Impact of N-Methyl-2-Pyrrolidone in Monoethanolamine Solution to the CO₂ Absorption in Packed Column: Analysis via Mathematical Modeling

L.S. TAN*, A.M. SHARIFF, W.H. TAY, K.K LAU, T. TSUJI & N.A.H. HAIRUL

ABSTRACT
This work investigates the reason behind the change of CO₂ absorption behaviour exhibited by monoethanolamine (MEA) solution via mathematical modeling analysis when physical absorbent, i.e. n-methyl-2-pyrrolidone (NMP), was added into the solution. The mathematical modeling included the heat model using time resolved numerical method. Based on the results, it was found that lower CO₂ removal performance with the addition of NMP into MEA solution at pressure of 0.1 MPa was mainly due to the lower temperature rise along the column, which resulted in lower reaction rate. However, at 3 and 5 MPa pressure conditions, the high physical absorption capability contributed by the presence of NMP in MEA hybrid solution enhanced the CO₂ absorption performance of MEA hybrid solution significantly. As such, temperature rise of solution was identified as the dominating factor affecting the performance of the hybrid solvent. The reaction rate of MEA was not affected by the addition of physical solvent. This finding shed crucial insight on the behaviour MEA-NMP hybrid solution which can be applied during scale-up of the process.

Keywords: CO₂ absorption; elevated pressure; hybrid solvent; packed column; physical absorbent

INTRODUCTION
Natural gas has become attractive in recent years as fuel of choice in power generation plants due to the lesser degree of pollution it produces compared to that from the combustion of oil or coal (Dong et al. 2017; Peters 2017). While renewable energy is the ultimate long term goal for sustainable living, natural gas could complement renewable energy as a clean energy source (Bailey & Feron 2005). However, natural gas reserves with low carbon dioxide (CO₂) content are fast reducing with the continuous extraction of the fossil fuel. Hence, there could be a need to consider the natural gas reservoir with high CO₂ content to sustain the worldwide power demand.

Many processes can be used for natural gas purification from carbon dioxide (CO₂) which include chemical absorption (Aouini et al. 2014; Haroun & Raynal 2016), physical absorption (Kohl & Nielsen 1997), adsorption process (Licciulli et al. 2017; Neishabori et al. 2017), membrane separation (Jusoh et al. 2016), gas hydrate formation (Dabrowski et al. 2009) and cryogenic
fractionation (Song et al. 2017). Out of the various processes available, chemical absorption system is the widely used technology for CO₂ removal.

Primary amine i.e. monoethanolamine (MEA) is a popular and effective solvent for capturing CO₂ due to its high reactivity with CO₂ and low solvent cost (Aouini et al. 2014; Sreedhar et al. 2017). However, the maximum CO₂ loading capacity for MEA is limited by its stoichiometry to 0.5 mol of CO₂/mol of amine (Dawodu & Meisen 1994).

The potential of n-methyl-2-pyrrolidone (NMP) to enhance the performance of MEA was studied by several researchers (Leites 1998; Tan et al. 2015; Vaidya & Mahajani 2005; Yuan & Rochelle 2018). At low CO₂ partial pressure range of 5 kPa or lesser (Vaidya & Mahajani 2005; Yuan & Hu 2018), it was observed that the solubility and the absorption rate of CO₂ was enhanced with the addition of NMP. However, in our previous work (Tan et al. 2015), the addition of NMP enhanced the CO₂ removal from natural gas in packed column at high pressure conditions. At lower pressure of 0.1 and 1 MPa, the CO₂ removal performance was lower when NMP was added into MEA aqueous solution. Huang et al. (2015) who studied the CO₂ solubility in MEA+diglyme, a type of aprotic polar organic solvent, also found that the CO₂ solubility in the physical-chemical hybrid mixture of absorbent was lower compared to MEA aqueous solution at low pressure condition. However, when the pressure exceeded 1 MPa, the CO₂ solubility was higher in MEA+diglyme than the solubility in MEA aqueous solution.

