. Hence, the effect of changing porosity when wetting occurs in the membrane is evaluated. Figure 7a illustrates that the porosity has less effect as more of the membrane pores get wetted. This is probably a response of the fact illustrated earlier with high mass transfer resistance and reduced separation performance with a wetted membrane.

Figure 7: Illustrates the effect of changing the porosity of the porous layer on the separation performance (a) The effect of the porosity in dry state, and when the membrane is wetted with: 1%, 5%, 10% and 50%. (b) The effect of the porosity when a dense layer is used to prevent the wetting with three different permeabilities: 100, 3,000 and 10,000 Barrer.

The effect of porosity was also evaluated when a composite membrane was used. In this case the dense membrane layer will prevent wetting of the porous membrane, but will introduce an extra mass transfer resistance. As shown in Figure 7b, the effect of porosity depends on the permeability of the dense layer. At low permeability the porosity does not have very large impact as the limiting factor under these conditions is the dense layer. With increased permeability, the porous layer will be more dominant and the porosity will affects the separation performance.

4.5. Fiber Diameter

The effect of changing the inner fiber diameter on the separation performance was evaluated. By changing the fiber diameter the number of fibers also changes when keeping the membrane area constant. With constant packing density, increasing the fiber diameter will result in increased gas velocity and decreased liquid velocity as the flow cross section is decreased for the gas phase and increased for the liquid phase. Based on this, to be able to evaluate the effect of the fiber diameter, the packing density was changed during this study. The cross section area for the gas phase was changed with the same ratio as the cross section of the fibers, based on outer diameter. The packing density can then be calculated with equation 2, where the

diameter of the shell is found from equation 54.

$$S_{\mathrm{g},j} = S_{\mathrm{g},k} \frac{S_{\mathrm{l,outer},j}}{S_{\mathrm{l,outer},k}} = \pi \left(\frac{d_{\mathrm{i},k}}{a_k} - \frac{d_{\mathrm{o},j}^2}{4}\right) \left(\frac{d_{\mathrm{o},j}^2 n_j}{d_{\mathrm{o},k}^2}\right)$$
(52)

$$S_{\text{tot}} = S_{\text{g},j} + S_{\text{l,outer},j} \tag{53}$$

$$D = \sqrt{\frac{4S_{\text{tot}}}{\pi}} \tag{54}$$

where k denotes the known value and j is the new dimension. $S_{\rm g}$, $S_{\rm l,outer}$ and $S_{\rm tot}$ are the cross sectional areas of respectively the gas phase, the fiber based on outer diameter and the total module. The selected basis values for the packing density calculation are a fiber diameter of 600 μ m and a packing density of 1,500 m_m²/m_t³.

When increasing the fiber diameter, the packing density is reduced. This also gives an increased liquid and gas cross section, resulting in a reduction in the velocity as the molar flow is constant. A reduction in the velocity is equivalent to increased residence time through the membrane module. The results shown in Figure 8 indicate that a smaller fiber diameter gives increased H_2O removal from the gas phase, which can be related to the lower residence time of the gas in the module. With smaller fibers, the H_2O concentration differences in the liquid from the membrane surface to the fiber center are lower than for larger fibers and the TEG solution is hence more efficiently used. In addition, smaller fibers with higher packing density will result in smaller module size. However, this will also give a higher pressure drop for both gas and liquid phase. To conclude, smaller fibers and higher packing density is preferred from a separation point of view, but the selection is restricted by acceptable pressure drop and the ability to produce the fiber with a dense layer on the inside. In addition, for practical operation possible impurities in the TEG solution which can block small fibers, should also be considered.

Figure 8: The effect of inner fiber diameter on separation performance with constant membrane area. When the packing density is changed to keep a constant ratio between the gas cross sectional area and the outer fiber cross sectional area. (a) H_2O content in the natural gas along the membrane length (b) H_2O content in the dehydrated natural gas outlet.

4.6. Packing Density

As mentioned above, high packing density is favourable from a module size perspective. But, increased packing density will give increased pressure drop of the gas through the module due to reduced cross sectional area for the gas flow. Therefore the effect of changing the packing density was evaluated for a case with the use of fibers with a diameter of 600 μ m.

As can be seen from the results in Figure 9a, the separation performance is increased with increased packing density up to a certain value. When the packing density is around 3,000, further increase of the packing density does not significantly change the separation performance. This can be related to the increase in pressure drop after this value, as shown in Figure 9b. From this evaluation it can be found that increasing the packing density towards 3,000 would be favourable in the case of a 600 μ m fiber diameter. But, as mentioned earlier, there is a limitation in packing density for a given fiber size, smaller fiber can give higher packing density. Some other factors to evaluate when considering increased packing density is the production of the membrane module and the effect of impurities in the system on the module, when the flow cross section is reduced. Based on practical considerations like this, King et al. reports a packing density of 500-1,500 m²/m³ as reasonable values [26].

