Plant-wide Assessment of High-Pressure Membrane Contactors in Natural Gas Sweetening – Part II: Process Analysis

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Abstract

This paper presents a model-based assessment of a natural gas sweetening process combining high-pressure membrane contactor with conventional amine regeneration. The analysis builds on a mathematical model of the membrane contactor developed in the companion paper, which is capable of quantitative predictions of the CO₂ and hydrocarbon absorption in the amine solvent and the solvent evaporative losses to the treated gas. The predictive capability of the plant-wide model is tested against data from a pilot plant operated under industrially relevant conditions at a natural gas processing facility in Malaysia, showing a close agreement of the predictions with the CO₂ outlet purity and the energy consumption at various CO₂ loading in the amine solvent. This enables a model-based analysis of various operational decisions on the plant-wide solvent losses and hydrocarbon recovery from the rich amine. A new semi-lean process configuration that replaces the energy-intensive stripper column by a simple flash separator is shown to reduce the overall energy consumption significantly while still meeting sales gas specification. This new configuration forms the basis for the scale-up of a commercial natural gas sweetening process, which shows a high intensification potential in terms of volume footprint and energy duty compared to conventional amine treating plants.

Keywords: membrane contactor, natural gas sweetening, high-pressure operation, process integration, semi-lean operation, experimental validation

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1. Introduction

Natural gas (NG) is a mixture of combustible hydrocarbon gases, that is typically composed of 70–90 vol% methane plus other hydrocarbons such as ethane and propane, alongside impurities such as carbon dioxide (CO₂) and hydrogen sulfide (H₂S). High volumes of these impurities can reduce the heating value of NG, increase the compression cost for pipeline transport and increase the risk of corrosion, among other problems. For bulk CO₂ removal the purity target is typically sales gas specification with a CO₂ content below 2–3 mol% [1]. For deep CO₂ removal applications the purity specification is 50 ppmv in liquefied natural gas (LNG) plants to avoid freezing in low-temperature chillers, and below 100 ppmv in ammonia plants to prevent catalyst poisoning [2, 3].

Membrane separation and chemical solvent absorption are both widely employed for NG sweetening [4, 5]. Membranes are attractive due to their potential for reducing physical footprint and capital and operating expenditures. However, current commercial membranes have a relatively low permeability and their low selectivity can lead to large hydrocarbon losses [6]. Chemical solvents, such as alkanolamines, can selectively react with the acid gases and thus minimize hydrocarbon losses. They are used extensively in absorption towers for deep CO₂ removal, but this conventional technology incurs high capital expenditures, has a large physical footprint, and can be subject to operational problems [7, 8].

The membrane contactor (MBC) technology combines the advantages of both conventional chemical absorption and membrane separation [9, 10]. Packaging into hollow-fiber membrane (HFM) modules offers a higher mass transfer area compared with conventional packed columns, giving MBC a high intensification potential [11–13]. This modularity also empowers a more flexible design and scale-up, while the ability to control the gas and liquid flow rates independently facilitates operations. The effectiveness of MBC for CO₂ removal has been extensively studied over the past few decades, including applications in CO₂ post-combustion capture and NG sweetening [11, 12, 14]. A host of mathematical modeling studies have also been conducted to support these assessments, for MBC operating near atmospheric pressure [15–17] and at high pressure [18, 19], and to get a better understanding of the effect of membrane wetting on MBC performance [19, 20].

In principle, either or both of the absorber and stripper columns in a conventional amine treating process could be replaced with an MBC module. Yeon et al. [21] conducted an experimental assessment of a hybrid process combining an atmospheric-pressure MBC using amine solvent for CO₂ removal from flue gas with a thermal stripping tower for the amine regeneration. They showed that this MBC-based process has a higher CO₂ removal efficiency than with a conventional packed column and that the CO₂ absorption rate per unit volume is 2 to 3 times higher with the MBC, thus confirming the intensification potential. Yan et al. [22] investigated a similar experimental set-up for the comparison of different absorbents. By contrast, Lee et al. [23] and Kosaraju et al. [24] studied a process not only employing an MBC for the CO₂ absorption, but also for the desorption. Simons et al. [25], and more recently Kim et al. [26], used this coupled MBC process for the separation of CO₂ from methane in biogas and investigated the influence of the type of membrane and various process parameters on the overall process performance.

The usual key performance indicators (KPIs) for NG sweetening processes consist of: (i) the CO₂ purity in the treated gas; and (ii) the energy per mass of CO₂ removed. From a techno-economic standpoint, other relevant KPIs include: (iii) the fraction of hydrocarbons lost via absorption in the amine solution; and (iv) the amount of solvent evaporative losses per volume of treated gas. Mathematical models can provide an effective tool to quantify these KPIs, and in

turn enable a better assessment and optimization of the whole process performance. But unlike modeling studies for stand-alone MBC modules, detailed models for the plant-wide simulation of MBC-based processes are still lacking. Recently, Pakšiová et al. [27] modeled a coupled MBC process operating at atmospheric pressure for both the separation of CO₂ from methane by absorption and the stripping of CO₂ from the amine solution. Although simplifying modeling assumptions based on mass transfer coefficient and non-wetted operation were made to describe the two MBC units, the plant-wide model could be used to analyze the effects of different liquid and gaseous flow rates on the overall energy consumption. To the best of the authors' knowledge however, there is no published literature on plant-wide modeling of MBC-based processes for NG sweetening that would simultaneously consider all four above-mentioned KPIs.