Vaidya and Mahajani (2005) deduced that chemical reaction between CO₂ and NMP could possibly take place on top of physical absorption. However, Huang et al. (2015) deduced that organic solvent was not able to ionize MEA as good as water, hence, limiting the ability of MEA to absorb CO₂ (Huang et al. 2015). However, at high pressure conditions, as the chemical absorption of CO₂ in MEA was getting saturated, the increase of CO₂ absorption with the increase of pressure was mainly due to complementary removal from the physical absorption. Hence, NMP, being aprotic polar organic solvent similar as diglyme, could possibly exhibited similar solubility behaviour too.

Zhang et al. (2018), through their recent ab initio calculations work, indicated that non-aqueous solvents could reduce the energy required during CO₂ desorption process from MEA solution. Hence, hybrid solution is a promising solvent to reduce the regeneration energy consumption in CO₂ capture using MEA based solution. Rate-based and computational fluid dynamic (CFD) model were applied on simulating CO₂ capture via chemical absorption (Asendrych & Niegodajew 2017; Majid 2017). However, modeling of hybrid chemical-physical absorption process is scarcely available in literature thus far, hence, there is limited insight on the process. Furthermore, the reason for the lower CO₂ removal performance for MEA-NMP hybrid solution at low operating pressure condition is still elusive. This is partly because the kinetics of CO₂ absorption using hybrid amines-physical organic solvents, in semi-aqueous or non-aqueous form, are still generally unknown (Descamps et al. 2008).

This work aims to study the reason behind the CO₂ absorption behaviour exhibited by MEA-NMP hybrid solution via time transient mathematical modeling with the inclusion of the physical and chemical properties, hydrodynamic parameters as well as the heat model. The chosen composition for the MEA hybrid solution was 20 MEA + 40 NMP + 40 wt. % water. Based on our previous experimental work (Tan et al. 2015), the CO₂ removal performance by the MEA hybrid solution was observed to inconsistent and it appeared to change based on the operating pressure of the absorption system. As such, understanding the contributing factors to such CO₂ removal behaviour could provide important insight on MEA-NMP hybrid solution.

We extended the application of SRP II model (Rocha et al. 1996) on the modeling of CO₂ absorption by the MEA hybrid solution. This model was previously applied to model rich CO₂ absorption by MEA aqueous solution in packed column (Tan et al. 2016) and had satisfactorily represented the mass transfer behavior at elevated pressure conditions. Some preliminary works of non-invasive scanning of NMP bubbled with CO₂ was also conducted in order to confirm the chemical reactivity of NMP with CO₂ before refining the mathematical model for the MEA hybrid solution. Physical properties measurement of the hybrid solution was also conducted in order to obtain further input for the mathematical model. The model for the CO₂ absorption performance was validated with experimental results before deciphering its details as part of the investigation work. The impact of NMP, which was the physical absorbent added into MEA solution, to the absorption of rich CO₂ content from natural gas in counter-current packed column could be investigated through the details from the validated model.

**MATERIALS AND METHODS**

**MATERIALS**

The chemicals used, i.e. MEA with 99% purity and NMP with 99% purity, were procured from Acros Organics (USA) and used without further purification. Double distilled water was used to prepare the solution for this work. CO₂ gas with 99.9% purity (Air Product, Malaysia) and natural gas with CH₄ content of 97 and 2% of CO₂ (PETRONAS Dagangan Bhd, Malaysia) were mixed according to the desired proportion for the experimental validation work.
NON-INVASIVE SCANNING OF NMP BUBBLED WITH CO₂

Raman spectroscopy was conducted on NMP solvent which had been bubbled with CO₂ for 9 h to verify deduction by Vaidya and Mahajani (2005) whether there was chemical reaction between CO₂ and NMP. This information is important because it would affect the mathematical model for the process. The scanning was done using Thermo Scientific DXR SmartRaman system with 785 nm high power laser at up to 150 mW. The NIR laser of 785 nm was used as it is a robust excitation source which is usually used to quench fluorescence background from most organic compounds (Wong et al. 2016).