Figure 9: The effect of packing density on the separation performance for an inner fiber diameter of 600 μ m. (a) The H₂O content in the dehydrated natural gas outlet as a function of packing density. (b) The total pressure drop over the module length for the gas side as a function of the packing density.

4.7. Membrane Length

When reducing the membrane length the number of fibers must be changed to maintain the same membrane area and the packing density is kept constant. Reducing the length, and hence increasing the number of fibers results in reduced gas and liquid velocity, but the residence time is kept constant. Based on the results in Figure 10a-10b, longer modules are preferred with respect to separation performance. However, the pressure drop is also increased with membrane length (Figure 10c).

Figure 10: The effect of module length on separation performance when the packing density and membrane area are kept constant. The liquid and gas velocities for a membrane length of 0.5 m, 0.75 m and 1 m is $v_g \text{ [m/s]} 0.203, 0.304, 0.405$ and $v_{l,av} \text{ [m/s]} 8.6e-4, 1.3e-3, 1.7e-3$. (a) H₂O content in the natural gas along the membrane length (b) H₂O outlet content (c) Total pressure drop in the fiber and shell side as a function of membrane length.

4.8. Operation Conditions

As the membrane contactor dehydration system will work together with a regeneration system for the TEG solvent, the optimization of the operation conditions should be done as a whole system. The optimized

conditions for the membrane contactor may not be the optimum for the regeneration and this must be taken into account. However, for the current study a simple evaluation is done on the operating conditions to estimate the changes of the separation performance in the membrane contactor alone.

4.8.1. Temperature and Pressure

We evaluate operating temperature and pressure changes in both the liquid and the gas phases, so the inlet temperature and pressure of both streams are the same. King et al. reported that the major operational issus from the pilot testing of natural gas dehydration with membrane contactor was to control the liquid temperature to avoid condensation within the membrane unit [26]. A liquid temperature lower than the natural gas could result in condensation, which is the reason for keeping the temperature of both phases to the same value and not having a lower temperature for the liquid flow. In the evaluation the change of pressure and temperature affects the inlet gas composition, the compressibility factor (Z), the correction factor for the H_2O diffusivity in the natural gas and the other temperature and pressure dependent physical properties. The values used for these parameters in this investigation are given in Table 4.

Table 4: Overview of the values for the compressibility factor, H_2O diffusivity in natural gas correction factor and H_2O inlet content for the different pressure and temperature conditions studied.

Temperature [°C]	Pressure [bar]	Z	Correction factor	$y_{\rm H_2O,inlet}$ [ppm]
20	30	0.9244	0.939	870
20	60	0.8577	0.876	497
20	80	0.8201	0.851	408
30	30	0.9324	0.939	1,571
30	60	0.8736	0.876	888
30	80	0.8407	0.851	722
50	30	0.9454	0.952	4,528
50	60	0.8991	0.910	2,511
50	80	0.8735	0.893	2,017

Increasing the temperature will give an increase in the vapor pressure of the aqueous TEG solution, which will reduce the driving force for the H_2O being absorbed in TEG. This leads to reduced separation performance as TEG absorbs less H_2O . However, increasing the temperature will reduce the viscosity of TEG and increase the H_2O diffusivity in the gas and TEG, which may increase the separation performance. The results in Figure 11 indicate that the reduced absorption of H_2O in TEG is the dominant effect as the increased temperature will reduce the separation performance.

Figure 11: The effect on the separation performance when changing the temperature of both phases from 20 to 50 °C at three different pressures: 30, 60 and 80 bar. In these studies the composition, compressibility, correction factor for the H_2O diffusivity in natural gas are changed for each pressure and temperature condition.

The results, illustrated in Figure 11, indicate that increased pressure is preferred for the separation. When the pressure is increased the velocity of the gas is decreased due to the compressibility of the gas. This results in an increased residence time for the gas in the module. From this analysis it seems like increasing pressure or decreasing temperature are favourable for the H_2O absorption into TEG. However, the viscosity of TEG is increased with reduced temperature and hence the temperature of the TEG solution should not be below 10°C [58].

4.8.2. Gas Velocity

Increasing the gas flow rate, keeping all other parameters constant, gives an increased gas velocity through the module and hence a reduced residence time in the module. This leads to a reduced separation performance, as shown in Figure 12a. The H_2O content in the dehydrated natural gas is increased with gas flow rate. However, the total flux of H_2O over the membrane is increased with the velocity, as shown in Figure 12b. This is related to the driving force over the membrane remains higher with higher gas velocity in the module, as the water content in the gas phase is kept almost constant. Nevertheless, the goal for the process is to reach the pipeline specification limits for water content and hence increasing the gas velocity to high values will not meet this criterion. As an increase in gas velocity up to 0.132 m/s does not significantly change the H_2O amount in the outlet, this can be considered as the optimal value for a system with the given liquid flow velocity and module configuration. At this conditions the inlet TEG solution and the outlet gas is at equilibrium which is the reason for no change in separation performance below this gas velocity.