The present paper addresses this gap by conducting a model-based analysis of an MBC-based process for NG sweetening. The process of interest is akin to a traditional amine treating process where the absorber column is simply replaced with an MBC. The enriched amine solvent from the MBC is regenerated by stripping the absorbed hydrocarbons and acid gases, before returning it to the MBC inlet. Both lean and semi-lean operations are possible in this process configuration depending on how much CO₂ remains in the amine solvent after its regeneration. Because solvent regeneration is the most energy intensive part [8, 28], the semi-lean operation can reduce the operating cost significantly yet to the detriment of CO₂ abatement. The benefit of using a high-pressure MBC rather than a conventional packed column for the CO₂ absorption is also a reduction in liquid-to-gas (L/G) ratio [29], which translates into less solvent to regenerate. The overall energy consumption may be further reduced by burning the light hydrocarbon gas recovered from the enriched amine solution, provided that it is compliant with the calorific value of fuel gas. Solvent make-up is furthermore needed to compensate for the evaporative losses due to both CO₂ absorption and stripping operations.

In order to conduct the techno-economic assessment, we develop a plant-wide model using the advanced process modelling platform gPROMS[®] [30], which builds on the MBC model presented in the companion paper [31]. This MBC model uses a combination of 1-d and 2-d mass-balance equations to predict the CO₂ absorption flux and membrane wetting for both lean and semi-lean amine solutions, and it has a unique capability for predicting the CO₂ and hydrocarbon absorption in the amine solvent and the solvent evaporative losses to the treated gas for a wide range of gas and solvent flowrates. We test the predictive capability of the plant-wide model against data from a pilot plant operated under industrially relevant conditions at a natural gas processing facility in Malaysia, and then use it to conduct process analysis and scale-up.

The rest of the paper is organized as follows. The experimental set-up of the pilot-scale MBC is described in Sec. 2 along with the corresponding plant-wide model and its implementation in gPROMS. Results of the experimental model verification are presented and discussed in Sec. 3. A model-based analysis is conducted in Sec. 4, where the effect of operational decisions on hydrocarbon recovery and solvent losses are investigated and two process configurations for lean and semi-lean operations are compared in terms of energy duty. The design and scale-up of a commercial-scale MBC under semi-lean operations is conducted in Sec. 5 and its intensification potential is assessed. Finally, Sec. 6 concludes the paper.

2. Material and Methods

2.1. Pilot Plant Setup

Experiments were conducted on a pilot plant at a NG processing facility in Malaysia. The CO₂-rich natural gas with up to 18 mol% CO₂ was produced by blending pure CO₂ from pres-

Figure 1: Diagram of the pilot plant setup.

surized gas cylinders into the NG feed stream, and a liquid-Gas coalescer was used to remove any water or hydrocarbon liquids. An aqueous mixture of methyldiethanolamine (MDEA) and piperazine (PZ) was used as the chemical solvent. The experimental setup is depicted on Fig. 1.

95 The CO₂-rich natural gas is fed to the tube side of the MBC at 54 bar, while the lean solvent is fed to the shell side also at a pressure of ca. 54 bar, in a counter-current and horizontal configuration. Circulating the solvent in the shell section of the MBC (instead of tube section) reduce the pressure drops significantly, while operating the MBC horizontally removes the need to overcome the static head and reduces membrane wetting [19]. The feed gas and solvent flow rates are controlled using a mass-flow controller (MFC) and pump stroke, respectively. The enriched amine solvent collected from the MBC shell outlet is directed to the rich-solution flash drum for degassing of the dissolved light hydrocarbons. The flashed liquid outlet stream is heated by cross exchange with hot lean solvent before feeding into the regenerator column where it is stripped of acid gas by a rising stream of vapors generated by the electrical reboiler. The acid gas leaving the top of this stripper column is cooled and feeds into the reflux drum for separating the condensed water from the acid gas. The condensed water is then returned to the top of the column, while the acid gas is flared. The lean solvent from the regenerator is cooled by passing through the lean-rich exchanger, then the lean solution cooler, and finally the amine chiller, before returning to the MBC. Since the solvent regenerator was designed for a maximal capacity 10-times larger than the MBC module, about 88% of the regenerated solvent is mixed with the rich amine and returned to the stripper—connection downstream of the LP amine pump shown in dashed line on Fig. 1. Both demineralized water and fresh MDEA and PZ are fed into the amine tank periodically to make up for evaporative solvent losses in the MBC and the stripper column.

115 The gas flowrates at the outlet of the MBC and of the flash drum were measured with a mass flowmeter. The gas compositions at the inlet and outlet of the MBC and at the outlet of the flash drum were analyzed using a gas chromatograph (PGC1000, ABB). These measurements were recorded over several hours of steady-state operation and averaged to filter out the noise. The

Table 1: Packing material and properties of stripper column.

Property	Value	Source
Packing height / diameter (m)	6.1 / 0.3	Manufacturer
Packing size (m)	0.025	Manufacturer
Surface area (m ⁻¹)	150	Manufacturer
Void fraction (–)	0.98	Manufacturer
Loading point constant, C_s (–)	3.491	[32]
Flooding point constant, C_{FL} (–)	2.2	[32]
Hydraulic constant, C_h (–)	0.75	[32]
Total particles constant, C_{p0} (–)	0.5	[32]
Liquid constant, C_L (–)	1.29	[32]
Vapor constant, C_v (–)	0.44	[32]

CO₂ loading in the enriched and regenerated amine solvents were measured by titration during steady-state operation.¹ All of the pieces of equipment in the pilot plant are electrically powered. The power consumption of the reboiler, overhead condenser, reflux pump, LP amine pump, lean solution cooler, HP amine pump, and amine chiller were monitored and added to obtain the total power consumption, also referred to as the process duty below.