PHYSICAL PROPERTIES MEASUREMENT

The density of the MEA hybrid solution at different temperatures from 303.15 to 333.15 K was measured using DMA 4500 M density meter from Anton Paar. The equipment can measure density with accuracy of ±0.00005 g.cm⁻³. The density meter consists of an oscillating U-tube made of borosilicate glass as a measuring cell in a thermostatic jacket. It was equipped with a built-in platinum resistance thermometer which could measure the temperature with an accuracy of ±0.03 °C.

Meanwhile, the viscosity of MEA hybrid solution at similar temperature range was measured using viscometer Lovis 2000M from Anton Paar. The viscosity measurement accuracy was up to ±0.5% and temperature accuracy was of ±0.02 °C. The capillary used for this study was of 1.59 mm size.

Surface tension was measured using tensiometer OCA 15 EC from Dataphysics with accuracy of ±0.1° for contact angles. The pendant drop method was used to measure the surface tension in which a drop was created in a thermostatic chamber. A camera installed in the equipment would identify and record the shape as well as contact angle properties of the drop inside the cell.

MODELING OF RICH CO₂ ABSORPTION FOR MEA HYBRID SOLUTION

The mathematical model for the absorption of CO₂ in the hybrid MEA solution was refined from the integrated mathematical modeling which was previously developed for prediction of rich CO₂ absorption in MEA aqueous solution (Tan et al. 2016). The process was modeled using Matlab 2013a based on the mass conservation concept (Rocha et al. 1996). The effective surface area, \( a_e \), applied in this study, consisted of Weber number for liquid, \( We_L \), and Reynolds number, \( Re_L \), as part of its calculation (Shi & Mersmann 1985).

\[
a_e = \frac{F_{SE}}{Re_L^{0.5} \alpha e^{0.6}(1 - 0.93 \cos \theta)(\sin \theta)^{0.3}}
\]  

(1)

where \( a_e \) is the specific surface area for the packing (m²/m³); \( F_{SE} \) is the factor for surface enhancement; \( F_r \) is the Froude number for liquid; \( S \) is the side dimension of corrugation of packing (m); \( \epsilon \) is the void fraction of packing; \( \gamma \) is the contact angle and \( \theta \) is the angle for corrugation channel. \( We_L \) and \( Re_L \) were calculated based on the density, surface tension, and viscosity of the liquid. Hence, this would enable the model to capture the variation of physical properties of the hybrid MEA solution from MEA aqueous solution accordingly. Specifically, the impact of variation of density, viscosity, and surface tension of the MEA hybrid solution to the effective surface area would be captured by the model and this would result in better representation of the absorption of CO₂ in hybrid MEA process.

In this work, the mathematical modeling was further improved by implementing the heat model. The temperature rise along the column due to heat of reaction between the MEA aqueous solution and CO₂ was integrated in the time resolved numerical model to elucidate a more realistic process and with that, more accurate results. The system was assumed to be in adiabatic condition. The general energy conservation can be written in (2):

\[
\rho \left( \frac{du}{dt} + \nabla (uH) \right) = k \nabla^2 T + q
\]  

(2)

where \( H \) is the specific enthalpy of fluid; \( k \) is thermal conductivity; \( \rho \) is density; \( C_p \) is heat capacity; \( q \) is the heat generated from the absorption, which can be estimated as (3):

\[
q = \Delta H_{MEA} n_{CO_2, react}
\]  

(3)

where \( \Delta H_{MEA} \) is the enthalpy of reaction for the solution (J/mol); \( n_{CO_2, react} \) is the amount of reacted CO₂ in mol; is the amount of CO₂ in feed gas in mol; \( C_p, feed, gas \) is the specific heat capacity at constant pressure for the feed gas (J/mol.K); \( n_{MEA} \) is the mole of MEA in the solution (mol); and \( C_p, MEA \) is the specific heat capacity at constant pressure for the MEA aqueous solution (J/mol.K).