Figure 12: The effect of increasing gas velocity on the separation performance. (a) H_2O content in the outlet gas as a function of gas velocity. (b) The total H_2O flux over the membrane in the membrane module as a function of gas velocity.

4.8.3. Liquid Velocity

When changing the liquid flow rate, the velocity of TEG in the fiber is changed and hence the residence time in the module. As illustrated in Figure 13 the separation performance is increased with increasing liquid flow rate. However, as can be seen, increasing the liquid velocity over 0.002 m/s gives no significant change in the separation performance. The reason for this is that equilibrium is achieved for water content between the outlet natural gas and the inlet TEG. Increasing the flow rate of the liquid also results in increased pressure drop. Increasing the liquid velocity results in larger energy demands due to pumping of larger amount of absorbent and more energy is needed for regeneration. Hence, when optimizing the liquid flow rate except for minimizing the operating and capital cost the required flow to meet the dehydration specification must be found.

Figure 13: The effect of increasing the TEG velocity in the module on the separation performance.

4.8.4. TEG Purity

The effect of the TEG purity was tested by changing the weight percent of H_2O in the liquid feed. The value tested was from 0.3 to 10 wt% H_2O and as expected higher purity of the feed solution will give better separation performance (Figure 14a). This is reasonable as the driving force for H_2O to pass the membrane will be larger with less H_2O in the feed. However, the purity of TEG for optimum operation needs to be considered together with the regeneration of the solvent. What is optimum for the membrane contactor for dehydration of the gas might not be the optimum for the regeneration. When the content of H_2O in the TEG feed is increased the membrane area required to reach the pipeline specifications for the dehydration natural gas is increased, as illustrated in Figure 14b. Under this evaluation the liquid flow rate was changes simultaneously with the membrane area to keep constant liquid flow rate. As can be seen from the result the purity of TEG can be reduced to 99.1 wt% before it gives any significant increase in the membrane area.

Figure 14: The effect of TEG purity in the liquid feed on the separation performance. (a) H_2O content in the outlet gas as a function of TEG purity, weight percent of H_2O in the liquid. (b) Membrane area as a function of TEG purity, while still reaching the pipeline specifications.

5. Conclusion

A mathematical model of a membrane contactor for subsea dehydration of natural gas was developed. The model predicts the amount of H_2O removed from the gas compared with high pressure experimental data within an average mean error of 3-7%. The modelling study clearly shows the effect of varying membrane and operation properties on the separation performance and the results reveal the following facts:

• Membrane wetting has significant effect on the separation performance, even with only 1% wetting. For subsea operation at high pressure it is favourable to use a thin dense top-layer to prevent wetting of the membrane.

- With a permeability of the dense layer of more than 3,000 Barrer the main contributor to mass transfer resistance is the porous membrane and the gas phase. The dense layer will then prevent the wetting, but the effect on the mass transfer resistance is reduced with increased permeability.
- Increasing the pressure and reducing the temperature are favourable for the separation performance, due to the increased solubility of H₂O in TEG. However, the viscosity of TEG is increased with reduced temperature and hence the temperature of the TEG solution should not be below 10° C.

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List of symbols

a	Membrane packing density $[m_m^2/m_t^3]$
$a_{ m L}$	Membrane area per volume liquid flow $[m_{\rm m}^2/m_{\rm l}^3$
A1-A6	Model parameters
$A_{i,j}$	Matrix of first derivative weights
$A_{ m m}$	Membrane area $[m_m^2]$
$B_{i,j}$	Matrix of second derivative weights
C^{ref}	Concentration reference value $[\rm kmol/m^3]$
C_i^{g}	Concentration of component i in gas bulk [kmol/m ³]
$C_i^{\mathrm{g,mem}}$	Concentration of component i at gas-membrane interface $[\rm kmol/m^3]$
$C_i^{\rm l,mem}$	Concentration of component i at membrane-liquid interface $\rm [kmol/m^3]$
$C_{\mathrm{l},i}$	Molar concentration of component i in the liquid phase $[\rm kmol/m^3]$
$C_{p,l}$	Heat capacity of the liquid phase [J/kgK]
$C_{p,i}$	Molar heat capacity of component i [J/kmolK]
d_h	Hydraulic diameter [m]
d_{i}	Inner fiber diameter [m]
$d_{ m o}$	Fiber outer diameter [m]
D	Inner diameter of the membrane module shell [m]
$D_{\mathrm{g},i}$	Diffusivity of component <i>i</i> in natural gas $[m^2/s]$
$D_{\mathrm{l},i}$	Diffusivity of component i in TEG $[m^2/s]$