The high pressure MBC module was packed with hydrophobic, polytetrafluoroethylene (PTFE) hollow fiber, with a steel tube insert at the center of the module to artificially reduce the specific membrane area. The main characteristics of these membranes and the geometrical properties of the MBC module are reported in the companion paper [31]. The stripper column was packed with Raschig Super-Ring No. 1 (RASCHIG GMBH). The properties of this packing material are listed in the top part of Table 1.

2.2. Pilot Plant Modeling

A plant-wide model of the pilot plant was developed using gPROMS ProcessBuilder (v1.3.1) and compiled into a gPROMS Model Library (gML) with the interface shown in Fig. 2. It was then combined with unit models of the solvent regeneration operations from both the standard and advanced gML, resulting in the process flowsheet displayed in Fig. 3. The corresponding operating conditions are summarized in Table 2 and further modeling details about the MBC, the stripper column, flash drum, heat exchangers and pumps are given next. All of the physical properties for the solvent regeneration operations are estimated using the RKSA equation of state, as available via the interface between gPROMS and Multiflash (v6.1).

¹The pH of 125 mL of methanol was first adjusted to 11.2 by adding 0.5 N KOH in a beaker. 20 ± 0.5 g of amine solvent was then transferred into the beaker, and the solution was titrated with 0.5 N KOH until reaching pH 11.2 ± 0.02 again. The same procedure was repeated on a fully regenerated amine (overnight reflux). The CO₂ content (wt%) and CO₂ loading (mol mol⁻¹) were calculated as:

$$\text{CO}_2 \text{ content} = \left(\frac{V_1}{m_1} - \frac{V_2}{m_2} \right) N \text{ MW}_{\text{CO}_2}$$

$$\text{CO}_2 \text{ loading} = \frac{\text{CO}_2 \text{ content}}{\text{MW}_{\text{CO}_2}} \frac{\text{MW}_{\text{amine}}}{\text{amine content}}$$

with V_1 (L) and m_1 (g) the volume and mass of KOH used to titrate the amine solvent; V_2 (L) and m_2 (g) the volume and mass of KOH used to titrate the fully-regenerated amine solvent; N the KOH normality (mol L⁻¹); MW_{CO_2} the molecular weight of CO₂; MW_{amine} the average molecular weight of MDEA and PZ; and the amine content as given in Table 2.

Table 2: Nominal operating conditions in the pilot experimental setup.

Absorption – NG sweetening	
MBC tube, inlet gas composition CO ₂ / CH ₄ / C ₂ H ₆ / C ₃ H ₈ (mol%)	5 / 85 / 7 / 3
inlet gas flowrate (kg h ⁻¹)	75
inlet gas pressure (kPa)	5400
inlet gas temperature (K)	298
MBC shell, inlet solvent composition MDEA / PZ (wt%)	39 / 5
inlet solvent flowrate (L h ⁻¹)	275
inlet solvent temperature (K)	303–308
outlet solvent pressure (kPa)	5430
inlet CO ₂ loading in solvent (mol mol ⁻¹)	0.01–0.23
Desorption – Solvent regeneration	
Rich solution drum pressure (kPa)	911
Solvent regenerator pressure (kPa)	258
Reboiler temperature (K)	376–403
Overhead condenser, outlet temperature (K)	333
Reflux pump, outlet pressure (kPa)	258
Lean-rich exchanger cold stream, outlet temperature (K)	371
outlet pressure (kPa)	368
hot stream, outlet pressure (kPa)	233
LP amine pump, outlet pressure (kPa)	711
Lean solution cooler, outlet temperature (K)	318
pressure drop (kPa)	35
HP amine HP pump, outlet pressure (kPa)	5460
Amine chiller, outlet temperature (K)	303–308
pressure drop (kPa)	30

Figure 3: Flowsheet of the pilot plant in gPROMS ProcessBuilder integrating the gML-compliant MBC model with the standard and advanced gML.

Modeling of Heat Exchangers. The process flowsheet comprises three heat exchangers—lean-rich heat exchanger, lean solution cooler, and amine chiller. The lean-rich heat exchanger is modeled as a two-stream countercurrent heat exchanger from the standard gML, with a specification on the outlet temperatures of the rich amine (cold stream) of 371 K. Both the lean solution cooler and the amine chiller are modeled as simple cooler elements in the standard gML, with a small pressure drop. The specification on the outlet temperature of the lean solution cooler is 318 K, while the outlet temperature of the amine chiller is set to the desired inlet solvent temperature, here in the range between 303–308 K. Both cooler models predict the power consumption required to meet these thermal specifications.

Modeling of Pumps. All three pumps in the process flowsheet—amine HP pump, amine LP pump, and reflux pump—are assumed to have mechanical and isentropic efficiencies of 85%. The model predicts the power consumption of each pump in order to meet the specified outlet pressures (see Table 2). The temperature of the pump outlet stream is furthermore calculated by defining the fluid compression relative to an ideal compression process, using an ideal efficiency.