Under constant pressure, the specific enthalpy is represented as (4):

\[
dH = C_p dT
\]  

(4)

Based on (2), the thermal conservation for liquid phase can be represented as (5):

\[
\rho v C_{p,MEA} \left[ \frac{dT}{dt} + \frac{d(eT)}{dx} \right] = k \frac{dT}{dx} T_L + k_{kr} (T_0 - T_L) + \Delta H_{REA,CO_2, react}
\]  

(5)

where \( T_L \) is the gas temperature; and \( T_0 \) is the solvent temperature. The heat of absorption is generated under liquid phase, thus transferred to gas phase through the thermal conductivity. Therefore, the thermal conservation
for gas phase is represented as (6).

\[ \rho C_p \text{feed gas} \left[ \frac{dT_p}{dt} + \frac{dT_v}{dz} \right] = k_v \frac{d^2}{dz^2} T_v + k(T_i - T_p) \] (6)

Therefore, the temperature rise along the column was estimated after the steady stage of the simulation.

The property value for MEA hybrid solution was included accordingly in the mathematical model in order to provide input necessary for the modelling of MEA hybrid solution. The correlation for physical properties, namely density, viscosity, and surface tension was generated from experimental measurement as input to the model, while the physical solubility (based on Henry’s law constant) and enthalpy of the MEA hybrid solvent were estimated based on literature data available for MEA aqueous solution and NMP (McCann et al. 2008; Murrieta-Guevara et al. 1992, 1988; Penttilä et al. 2011; Rajasingam et al. 2004).

**PACKED COLUMN EXPERIMENTAL SET UP AND PROCEDURE**

Experimental work on \( \text{CO}_2 \) absorption performance of the MEA hybrid solution was conducted in order to obtain \( \text{CO}_2 \) concentration profile for model validation. The \( \text{CO}_2 \) absorption experiment at varying pressure, i.e. 0.1, 1, 3, and 5 MPa, was conducted in a counter-current packed column set-up with an inner diameter (ID) of 0.145 m and structured packing of FLEXIPAC 1Y from Koch-Glitsch, USA. The height of the column was 1.64 m. The inlet \( \text{CO}_2 \) concentration was fixed at 50% of the gas mixture. Total gas flow rate was set at 100 standard litre per minute (slpm) while the liquid flow rate flowing into the system was set at 1 L per minute. The \( \text{CO}_2 \) concentration data was collected when the system was at steady state condition. Details on the set-up and procedure was explained in our previous work (Tan et al. 2015).

**RESULTS AND DISCUSSION**

**VERIFICATION OF REACTION BETWEEN \( \text{CO}_2 \) AND NMP**

The Raman spectroscopy results for fresh NMP and NMP bubbled with \( \text{CO}_2 \) for 9 h is shown in Figure 1. The red line represents Raman profile for fresh NMP while the green line represents Raman profile for \( \text{CO}_2 \)-bubbled NMP. A cross-check of the Raman profile for the \( \text{CO}_2 \) bubbled NMP solvent with the HR Aldrich Raman database available in the software indicated more than 95% of similarity with NMP profile in the database as shown in Figure 1(b). As such, it was confirmed that only physical solubility occurred in NMP. This confirmation is important as necessary amendment need to be done at the mathematical model should there be chemical reaction between NMP and \( \text{CO}_2 \).

![Figure 1. (a) Raman spectroscopy results for fresh NMP (red line) and NMP bubbled with \( \text{CO}_2 \) for 9 h (green line), (b) Cross-check of Raman profile for \( \text{CO}_2 \) bubbled NMP solvent with database](image-url)
PHYSICAL PROPERTIES ANALYSIS

Density and viscosity of MEA hybrid solution measurement in this study is validated with measurement by Blanco et al. (2012). The authors did measurement at slightly lower temperature range compared to this work, hence, provided good comparison platform for several similar temperature points. Meanwhile, the surface tension measurement in this work was validated by comparing measurement results with data from literature for water, pure NMP and 20 wt. % MEA aqueous solution (Han et al. 2012; Kahl et al. 2003) since surface tension data for the hybrid solution is not available in open literature thus far. The validity of the measured data was evaluated based on the percent average absolute deviation (% AAD) between experimentally measured values with literature values. The calculation was based on (7):

\[
\%\text{ AAD} = \frac{1}{n} \sum |\frac{X_{\text{exp}} - X_{\text{lit}}}{X_{\text{lit}}}| \times 100
\]  