$\tilde{D}_{\mathrm{g},i}$	Effective diffusivity in dry porous membrane $[m^2/s]$
$\tilde{D}_{\mathrm{l},i}$	Effective diffusivity in wetted porous membrane $[m^2/s]$
$f_{D,g}$	Shell side friction factor
$f_{D,1}$	Fiber side friction factor
$f_{\rm NG}$	Molar flow of natural gas [kmol/s]
$f_{\rm TEG}$	Molar flow of triethylene glycol (TEG) [kmol/s]
$h_{ m g}$	Gas phase boundary heat transfer resistance $[\mathrm{W}/\mathrm{m}^2\mathrm{K}]$
$h_{ m mem}$	Membrane heat transfer resistance $[W/m^2K]$
$k_{ m g}$	Gas mass transfer resistance coefficient [m/s]
$k_{\rm mem}$	Membrane mass transfer resistance coefficient [m/s]
L	Membrane length [m]
L_e	Velocity profile entry length [m]
n	Number of fibers
n^{ref}	Molar flow reference value $[\rm kmol/m_t^2 s]$
$n^s_{\rm g,i}$	Molar flux of component $i [\text{kmol/m}_t^2 \text{s}]$
J_i	Molar flux of component i over the membrane $[\text{kmol/s } m_m^2]$
P^{ref}	Pressure reference value [kPa]
P_{bar}	System pressure in bar [bar]
$P_{\rm g}$	Total gas phase pressure [kPa]
$P_{\mathrm{g},i}$	Partial pressure of component i in gas bulk [kPa]
$P_i^{\rm g,mem}$	Partial pressure of component i at gas-membrane interface [kPa]
P_1	Liquid phase pressure [kPa]
$P_{{\rm l},i}^{VLE}$	Equilibrium partial pressure of component i at membrane-liquid interface[kPA]
$P_{\rm mem}$	Membrane permeability of the dens layer $[\text{kmolm/m}^2\text{skPa}]$
q_j	Quadrature weights
Q	Heat flux over the membrane $[W/m_m^2]$
r	Radial coordinate
$R_{\rm g}$	Ideal gas constant [J/molK]
$R_{\rm i}$	Inner fiber radius [m]
$R_{\rm id}$	Fiber radius to interface between porous and dense membrane layer [m]
$R_{\rm o}$	Outer fiber radius [m]
$R_{\rm w}$	Fiber radius to the interface between dry and wetted membrane pores [m]
Re_{g}	Shell side Reynolds number
Re_{l}	Fiber side Reynolds number

$S_{ m g}$	Gas phase cross section area $[m^2]$
$S_{\rm l,outer}$	Cross section area of the fiber, based on outer diameter $[m^2]$
$S_{ m tot}$	Cross section area of membrane module $[m^2]$
Sh_{g}	Shell side Sherwood numbers
T^{ref}	Temperature reference value [K]
$T_{\rm g}$	Temperature in bulk gas [K]
T_1	Temperature in bulk liquid [K]
$T_{\rm l,mem}$	Temperature in liquid phase at memrbane surface [K]
$U_{\rm tot}$	Total heat transfer resistance $[W/m^2K]$
$v_{ m g}$	Gas velocity [m/s]
v_z	Liquid velocity [m/s]
$v_{z,\mathrm{av}}$	Average liquid velocity [m/s]
$V_{ m mod}$	Module volume $[m_t^3]$
$x_{ m d}$	Dense membrane thickness [m]
x_i	Molfraction of component <i>i</i> in liquid phase
$x_{ m p}$	Porous membrane thickness [m]
y_i	Molfraction of component i in gas phase
z	Axial coordinate
$\Delta H_{i,\mathrm{abs}}$	Absorption heat [J/mol]
$\epsilon_{ m p}$	Membrane porosity
ϵ_{RR}	Relative roughness
γ	Normalized radial coordinate
λ_1	Thermal conductivity of the liquid phase [W/mK]
$\phi_{\rm H_2O}$	$\rm H_2O$ fugacity coefficient
$ ho_{ m g}$	Gas density $[kg/m^3]$
$ ho_{ m l}$	Liquid phase density $[kg/m^3]$
τ	Membrane tortuosity
ξ	Normalized axial coordinate
*	Normalized variables

6. References

- Ramberg R.M., Davies S.R.h., Rognoe H., Oekland O. Steps to the Subsea Factory. In: OTC Brasil. October; Offshore Technology Conference. ISBN 978-1-61399-287-6; 2013, p. 29-31. URL: https://www.onepetro.org/conference-paper/ OTC-24307-MShttp://www.onepetro.org/doi/10.4043/24307-MS. doi:10.4043/24307-MS.
- [2] Dalane K., Dai Z., Mogseth G., Hillestad M., Deng L. Potential applications of membrane separation for subsea

natural gas processing: A review. Journal of Natural Gas Science and Engineering2017;39:101-17. URL: http://dx.doi. org/10.1016/j.jngse.2017.01.023. doi:10.1016/j.jngse.2017.01.023.