Modeling of Solvent Make-up. The desired flowrate and composition of the amine solution in the MBC are set using three separate control elements: one for adjusting the flowrate to 275 L h^{-1} ; the other two for adjusting the mass fractions of MDEA and PZ to 39 wt% and 5 wt%, respectively. The outlet streams from the control elements are mixed together with the regenerated amine solution before feeding into the MBC unit.

2.3. Numerical Simulation

The numerical discretization approach used to implement the MBC model was described in the companion paper [31]. In order to reduce the computational burden, a coarser uniform mesh grid consisting of 35 elements—compared with 70 elements previously—was adopted to perform the plant-wide simulations, which still provides solutions within 2% of finer discretizations. For the solvent regenerator, a first-order finite difference scheme was applied to both the bulk liquid and vapor phases. With these settings, a steady-state simulation takes about 10 minutes to run on a desktop computer running Windows 7 with Intel® Core™ i7-4790 CPU at 3.60GHz and 32GB of RAM.

3. Experimental Plant-wide Model Verification

Predictions of the plant-wide model in terms of CO_2 removal in the MBC, CO_2 loading in both the enriched and regenerated amine solutions, and total process duty are compared against experimental data from the pilot plant in Fig. 4. All of these experiments were conducted at constant gas (75 kg h^{-1}) and solvent (275 L h^{-1}) flow rates by varying the reboiler temperature in the stripper column, which resulted in different CO_2 loadings in the regenerated amine solution—additional experiments conducted for different L/G ratios in the MBC can be found in the companion paper [31].

Overall, the model predictions are in excellent agreement with the experimental data. Prediction errors are within 5% for the CO_2 absorption flux (Fig. 4A), the CO_2 removal efficiency (Fig. 4B, right axis), the CO_2 loading in both the enriched and regenerated amine solutions (Fig. 4C), and the total process duty (Fig. 4D). Notice the somewhat larger prediction error for the outlet CO_2 molar fraction (Fig. 4B, left axis)—e.g., the prediction error close to 15% for

Figure 4: Comparison of plant-wide model predictions against experimental data from the pilot plant with a gas flowrate of 75 kg h⁻¹ and solvent flowrate of 275 L h⁻¹. **A:** CO₂ absorption flux in MBC at various solvent regeneration temperatures; **B:** CO₂ purity at MBC gas outlet and CO₂ removal efficiency at various CO₂ loadings in amine solvent; **C:** CO₂ loading levels at various solvent regeneration temperatures; **D:** total process duty at various CO₂ loadings in amine solvent.

the second experimental point—which is nonetheless acceptable given the relatively low CO₂ concentration at the MBC outlet.

The capability of the MBC model to make quantitative predictions of the CO₂ removal efficiency under both lean and semi-lean conditions (Fig. 4B) was discussed in the companion paper [31], where an increase in CO₂ loading of the amine solution can reduce the absorption flux by 20% or more. In order to achieve deep CO₂ removal, in particular to meet the LNG specification of 50 ppmv, operating the MBC with a regenerated lean amine is necessary. On the other hand, operation with a regenerated semi-lean amine appears to be sufficient to meet the typical sales gas specification of 2–3 mol% CO₂.

On top of this, the plant-wide model correctly describes the effect of reducing the solvent regeneration (reboiler) temperature on increasing the CO₂ loading in the regenerated amine (Fig. 4C), which in turn decreases the CO₂ absorption flux in the MBC (Fig. 4A). Notice, in particular, how accurately the model describes the difference in CO₂ loading between the enriched and regenerated solvents, which narrow down as the reboiler temperature is lowered. The corresponding reduction in heating and cooling duties is accurately predicted, too (Fig. 4D).

These experimental data suggest that the energy consumption for meeting sales gas specification (2–3 mol% CO₂) could be reduced dramatically, by up to 80%, upon operating the pilot plant with a semi-lean solvent (regeneration temperature of 376 K) instead of a lean solvent (regeneration temperature of 423 K). This observation is consistent with previous studies by Alie [33] and Xu et al. [34], which reported significant reductions in the reboiler duty upon increasing the CO₂ loading of the regenerated amine to 0.2 mol mol⁻¹ or higher. The plant-wide model is used to further this analysis in Sec. 4, before investigating the scale-up of a semi-lean MBC-based process of NG sweetening under industrially-relevant conditions in Sec. 5.

4. Model-based Analysis of Pilot Setup

4.1. Process-wide Solvent Losses

Although the amine solvent is not consumed during the acid gas removal process, losses via evaporation or entrainment are inevitable. Unlike conventional packed columns, solvent entrainment cannot occur in MBC because the microporous membrane prevents the dispersion of the gas and liquid phases into one another. However, water, MDEA or PZ losses may still occur with the treated gas, flash gas and acid gas streams. These losses are dependent on the type and concentration of amine, but also on the operating temperature and pressure of the MBC, flash drum and stripper column from a process-wide viewpoint (cf. Fig. 1). The solvent makeup stream compensates for such losses by maintaining a desired solvent amount and composition in the process.