TABLE 1. The physical properties of MEA hybrid solution (20 wt. % MEA + 40 wt. % NMP + 40 wt. % water) measured in this work

| Temperature (K) | Density (g.cm\(^{-3}\)) | Viscosity (mPa.s) | Surface tension (mN.m\(^{-1}\)) |
|----------------|--------------------------|-------------------|-------------------------------|
| 303.15         | 1.0325                   | 4.365             | 49.75                         |
| 313.15         | 1.0244                   | 3.050             | 48.60                         |
| 323.15         | 1.0162                   | 2.244             | 47.76                         |
| 333.15         | 1.0077                   | 1.707             | 47.01                         |

Based on the trend of data, the best fit for density and surface tension was linear function while the best fit for viscosity was exponential function. The following equations were used to fit the physical properties data.

**Density:**

\[
\rho = A_0 + A_1 T
\]  

**Viscosity:**

\[
\eta = A_0 \exp (A_1 T)
\]  

**Surface tension:**

\[
\sigma = A_0 + A_1 T
\]

where \( \rho \) is density (g.cm\(^{-3}\)); \( \sigma \) is the viscosity (mPa.s); \( \eta \) represents surface tension (mN.m\(^{-1}\)); \( A_0 \) and \( A_1 \) are the fitting parameters while \( T \) is the temperature (K).

The fitting equation parameters are listed in Table 2 with standard deviations (SD) calculated using (11).

\[
\text{SD} = \left[ \frac{\sum_{i=1}^{n} (X_{\text{exp}} - X_{\text{calc}})^2}{n} \right]^{0.5}
\]  

where \( n \) is the number of experimental data points; \( X_{\text{exp}} \) and \( X_{\text{calc}} \) are experimental and calculated values, respectively. Based on data in Table 2, the coefficient of determination, \( R^2 \), of the fitted data was approximately 0.99 for all three properties. This indicated that the predicted data are in good relation with the measured data. Therefore, the fitted equations can be used for prediction of physical properties for modelling MEA hybrid solution.

TABLE 2. Fitting parameters and standard deviation for physical properties of MEA hybrid solution

| Properties          | \( R^2 \)   | SD             |
|---------------------|-------------|----------------|
| Density             | 1.283       | -0.00083       | 0.9999         | 1.16 \times 10^8 |
| Viscosity           | 78390       | -0.0323        | 0.9968         | 5.08 \times 10^3 |
| Surface tension     | 77.1        | -0.0906        | 0.9898         | 1.07 \times 10^2 |
PREDICTION AND ANALYSIS OF RICH CO\textsubscript{2} ABSORPTION FOR MEA HYBRID SOLUTION

Figure 2 shows the experimental and predicted profile of the CO\textsubscript{2} concentration along the absorption column at pressure condition of 0.1, 1, 3, and 5 MPa. The MEA hybrid solution model under-predicted the CO\textsubscript{2} mole fraction in the middle of the column for pressure condition of 0.1 MPa but it managed to predict the CO\textsubscript{2} mole fraction at the top of the column quite well. Generally, the model was able to provide quite decent prediction of CO\textsubscript{2} mole fraction profile which exhibited the change of CO\textsubscript{2} absorption behaviour for MEA hybrid solution when the pressure of the system progressed from low pressure to high pressure condition.

![Graphs showing predicted and measured CO\textsubscript{2} mole fraction for absorption using MEA hybrid solution at different pressures.](image)

FIGURE 2. Profile of the predicted and measured CO\textsubscript{2} mole fraction for absorption using MEA hybrid solution at pressure condition of (a) 0.1 MPa, (b) 1 MPa, (c) 3 MPa and (d) 5 MPa