- [3] Criscuoli A., Drioli E. Membrane Contactors for Gaseous Streams Treatments. In: Pabby A.K., Rizvi S.S.H., Sastre A.M., editors. Handbook of Membrane Separations. CRC Press; 2008, p. 1041-55. URL: http://www.crcnetbase.com/ doi/10.1201/9781420009484.ch38. doi:10.1201/9781420009484.ch38.
- [4] Gabelman A., Hwang S.t. Hollow fiber membrane contactors. Journal of Membrane Science1999;159(1-2):61-106. URL: http://linkinghub.elsevier.com/retrieve/pii/S037673889900040X. doi:10.1016/S0376-7388(99)00040-X.
- [5] Boributh S., Rongwong W., Assabumrungrat S., Laosiripojana N., Jiraratananon R. Mathematical modeling and cascade design of hollow fiber membrane contactor for CO 2 absorption by monoethanolamine. Journal of Membrane Science2012;401-402:175-89. URL: http://dx.doi.org/10.1016/j.memsci.2012.01.048. doi:10.1016/j.memsci.2012.01.048.
- [6] Rongwong W., Assabumrungrat S., Jiraratananon R. Rate based modeling for CO2 absorption using monoethanolamine solution in a hollow fiber membrane contactor. Journal of Membrane Science2013;429:306-408. URL: http://dx.doi. org/10.1016/j.memsci.2012.11.050. doi:10.1016/j.memsci.2012.11.050.
- [7] Rode S., Nguyen P.T., Roizard D., Bounaceur R., Castel C., Favre E. Evaluating the intensification potential of membrane contactors for gas absorption in a chemical solvent: A generic one-dimensional methodology and its application to CO2 absorption in monoethanolamine. Journal of Membrane Science2012;389:1-16. URL: http://dx.doi. org/10.1016/j.memsci.2011.09.042http://linkinghub.elsevier.com/retrieve/pii/S0376738811007307. doi:10.1016/ j.memsci.2011.09.042.
- [8] Albarracin Zaidiza D., Billaud J., Belaissaoui B., Rode S., Roizard D., Favre E. Modeling of CO2 post-combustion capture using membrane contactors, comparison between one- and two-dimensional approaches. Journal of Membrane Science2014;455:64-74. URL: http://dx.doi.org/10.1016/j.memsci.2013.12.012. doi:10.1016/j.memsci.2013.12.012.
- [9] Albarracin Zaidiza D., Belaissaoui B., Rode S., Neveux T., Makhloufi C., Castel C., et al. Adiabatic modelling of CO2 capture by amine solvents using membrane contactors. Journal of Membrane Science2015;493:106-19. doi:10.1016/ j.memsci.2015.06.015.
- [10] Zhang H.Y., Wang R., Liang D.T., Tay J.H. Modeling and experimental study of CO2 absorption in a hollow fiber membrane contactor. Journal of Membrane Science2006;279(1-2):301-10. URL: http://www.sciencedirect.com/science/ article/pii/S0376738805009051. doi:10.1016/j.memsci.2005.12.017.
- [11] Hoff K.A. Modeling and Experimental Study of Carbon Dioxide Absorption in a Membrane Contactor. Ph.D. thesis; 2003.
- [12] Hoff K.A., Juliussen O., Falk-Pedersen O., Svendsen H.F. Modeling and Experimental Study of Carbon Dioxide Absorption in Aqueous Alkanolamine Solutions Using a Membrane Contactor. Industrial & Engineering Chemistry Research2004;43(16):4908-21. URL: http://www.scopus.com/inward/record.url?eid=2-s2. 0-3542993250{&}partnerID=40{&}md5=5135ac0a3b23c636a49dd913213c2d11http://pubs.acs.org/doi/abs/10.1021/ ie034325a. doi:10.1021/ie034325a.
- [13] Boucif N., Corriou J.P., Roizard D., Favre E. Carbon dioxide absorption by monoethanolamine in hollow fiber membrane contactors: A parametric investigation. AIChE Journal2012;58(9):2843-55. doi:10.1002/aic.12791.
- [14] Eslami S., Mousavi S.M., Danesh S., Banazadeh H. Modeling and simulation of CO2 removal from power plant flue gas by PG solution in a hollow fiber membrane contactor. Advances in Engineering Software2011;42(8):612-20. URL: http://dx.doi.org/10.1016/j.advengsoft.2011.05.002. doi:10.1016/j.advengsoft.2011.05.002.
- [15] Faiz R., Al-Marzouqi M. CO2 removal from natural gas at high pressure using membrane contactors: Model validation and membrane parametric studies. Journal of Membrane Science2010;365(1-2):232-41. URL: http://dx.doi. org/10.1016/j.memsci.2010.09.004http://linkinghub.elsevier.com/retrieve/pii/S0376738810007015. doi:10.1016/

j.memsci.2010.09.004.