Predictions of the evaporative solvent losses across the entire NG sweetening process are presented in Fig. 5, for the same gas and solvent flowrates as in the experimental verification above. Notice that the water evaporative losses are 100-fold larger than the PZ losses, which are themselves 2–3 times larger than the MDEA losses, in agreement with their respective vapor pressures. Interestingly, varying the reboiler temperature in the stripper column shows an opposite effect on the total water losses and on the total amine losses (Fig. 5A). The water losses increase by over 20% in raising the reboiler temperature from 376 K to 403 K, whereas the amine losses are about halved at the same time. This counter-intuitive behavior—one would expect the amine losses to increase with the reboiler temperature instead—is attributed to non-ideality and association effects in the water-MDEA-PZ mixture. It could be reproduced with different thermodynamic

Figure 5: Effect of solvent regeneration temperature in stripper column on process-wide evaporative losses, with a gas flowrate of 75 kg h^{-1} and solvent flowrate of 275 L h^{-1} . **A**: water and amine losses per volume of treated gas; **B**: comparison of solvent losses in treated gas and acid gas streams.

property packages in gPROMS, including RKSA and SAFT-VR, but the process model predictions could be subject to large errors due to the low residual concentrations of MDEA and PZ in the acid gas. A breakdown of these losses reveals that: (i) evaporative losses with the flash gas contribute only 1–3% of the overall losses; (ii) evaporative losses with the treated gas show very little variations (2–4%) over the reboiler temperature range of interest; and (iii) both the water and amine losses with the acid gas make by far the largest share (70–90%) of the evaporative losses in the process (Fig. 5B). This latter observation suggests that a reduction in the overhead condenser temperature, for instance from 333 K to 318 K, could significantly curtail the overall water and amine losses. In practice, it is also expected that more MDEA and PZ will be conveyed upwards through mist entrainment than strictly as vaporization losses [35], which are not accounted for in the stripper model. The use of MBC technology to replace the stripper column could help further reduce solvent losses, by preventing such entrainment losses.

The total amine (MDEA + PZ) losses in the pilot plant are predicted to be between 27–54 mg per Sm^3 of treated gas, which is commensurate with reported average amine losses of ca. 48 mg Sm^{-3} (3 lb MMSCF^{-1}) in existing gas processing plants using monoethanolamine (MEA), diethanolamine (DEA) and MDEA [35]. The predicted amine losses per CO_2 removed are between $0.24\text{--}0.63 \text{ kg ton}^{-1}$, which is again consistent with conventional NG sweetening plants ($0.35\text{--}3 \text{ kg ton}^{-1}$) [7, 36].

In the current setup, the total solvent losses amount to about 0.1–0.15% of the solvent circulation rate (275 L h^{-1}) and water makes over 99 wt% of these losses. This suggests that pure water makeup should be sufficient to maintain the solvent concentration during normal operations, complemented with regular injection of fresh amine into the process when the amine inventory has dropped below a certain threshold or has thermally degraded.

Figure 6: Effect of pressure in rich solution flash drum on hydrocarbon recovery and LHV of flash gas, with a gas flowrate of 75 kg h^{-1} and solvent flowrate of 275 L h^{-1} . **A**: lean amine operation (inlet CO_2 loading: 0.01); **B**: semi-lean amine operation (inlet CO_2 loading: 0.23). Dotted line: lower limit of NG fuel gas specification.

4.2. Process-wide Hydrocarbon Losses

Hydrocarbons absorbed alongside CO_2 by the solvent might end up in the acid gas stream if they are not recovered. Although these losses are typically a tiny fraction of the treated gas, they could add up to a large economic loss and cause problems in the downstream processing of the acid gas [37]. A large fraction of these hydrocarbons may be recovered in the rich solution flash drum downstream of the MBC liquid outlet (Fig. 1). It is customary to use the flash gas in a gas turbine for heat recovery. A usual specification for the fuel gas is based on the lower heating value (LHV) of 47.1 MJ kg^{-1} for NG [38], although specially-designed gas turbines may still be used for NG with higher CO_2 content and lower LHV [39]. Alternatively, the flash gas could be compressed and returned to the MBC gas inlet, or simply mixed with the treated gas subject to meeting the required CO_2 purity.

Adjusting the operating pressure of the rich solution flash drum provides an effective strategy to mitigating hydrocarbon losses. The results of a case study that considers the same gas and solvent flowrates as before are shown in Fig. 6, for both lean and semi-lean conditions. The hydrocarbon recovery is calculated on a mole basis with respect to the hydrocarbon content of the MBC liquid outlet. The LHV of the flash gas is calculated based on the LHV of methane, ethane and propane [40], weighted by their respective mass fractions and using an LHV of zero for CO_2 . From thermodynamic considerations, operating the rich solution flash drum at a lower pressure increases the amount of flash gas, thereby increasing fuel gas recovery. But those species with a lower vapor pressure, such as CO_2 , also flash off of the amine solvent at lower pressure, thereby reducing the LHV of the flash gas. This defines a clear trade-off in terms of the flash drum pressure.

Upon reducing the rich solution flash drum pressure from 1500 kPa to 700 kPa, the predicted hydrocarbons recovery increases from about 81% to 90% under lean conditions (Fig. 6A) and from 77% to 88% under semi-lean conditions (Fig. 6B). Under lean conditions, the flash gas meets the LHV specification of 47.1 MJ kg^{-1} (dotted line) at all pressure values, with a corresponding maximal recovery of over 90% at 700 kPa. By contrast, the LHV of the flash gas only

reaches 47.1 MJ kg^{-1} at 1500 kPa, yet with a much lower recovery of 77%. This higher CO_2 content is due to a richer amine under semi-lean conditions ($0.37 \text{ mol mol}^{-1}$ at MBC liquid outlet, see Fig. 4D) compared to lean conditions ($0.20 \text{ mol mol}^{-1}$ at MBC liquid outlet). One might therefore decide to use a different design strategy in terms of flash gas utilization or reprocessing for the lean and semi-lean modes of operation.