The predicted result also manifested similar behaviour of MEA hybrid solution as per our previous experimental results (Tan et al. 2015) whereby MEA hybrid solution showed lower CO\textsubscript{2} removal performance at low pressure condition i.e. 0.1 MPa compared to MEA aqueous solution. Since the profile of high concentration CO\textsubscript{2} removal using MEA aqueous solution had been modelled (Tan et al. 2016), the comparison of the predicted CO\textsubscript{2} concentration along the column between the aqueous and hybrid solution is presented in Figure 3. The model developed in this work successfully captured the change CO\textsubscript{2} absorption performance of MEA-NMP hybrid solution in comparison to MEA aqueous solution, i.e. from inferior when at low pressure of 0.1 MPa to better performance when at high pressure of 3.0 and 5.0 MPa. This indicated that a change of physical properties as well as the Henry’s law constant, which represented the physical solubility of CO\textsubscript{2} into the solution, indeed could alter the performance of CO\textsubscript{2} absorption.
It was previously deduced that the reaction process could have been partially impeded with the reduced ability of NMP to ionize MEA as good as water (Huang et al. 2015). However, the mathematical model developed in this study for MEA hybrid solution utilized similar correlation for reaction rate constant, $k_2$, used for MEA aqueous solution. The model was mainly altered at the liquid’s physical properties, physical solubility (Henry’s law constant), enthalpy of CO$_2$ solution into the solvent and heat capacity of the MEA solution.

The temperature rise along the column affected the physical properties of the MEA solutions during the CO$_2$ absorption process. The variation of density for the MEA hybrid solution compared to MEA aqueous solution was calculated to be only about 2%. As such, it was not expected to affect the model much. However, the surface tension of the MEA hybrid solution was approximately 20% lower than surface tension of MEA aqueous solution while the viscosity of MEA hybrid solution was approximately double than that of MEA aqueous solution. These changes of liquid behaviour were captured by the correlations for effective packing area, $a_e$, and it was observed to be vital to the model developed. All these physical property changes resulted in approximately 20% of increase in calculated for the MEA hybrid solution model compared to MEA aqueous solution as shown in Figure 4.

**FIGURE 3.** Comparison of the predicted CO$_2$ concentration along the column between MEA aqueous solution and MEA hybrid solution

**FIGURE 4.** Estimation of the effective packing area, $a_e$, for the MEA solutions
Nevertheless, despite the higher $a$, for MEA hybrid solution in comparison to MEA aqueous solution, the MEA hybrid solution exhibited lower CO$_2$ removal efficiency at low pressure condition. Furthermore, for the estimated Henry law’s constant for MEA hybrid solution, the generated value that was approximately 30% lower than Henry law’s constant for MEA aqueous solution. Lower Henry law’s constant would translate into high overall mass transfer coefficient, $K_G$, which was supposed to render higher CO$_2$ removal efficiency.

Further analysis on the modeling results indicated that there was indeed a reduction in reaction rate constant, $k_2$, for MEA hybrid solvent as shown in Figure 5. This was mainly due to lower temperature rise along the column as indicated in Figure 6. Lower temperature rise was obtained for the MEA hybrid solution model as the enthalpy of solution of CO$_2$ in the MEA hybrid solution was approximately 30% lower than the enthalpy of solution of CO$_2$ in MEA aqueous solution (Arcis et al. 2011; Murrieta-Guevara et al. 1988). On top of that, the heat of capacity of the MEA hybrid solution was higher than MEA aqueous solution (Mundhwa et al. 2009; Weiland et al. 1997).

![FIGURE 5. Comparison of second order reaction constant, $k_2$, profile for MEA aqueous and hybrid solutions at for operating pressure of (a) 0.1 MPa, (b) 1 MPa, (c) 3 MPa and (d) 5 MPa](image)

It appeared that at low pressure conditions, the lower reaction rate resulted from the lower temperature rise along the column could not be compensated even with higher in the system and lower Henry law’s constant of the solution. Hence, lower CO$_2$ removal efficiency was obtained when the rich CO$_2$ absorption process was conducted using MEA hybrid solution compared to MEA aqueous solution.