- [16] Faiz R., Al-Marzouqi M. Mathematical modeling for the simultaneous absorption of CO2 and H2S using MEA in hollow fiber membrane contactors. Journal of Membrane Science2009;342(1-2):269-78. doi:10.1016/j.memsci.2009.06.050.
- [17] Yan Y., Zhang Z., Zhang L., Chen Y., Tang Q. Dynamic Modeling of Biogas Upgrading in Hollow Fiber Membrane Contactors. Energy & Fuels2014;28(9):5745-55. URL: http://pubs.acs.org/doi/abs/10.1021/ef501435q. doi:10.1021/ ef501435q.
- [18] Rezakazemi M., Niazi Z., Mirfendereski M., Shirazian S., Mohammadi T., Pak A. CFD simulation of natural gas sweetening in a gas-liquid hollow-fiber membrane contactor. Chemical Engineering Journal2011;168(3):1217-26. URL: http://dx.doi.org/10.1016/j.cej.2011.02.019. doi:10.1016/j.cej.2011.02.019.
- [19] Razavi S.M.R., Razavi S.M.J., Miri T., Shirazian S. CFD simulation of CO2 capture from gas mixtures in nanoporous membranes by solution of 2-amino-2-methyl-1-propanol and piperazine. International Journal of Greenhouse Gas Control2013;15:142-9. URL: http://dx.doi.org/10.1016/j.ijggc.2013.02.011. doi:10.1016/j.ijggc.2013.02.011.
- [20] Zhang Z., Yan Y., Zhang L., Chen Y., Ran J., Pu G., et al. Theoretical Study on CO 2 Absorption from Biogas by Membrane Contactors : E ff ect of Operating Parameters. Industrial & Engineering Chemistry Research2014;.
- [21] Chabanon E., Roizard D., Favre E. Modeling strategies of membrane contactors for post-combustion carbon capture: A critical comparative study. Chemical Engineering Science2013;87:393-407. URL: http://dx.doi.org/10.1016/j.ces. 2012.09.011. doi:10.1016/j.ces.2012.09.011.
- [22] Albarracin Zaidiza D., Wilson S.G., Belaissaoui B., Rode S., Castel C., Roizard D., et al. Rigorous modelling of adiabatic multicomponent CO2 post-combustion capture using hollow fibre membrane contactors. Chemical Engineering Science2016;145:45-58. URL: http://dx.doi.org/10.1016/j.ces.2016.01.053. doi:10.1016/j.ces.2016.01.053.
- [23] Boributh S., Assabumrungrat S., Laosiripojana N., Jiraratananon R. A modeling study on the effects of membrane characteristics and operating parameters on physical absorption of CO2 by hollow fiber membrane contactor. Journal of Membrane Science2011;380(1-2):21-33. URL: http://linkinghub.elsevier.com/retrieve/pii/S0376738811004686. doi:10.1016/j.memsci.2011.06.029.
- [24] Farjami M., Moghadassi A., Vatanpour V. Modeling and simulation of CO2 removal in a polyvinylidene fluoride hollow fiber membrane contactor with computational fluid dynamics. Chemical Engineering and Processing: Process Intensification2015;98:41-51. doi:10.1016/j.cep.2015.10.006.
- [25] Dai Z., Usman M., Hillestad M., Deng L. Modelling of a tubular membrane contactor for pre-combustion CO 2 capture using ionic liquids: Influence of the membrane configuration, absorbent properties and operation parameters. Green Energy and Environment2016;1(3):266-75. URL: http://dx.doi.org/10.1016/j.gee.2016.11.006. doi:10.1016/j.gee.2016.11.006.
- [26] King S.I., Falk-Pedersen O., Stuksrud D.B., Grønvold M.S., Svendsen H.F., Palla R., et al. Membrane Gas/Liquid Contactors for Natural Gas Dehydartion. In: The 52nd Annual Laurance Reid Gas Conditioning Conference. 2002,.
- [27] Meyer H.S., Palla R., King S.I. Field Tests Support Reliability of Membrane Gas/Liquid Contactor Gas Dehydration System. Gas Technology Institute2002;8:37–40.
- [28] Usman M., Dai Z., Hillestad M., Deng L. Mathematical modeling and validation of CO 2 mass transfer in a membrane contactor using ionic liquids for pre-combustion CO 2 capture. Chemical Engineering Research and Design2017;123:377-87. URL: http://linkinghub.elsevier.com/retrieve/pii/S0263876217303155. doi:10.1016/j.cherd.2017.05.026.
- [29] Boributh S., Assabumrungrat S., Laosiripojana N., Jiraratananon R. Effect of membrane module arrangement of gas-liquid membrane contacting process on CO2 absorption performance: A modeling study. Journal of Membrane Science2011;372(1-2):75-86. URL: http://dx.doi.org/10.1016/j.memsci.2011.01.034http://linkinghub. elsevier.com/retrieve/pii/S0376738811000536. doi:10.1016/j.memsci.2011.01.034.
- [30] Dindore V.Y., Brilman D.W.F., Versteeg G.F. Hollow fiber membrane contactor as a gas-liquid model contactor.