4.3. Improved Semi-lean Process to Meet Sales Gas Specification

The pilot plant experiments in Sec. 3 demonstrate that sales gas specification with less than 2–3 mol% of CO_2 can be achieved under both lean and semi-lean conditions, yet with the semi-lean operation consuming 80% less energy compared to lean operation. However, this comparison might be misleading as these experiments were all conducted with the same solvent flowrate of 275 L h^{-1} . To allow for a fairer comparison, a case study is conducted here for treating 75 kg h^{-1} of sour NG with a target CO_2 purity of 1.5 mol% by adjusting the solvent flowrate.

- The configuration of the lean amine process follows the flowsheet in Fig. 3, yet without the internal amine recycle to the stripper column (cf. dashed line in Fig. 1). In order to achieve a CO_2 loading of $0.01 \text{ mol mol}^{-1}$ at the MBC liquid inlet, the reboiler temperature is set to 403 K.
- A modified configuration is adopted for the semi-lean amine process, whereby the stripper column and reboiler are replaced with a low-pressure flash drum and heater, respectively. The corresponding flowsheet is depicted in Fig. 7. The target CO_2 loading of $0.23 \text{ mol mol}^{-1}$ in the solvent feed to the MBC is achieved by imposing a temperature of 376 K in the flash drum heater.

Most of the composition, temperature and pressure specifications in Table 2 remain in effect in both processes. The modified or extra specifications are reported in Table 3, together with several KPI predictions for each process configuration.

The solvent flowrate in the lean amine process (106 L h^{-1}) is 30% lower than in the semi-lean process (150 L h^{-1}) in order to meet the same CO_2 purity of 1.5 mol%. This is mainly due to the higher CO_2 absorption capacity of the fully-regenerated solvent. The corresponding solvent-to-absorbed- CO_2 ratios of $0.54 \text{ m}^3 \text{ kmol}^{-1}$ in the lean process and $0.77 \text{ m}^3 \text{ kmol}^{-1}$ in the semi-lean process are at the lower end of the range $0.6\text{--}1.1 \text{ m}^3 \text{ kmol}^{-1}$ that is typical of conventional packed columns [41–43].

A lower solvent flowrate in the lean amine process translates into a lower energy consumption in all of the pumps. Nevertheless, the total process duty of the lean process (13.7 kW) remains 16% higher compared to the semi-lean process (11.6 kW). This is attributed to: (i) the higher reboiler temperature needed to fully regenerate the solvent in the lean process; and (ii) the greater cooling duty in the lean solution cooler since the temperature of the solvent leaving the stripper column is higher in the lean process despite the heat integration provided by the lean-rich heat exchanger.

A breakdown of the plant-wide energy consumption by main equipment is shown in Fig. 8 for both the lean and semi-lean processes. The reboiler duty makes up the largest share with about 40–49% of the plant-wide energy consumption, which is consistent with the figures from conventional amine-based processes [8, 28]. By contrast, the pumping energy required by the MBC is only a few percentage points. The lean solution cooler and amine chiller come second and third, with respective shares of 29–36% and 9–16%. This analysis suggests that the process duty could be further reduced by feeding the regenerated solvent to the MBC at a temperature of

Table 3: Modified operating conditions and performance indicators in the pilot experimental setup in order to achieve a CO₂ purity of 1.5 mol% under lean and semi-lean operations.

	Lean process	Semi-lean process
Absorption – NG sweetening		
MBC tube, inlet gas temperature (K)	298	298
outlet gas CO ₂ composition (mol%)	1.5	1.5
MBC shell, inlet solvent flowrate (L h ⁻¹)	106	150
inlet solvent temperature (K)	303	303
inlet CO ₂ loading in solvent (mol mol ⁻¹)	0.01	0.23
Desorption – Solvent regeneration		
Reboiler temperature (K)	403	376
Amine chiller, outlet temperature (K)	303	303
Performance indicators		
LHV of flash gas (MJ kg ⁻¹)	48.4	45.6
Amine loss with treated gas (mg Sm ⁻³)	7.9	8.4
acid gas (mg Sm ⁻³)	53.1	40.6
flash gas (mg Sm ⁻³)	0.7	4.2
Total process duty (kW)	13.7	11.6

318 K, thereby removing the amine chiller. This process modification would furthermore reduce the physical footprint of the whole process and it is adopted in the final scale-up study conducted in Sec. 5 below. However, we note that removing the amine chiller could also have adverse consequences since a higher solvent temperature will raise the amine vapor pressure, resulting in increased amine losses. A higher solvent temperature will also increase the outlet gas temperature and in turn the water content of the gas, thereby increasing the loading of downstream dehydration equipment [44].

By and large, the semi-lean configuration presents a better intensification potential than its lean counterpart to achieve sales gas specification since it reduces both the energy consumption and the physical footprint of the process. The predicted amine losses under this mode of operation are also comparable to those of the lean process (see Table 3), while its only downside would be a reduction in LHV of the flash gas that could prevent its use in a conventional combustion turbine. It is expected that these benefits will translate into a significant reduction in capital and operating expenditures compared with the lean mode of operation in a commercial-scale sweetening process.

5. Model-based Scale-up of a Commercial Semi-lean Process for Natural Gas Sweetening

The final section investigates the design of a commercial process by leveraging knowledge acquired in this paper and its companion [31] from both the experimental and modeling studies. We consider an industrially-relevant scenario, whereby 233 MMSCFD of sour NG with a CO₂ content of 24 mol% need to be sweetened to 6.5 mol% before sending the gas onshore for further processing. The focus is on the semi-lean process (Fig. 7), which has shown superior performance in the pilot-plant experiments and is also supported by the modeling results.