However, at high pressure condition of 3 and 5 MPa, MEA hybrid solution performance overtook that of MEA aqueous solution mainly because the physical absorption capability of NMP was much greater than water at high pressure condition (Huang et al. 2015). Organic physical solvents usually prevails over chemical solvent at high pressure conditions (Chakma 1999) and similar behaviour was also observed for this combination of MEA-NMP-water hybrid solution.
The mathematical model was able to predict CO₂ mole fraction profile reasonably close to the measured experimental data at varied pressure conditions. The model indicated lower CO₂ removal performance by MEA hybrid solution compared to MEA aqueous solution at low pressure condition. This was mainly due to the lower temperature rise along the column, which resulted in lower reaction rate. However, at high pressure conditions, the high physical absorption capability contributed by the presence of NMP in MEA hybrid solution enhanced the CO₂ absorption performance of MEA hybrid solution significantly. As such, temperature rise of solution was identified as the dominating factor affecting the performance of the hybrid solvent. The reaction rate constant of MEA was not affected by the addition of physical solvent. This finding shed crucial insight on the behaviour MEA-NMP hybrid solution which can be applied during scale-up of the process operating in elevated pressure conditions.

ACKNOWLEDGEMENTS

Financial support by UTM Collaborative Research Grant (PY/2019/03294) and facility support by CO₂ Research Centre (CO2Res), Universiti Teknologi PETRONAS are gratefully acknowledged.
Descamps, C., Boullou, C. & Kanniche, M. 2008. Efficiency of an integrated gasification combined cycle (IGCC) power plant including CO₂ removal. *Energy* 33(6): 874-881.

Dong, X., Pi, G., Ma, Z. & Dong, C. 2017. The reform of the natural gas industry in the PR of China. *Renewable and Sustainable Energy Reviews* 73: 582-593.

Han, J., Jin, J., Eimer, D.A. & Melaaen, M.C. 2012. Density of water (1) + monoethanolamine (2) + CO₂ (3) from (298.15 to 413.15) K and surface tension of water (1) + monoethanolamine (2) from (303.15 to 333.15) K. *Journal of Chemical & Engineering Data* 57(4): 1095-1103.

Haroun, Y. & Raynal, L. 2016. Use of computational fluid dynamics for absorption packed column design. *Oil Gas Sci. Technol. - Rev. IFP Energies Nouvelles* 71(3): 43.

Huang, W., Mi, Y., Li, Y. & Zheng, D. 2015. An aprotic polar solvent, diglyme, combined with monoethanolamine to form CO₂ capture material: Solubility measurement, model correlation, and effect evaluation. *Industrial & Engineering Chemistry Research* 54(13): 3430-3437.

Jusoh, N., Lau, K.K., Yeong, Y.F. & Shariff, A.M. 2016. Bulk CO₂/CH₄ separation for offshore operating conditions using membrane process. *Sains Malaysia* 45(11): 1707-1714.

Kahl, H., Wardetzky, T. & Winkelmann, J. 2003. Surface tension of pure liquids and binary liquid mixtures. *Journal of Chemical & Engineering Data* 48(3): 580-586.

Koh, A.L. & Nielsen, R.B. 1997. *Gas Purification*. 5th ed. Texas: Gulf Publishing Company.

Leites, I.L. 1998. Thermodynamics of CO₂ solubility in mixtures monoethanolamine with organic solvents and water and commercial experience of energy saving gas purification technology. *Energy Conversion and Management* 39(16-18): 1665-1674.

Licciuli, A., Maurizio, N., Stefania, D.S., Carlo, T. & Sanosh, K.P. 2017. CO₂ capture on amine impregnated mesoporous alumina-silica mixed oxide spheres. *Fuel Processing Technology* 166: 202-208.

Majid, S. 2017. Rate based modeling of CO₂ absorption into piperezine- activated aqueous n-methylidethanolamine solution: Kinetic and mass transfer analysis. *International Journal of Chemical Kinetics* 49(9): 690-708.

McCann, N., Marcel, M. & Moetaz, A. 2008. Simulation of enthalpy and capacity of CO₂ absorption by aqueous amine systems. *Industrial & Engineering Chemistry Research* 47(6): 2002-2009.

Mundhwa, M., Elmahmudi, S., Maham, Y. & Henni, A. 2009. Molar heat capacity of aqueous sulfolane, 4-formylmorpholine, 1-methyl-2-pyrrolidinone, and triethyleneglycol dimethyl ether solutions from (303.15 to 353.15) K. *Journal of Chemical & Engineering Data* 54(10): 2895-2901.