Chemical Engineering Science2005;60(2):467-79. doi:10.1016/j.ces.2004.07.129.

- [31] Boucif N., Roizard D., Corriou J.P., Favre E. To What Extent Does Temperature Affect Absorption in Gas-Liquid Hollow Fiber Membrane Contactors?Separation Science and Technology2015;50(9):1331-43. URL: http://www.tandfonline.com/ doi/full/10.1080/01496395.2014.969807. doi:10.1080/01496395.2014.969807.
- [32] DeMontigny D., Tonitwachwuthikul P., Chakma A. Using polypropylene and polytetrafluoroethylene membranes in a membrane contactor for CO2 absorption. Journal of Membrane Science2006;277(1-2):99-107. URL: http://linkinghub. elsevier.com/retrieve/pii/S0376738805007490. doi:10.1016/j.memsci.2005.10.024.
- [33] Colebrook C.F., Blench T., Chatley H., Essex E.H., Finniecome J.R., Lacey G., et al. Correspondence. Turbulent Flow in Pipes, With Particular Reference To the Transition Region Between the Smooth and Rough Pipe Laws. (Includes Plates). Journal of the Institution of Civil Engineers1939;12(8):393-422. URL: http://www.icevirtuallibrary.com/doi/ 10.1680/ijoti.1939.14509. doi:10.1680/ijoti.1939.14509.
- [34] Bird R.B., Stewart W.E., Lightfoot E.N. Transport phenomena. 1960.
- [35] Geankoplis C.J. Transport Processes and Separation Process Principles. 2003.
- [36] Iversen S.B., Bhatia V.K., Dam-Johansen K., Jonsson G. Characterization of microporous membranes for use in membrane contactors. Journal of Membrane Science1997;130(1-2):205-17. doi:10.1016/S0376-7388(97)00026-4.
- [37] Lu J.G., Zheng Y.F., Cheng M.D. Wetting mechanism in mass transfer process of hydrophobic membrane gas absorption. Journal of Membrane Science2008;308(1-2):180-90. URL: http://linkinghub.elsevier.com/retrieve/pii/ S0376738807007132. doi:10.1016/j.memsci.2007.09.051.
- [38] Keshavarz P., Fathikalajahi J., Ayatollahi S. Analysis of CO2 separation and simulation of a partially wetted hollow fiber membrane contactor. Journal of Hazardous Materials2008;152(3):1237-47. doi:10.1016/j.jhazmat.2007.07.115.
- [39] Dai Z., Deng L. Membrane absorption using ionic liquid for pre-combustion CO2 capture at elevated pressure and temperature. International Journal of Greenhouse Gas Control2016;54:59-69. URL: http://dx.doi.org/10.1016/j.ijggc. 2016.09.001http://linkinghub.elsevier.com/retrieve/pii/S1750583616305540. doi:10.1016/j.ijggc.2016.09.001.
- [40] Poling B.E., Prausnitz J.M., O'Connell J.P. The properties of gases and liquids; vol. 1. Fifth edited.; 2001. ISBN 0071499997. doi:10.1016/0070116822. arXiv:arXiv:1011.1669v3.
- [41] DOW Triethylene Glycol. 2007. URL: http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh{_}0952/ 0901b80380952386.pdf?filepath=ethyleneglycol/pdfs/noreg/612-00004.pdf{&}fromPage=GetDoc.
- [42] Sun T., Teja A.S. Density, viscosity and thermal conductivity of aqueous solutions of propylene glycol, dipropylene glycol, and tripropylene glycol between 290 K and 460 K. Journal of Chemical and Engineering Data2004;49(5):1311-7. doi:10.1021/je049960h.
- [43] Lee A.L., Starling K.E., Dolan J.P., Ellington R.T. Viscosity correlation for light hydrocarbon systems. AIChE Journal1964;10(5):694-7. doi:10.1002/aic.690100523.
- [44] Parrish W.R., Won K.W., Baltatu M.E. Phase Behavior of the Triethylenen Glycol-Water System and Dehydration/Regeneration Design for Extremely Low Dew Point Requirements. In: 65th Annual GPA Convention. 1986,.
- [45] Duan Z., Mao S. A thermodynamic model for calculating methane solubility, density and gas phase composition of methane-bearing aqueous fluids from 273 to 523 K and from 1 to 2000 bar. Geochimica et Cosmochimica Acta2006;70(13):3369-86. doi:10.1016/j.gca.2006.03.018.
- [46] Hillestad M., Sørlie C., Anderson T.F., Olsen I., Hertzberg T. On estimating the error of local thermodynamic models-a general approach. Computers and Chemical Engineering1989;13(7):789–96. doi:10.1016/0098-1354(89)85052-5.
- [47] Olds R., Sage B., Lancey W. Phase Equilibria in Hydrocarbon Systems1942;189(March):1108–17.
- [48] Chapoy A., Mohammadi A.H., Tohidi B., Richon D. Estimation of Water Content for Methane+ Water and Methane+Ethane + n-Butane + Water Systems Using a New Sampling Device. J Chem Eng Data2005;50:1157–61.
- [49] Frost M., Karakatsani E., von Solms N., Richon D., Kontogeorgis G.M. Vapor-Liquid Equilibrium of Methane with