Figure 8: Breakdown of the plant-wide energy consumption by main equipment. **A**: lean amine process using a stripper column. **B**: semi-lean amine process using a low-pressure flash drum.

5.1. Commercial Process Specifications

We assume that the high-pressure MBC cartridges are packed with the same PTFE hollow fibers and have the same geometry (radius: 0.115 m, length: 2.3 m) as in the lab and pilot-plant setups [31, Table 2], yet without the steel tube insert (compare Sec. 2.1). The cartridges are assembled into MBC modules as illustrated in Fig. 9, and a number of these modules are then operated in parallel as a strategy to scale up the throughput—this modular configuration is adopted in an effort to limit the number of high-pressure vessels in the process. In order to determine how many modules are needed for treating 233 MMSCFD of NG, we use the average absorption flux of $7.1 \text{ mol m}^{-2} \text{ h}^{-1}$ that was measured under the same NG composition and semi-lean conditions in the lab setup [31, Fig. 7B–C]. The corresponding total membrane area is estimated to be $287\,000 \text{ m}^2$, which requires in excess of 2120 MBC cartridges and thus 69 MBC modules. The estimated total volume and weight for these MBC modules are 320 m^3 and 830 ton, respectively a 50% and 10% reduction against a state-of-the-art packed column designed by PETRONAS for similar gas flowrate, solvent composition and CO_2 abatement; check Ref. [45] for a detailed comparison of MBC vs. packaged column in terms of volume footprint. In addition to this large intensification factor, the solvent flowrate ($1675 \text{ m}^3 \text{ h}^{-1}$) is minimized in order to meet the desired CO_2 purity (6.5 mol%), so that the energy required to regenerate the solvent is also minimized. The specifications in the CO_2 absorption section are summarized in the top part of Table 4.

Following the recommendations in Sec. 4, we also depart from the pilot-plant setup by (i) removing the amine chiller to reduce the process duty and the physical footprint, and (ii) reducing the temperature of the overhead condenser to mitigate the solvent evaporative losses with the acid gas. The new set of specifications in the solvent regeneration section is reported in the bottom part of Table 4.

5.2. Commercial Process Performance

A set of KPIs for the scale-up semi-lean MBC process are listed in Table 5. The variation ranges for these KPIs correspond to a $\pm 5\%$ change in the Henry constants of N_2O , CH_4 , C_2H_6 and C_3H_8 in amine solvent, which is consistent with the predicted uncertainty in the regressions

Table 4: Specifications of commercial semi-lean process for NG sweetening.

Absorption – NG sweetening	
MBC tube, inlet gas composition CO ₂ / CH ₄ / C ₂ H ₆ / C ₃ H ₈ (mol%)	24 / 73 / 2 / 1
inlet gas flowrate (kmol h ⁻¹)	11630
inlet gas pressure (kPa)	5400
inlet gas temperature (K)	298
MBC shell, inlet solvent composition MDEA / PZ (wt%)	39 / 5
inlet solvent flowrate (m ³ h ⁻¹)	1675
inlet solvent temperature (K)	318
outlet solvent pressure (kPa)	5430
MBC cartridge, inner radius (m)	0.115
number of fibers	17,000
MBC module, number of cartridges	31
inner radius (m)	0.8
Number of MBC modules	69
Desorption – Solvent regeneration	
Rich solution drum, pressure (kPa)	911
Solvent regeneration flash drum, pressure (kPa)	258
heater, temperature (K)	377
Overhead condenser, outlet temperature (K)	318
Reflux pump, outlet pressure (kPa)	258
Lean-rich exchanger cold stream, outlet temperature (K)	364
outlet pressure (kPa)	368
hot stream, outlet pressure (kPa)	233
LP amine pump, outlet pressure (kPa)	711
Lean solution cooler, outlet temperature (K)	318
pressure drop (kPa)	35
HP amine HP pump, outlet pressure (kPa)	5430

Figure 9: Cross-section of commercial-scale MBC module with radius of 0.8 m, containing 31 smaller MBC cartridges with radius of 0.115 m each.

Table 5: Key performance indicators of commercial semi-lean process for NG sweetening. The variation ranges are calculated for a $\pm 5\%$ change in the Henry constants of N_2O , CH_4 , C_2H_6 and C_3H_8 in amine solvent.

Performance indicator	Nominal value	Variation range
CO_2 purity of treated gas (mol%)	6.4	6.2–6.6
CO_2 absorption flux ($\text{mol m}^{-2} \text{h}^{-1}$)	7.6	7.5–7.7
Solvent-to-absorbed- CO_2 ratio ($\text{m}^3 \text{kmol}^{-1}$)	0.76	0.75–0.78
Reboiler energy per CO_2 removed (GJ ton^{-1})	2.20	2.18–2.21
Recovered hydrocarbons in flash gas (ton h^{-1} , %)	1.04 (82%)	0.98 (81%)–1.10 (83%)
LHV of flash gas (MJ kg^{-1})	29.5	29.1–29.8
Amine loss per CO_2 removed (kg ton^{-1})	0.270	0.268–0.272