Florentino, M-G., Esther, R-L. & Arturo, T. 1992. Solubility of carbon dioxide in binary mixtures of N-methylpyrrolidone with alkanolamines. *Journal of Chemical & Engineering Data* 37(1): 4-7.

Florentino, M-G., Ascencio, R-M. & Arturo, T. 1988. Solubilities of carbon dioxide and hydrogen sulfide in propylene carbonate, N-methylpyrrolidone and sulfolane. *Fluid Phase Equilibria* 44(1): 105-115.

Neishabiri, S., Rasoul, F.R. & Sahram, S. 2017. Adsorption of carbon dioxide, nitrogen and methane on modified titanosilicate type molecular sieves. *Journal of Natural Gas Science and Engineering* 46(Supplement C): 730-737.

Penttilä, A., Claudia, D., Petri, U. & Ville, A. 2011. The Henry’s law constant of NO₂ and CO₂ in aqueous binary and ternary amine solutions (MEA, DEA, DIPA, MDEA, and AMP). *Fluid Phase Equilibria* 311: 59-66.

Peters, J.C. 2017. Natural gas and spillover from the US clean power plan into the Paris agreement. *Energy Policy* 106: 41-47.

Rajasingam, R., Liwan, L.O., Tuan, P. & Frank, P.L. 2004. Solubility of carbon dioxide in dimethylsulfoxide and N-methyl-2-pyrrolidone at elevated pressure. *The Journal of Supercritical Fluids* 31(3): 227-234.

Rocha, J.A., Jose, L.B. & James, R.F. 1996. Distillation columns containing structured packings: A comprehensive model for their performance. 2. mass-transfer model. *Industrial & Engineering Chemistry Research* 35(5): 1660-1667.

Shi, M.G. & Mersmann, A. 1985. Effective surface area in packed column. *German Chemical Engineering* 8: 87-96.

Song, C., Liu, Q., Ji, N., Deng, S., Zhao, J. & Kitamura, Y. 2017. Advanced cryogenic CO₂ capture process based on stirling coolers by heat integration. *Applied Thermal Engineering* 114: 887-895.

Sreedhar, I., Nahar, T., Venugopal, A. & Srinivas, B. 2017. Carbon capture by absorption - path covered and ahead. *Renewable and Sustainable Energy Reviews* 76: 1080-1107.

Tan, L.S., Shariff, A.M., Tay, W.H., Lau, K.K. & Halim, H.N.A. 2016. Integrated mathematical modeling for prediction of rich CO₂ absorption in structured packed column at elevated pressure conditions. *Journal of Natural Gas Science and Engineering* 28: 737-745.

Tan, L.S., Shariff, A.M., Lau, K.K. & Bustam M.A. 2015. Impact of high pressure on high concentration carbon dioxide capture from natural gas by monoethanolamine/n-methyl-2-pyrrolidone solvent in absorption packed column. *International Journal of Greenhouse Gas Control* 34: 25-30.

Vaidya, P.D. & Mahajani, V.V. 2005. Kinetics of the reaction of CO₂ with aqueous formulated solution containing monoethanolamine, n-methyl-2-pyrrolidone, and diethylene glycol. *Industrial & Engineering Chemistry Research* 44(6): 1868-1873.

Weiland, R.H., Dingman, J.C., Cronin, D.B. & Browning, G.J. 1998. Density and viscosity of some partially carbonated aqueous alkanolamine solutions and their blends. *Journal of Chemical & Engineering Data* 43(3): 378-382.

Wong, M.K., Bustam, M.A. & Shariff, A.M. 2016. In situ measurement of physical solubility of carbon dioxide in loaded aqueous monoethanolamine by Raman spectroscopy. *Journal of Natural Gas Science and Engineering* 36(Part A): 305-313.

Yuan, Y. & Rochelle, G.T. 2018. CO₂ absorption rate in semi-aqueous monoethanolamine. *Chemical Engineering Science* 182: 56-66.

Zhang, T., Yu, Y. & Zhang, Z. 2018. Effects of non-aqueous solvents on CO₂ absorption in monoethanolamine: *ab initio* calculations. *Molecular Simulation* 44(10): 815-825.