Water and Methanol. Measurements and Modeling. Journal of Chemical & Engineering Data2013;59(4):961-7. URL: http://pubs.acs.org/doi/abs/10.1021/je400684k. doi:10.1021/je400684k.

- [50] Sharma S.C. Equilibrium water content of gaseous mixtures. Ph.D. thesis; The University of Oklahoma; 1969.
- [51] Mohammadi A.H., Chapoy A., Richon D., Tohidi B. Experimental Measurement and Thermodynamic Modeling of Water Content in Methane and Ethane Systems. Industrial & engineering chemistry research2004;43:7148-62. doi:10. 1021/ie049843f.
- [52] Rigby M., Prausnitz J.M. Solubility of water in compressed nitrogen, argon, and methane. The Journal of Physical Chemistry1968;72(1):330-4. URL: http://pubs.acs.org/doi/abs/10.1021/j100847a064. doi:10.1021/j100847a064.
- [53] Yarrison M., Cox K.R., Chapman W.G. Measurement and modeling of the solubility of water in supercritical methane and ethane from 310 to 477 K and pressures from 3.4 to 110 MPa. Industrial and Engineering Chemistry Research2006;45(20):6770-7. doi:10.1021/ie0513752.
- [54] Chapoy A., Coquelet C., Richon D. Erratum: Revised solubility data and modeling of water in the gas phase of the methane/water binary system at temperatures from 283.08 to 318.12 K and pressures up to 34.5 MPa (Fluid Phase Equilibria (2003) 214 (101-117)). Fluid Phase Equilibria2005;230(1-2):210-4. doi:10.1016/j.fluid.2004.07.005.
- [55] Ng H.J., Jia N., Cheng Y., Schmidt K.A.G., Schroeder H. Vapour-Liquid Equilibrium, Viscosity and Interfacial Tension Modelling of Aqueous Solutions of Ethylene Glycol or Triethylene Glycol in the Presence of Methane, Carbon Dioxide and Hydrogen Sulfide. Gas Injection for Disposal and Enhanced Recovery2009;(September):111-27. doi:10.1002/ 9781118938607.ch7. arXiv:1011.1669v3.
- [56] Ng H.J., Jia N., Cheng Y., Schmidt K.A.G., Schroeder H. Erratum:Vapour-Liquid Equilibrium, Viscosity and Interfacial Tension Modelling of Aqueous Solutions of Ethylene Glycol or Triethylene Glycol in the Presence of Methane, Carbon Dioxide and Hydrogen Sulfide. Gas Injection for Disposal and Enhanced Recovery2009;.
- [57] Chabanon E., Roizard D., Favre E. Membrane contactors for postcombustion carbon dioxide capture: A comparative study of wetting resistance on long time scales. Industrial and Engineering Chemistry Research2011;50(13):8237-44. doi:10.1021/ie200704h.
- [58] Netusil M., Ditl P. Natural Gas Dehydration. In: Natural Gas Extraction to End Use; chap. 1. InTech. ISBN 978-953-51-0820-7; 2012, p. 223-63. URL: http://linkinghub.elsevier.com/retrieve/pii/B9780128014998000079http: //www.intechopen.com/books/natural-gas-extraction-to-end-use/natural-gas-dehydration. doi:10.5772/45802.

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