embedded in the MBC model [31, Figs. 5–6]. The effect of this uncertainty on the KPIs is rather small overall. First of all, it can be checked that the CO_2 concentration in the treated gas meets the desired target of 6.5 mol%. The predicted CO_2 absorption flux ($7.6 \text{ mol m}^{-2} \text{h}^{-1}$) is 7% higher than the same flux measured in the lab setup ($7.1 \text{ mol m}^{-2} \text{h}^{-1}$), a difference caused by the higher solvent temperature in the MBC after removing the amine chiller. Such an increase in the CO_2 absorption flux at higher solvent temperature was also observed experimentally [19, 31]. The predicted solvent-to-absorbed- CO_2 ratio ($0.76 \text{ m}^3 \text{kmol}^{-1}$) is comparable to the pilot-scale process (Sec. 4.3) and again in the lower range of typical values for conventional packed columns [41–43]. Furthermore, the reduction in reboiler energy per CO_2 removed (2.2 GJ ton^{-1}) compared to conventional amine treating processes (2.4 – 4.2 GJ ton^{-1} , see [46–48]) is mostly attributed to operating the MBC process under semi-lean conditions (Sec. 4.3).

The predicted hydrocarbon recovery of over 80% with the flash gas is in agreement with the pilot-plant results (Fig. 6). Though the corresponding LHV below 30 MJ kg^{-1} indicates a much higher CO_2 concentration in the flash gas compared to the pilot plant, which results from the higher CO_2 content in the gas feed and consequently a richer amine ($0.59 \text{ mol mol}^{-1}$). A scenario analysis reveals that the LHV could be raised to 37 MJ kg^{-1} upon increasing the flash

drum pressure to 1500 kPa, but this would then lower the hydrocarbon recovery to below 70%. The variation range in the recovered hydrocarbon flow rate ($0.98\text{--}1.10\text{ ton h}^{-1}$) is on a par with the $\pm 5\%$ uncertainty imposed on the Henry constant of the light hydrocarbons. A quick estimate of the corresponding annual cost savings is in the range of US\$543k–626k, assuming 8,000 operating hours per year and an energy cost of US\$0.24 MJ⁻¹ [49]. In turn, this estimate could feed into an economic assessment to decide between sweetening the flash gas and using it in a gas turbine, recompressing and returning the flash gas to the MBC gas inlet, or simply disposing of the flash gas by flaring.

By and large, the scaled-up semi-lean MBC process shows a promising intensification potential compared to conventional amine-based processes in order to meet sales gas specification, via: (i) reducing the physical volume of the absorption section and substituting the stripper column by a flash drum; and (ii) reducing the reboiler energy per amount of CO₂ removed and thus the overall process duty. The ability to recover the hydrocarbons dissolved in the enriched amine could also contribute to generating extra energy or revenue for the gas sweetening plant.

6. Conclusions

This paper has presented a model-based assessment of a natural gas sweetening process combining a high-pressure MBC with the solvent regeneration. The plant-wide model builds upon the MBC model developed in the companion paper [31] and is capable of quantitative predictions of a broad set of KPIs, including the CO₂ and hydrocarbon absorption by the amine solvent in the MBC, the solvent evaporative losses across the process, the recovery of dissolved hydrocarbons from the enriched amine, and the process duty and its breakdown between units. Its predictive capability has been tested against experimental data from a pilot plant in Malaysia for a wide range of CO₂ loadings in the amine solvent, showing an excellent agreement in terms of CO₂ outlet purity and energy consumption.

A detailed model-based investigation has compared two configurations of the amine regeneration section of the plant, whereby the amine solvent is either fully regenerated using a conventional stripper column leading to lean operation, or partially regenerated in a low-pressure flash drum resulting in semi-lean operation. Only the former can meet LNG specification and achieve deep CO₂ removal to ppm levels, but semi-lean operation was shown to be suitable for bulk CO₂ removal in order to meet sales gas specification. In particular, it was found that the semi-lean process configuration can reduce the overall energy consumption significantly and does not increase the solvent evaporative losses in either the adsorption or regeneration section of the plant. A possible drawback of the semi-lean mode of operation is the higher CO₂ content of the flash gas, which reduces its LHV and could prevent its direct use in a gas turbine.

In the final part of the paper, the scale-up of a commercial semi-lean MBC process has been conducted for sweetening of an industrial natural gas stream with 24 mol% CO₂ down to 6.5 mol%. This case study provides compelling evidence of the large intensification potential of semi-lean MBC operations compared to conventional amine-based processes. A key benefit, besides the smaller volume footprint of both the absorption and stripping sections, is the reduction in energy consumption for the amine regeneration. This reduction is enabled by operating the MBC with a semi-lean amine and at a lower L/G ratio than conventional packed columns, thereby highlighting the need to assess NG sweetening in a plant-wide manner. A simple economic assessment has also quantified the extra income expected to be generated from recovering the dissolved hydrocarbons in the amine solvent.

Future work will consider the application of systematic model-based optimisation techniques to further improve the design and operation of commercial MBC modules and processes. It will also be interesting to investigate the performance and intensification potential of processes that use the MBC technology both for the CO₂ absorption and desorption.

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Nomenclature

Acronyms

HFM	hollow-fiber membrane	MMSCFD	million standard cubic feet per day
KPI	key performance indicator	NG	natural gas
LHV	lower heating value	PTFE	polytetrafluoroethylene
MBC	membrane contactor	PZ	piperazine
MDEA	methyldiethanolamine	Sm ³	standard cubic meter (at 15 °C, 1 atm)
MFC	mass-flow controller		

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