Effect of solvent concentration on the energy demand of an absorption-based natural gas sweetening plant

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Abstract

The removal of CO_2 from natural gas will enhance its energy content, decrease the volume to be transported and –if coupled with storage technology- it will also contribute to the control of CO_2 emissions. Amine-based chemical absorption is the most advanced CO_2 capture system. Yet, high energy requirement is a major hinder to its wide deployment. Among the possible routes of improvement is the use of novel amines that can achieve the trade-off between robustness and low regeneration energy.

In this paper, we have studied the use of MDEA/DEA as solvent for the capture of CO_2 from natural gas. The presence of BTEX (Benzene, Toluene, Ethyl Benzene and Xylene) in the raw natural gas was taken into account. AspenHysys v9 was used to simulate the chemical absorption system. The impact of solvent composition on key process variables, the required flow rate to achieve transport specification, required reboiler duty, pumping energy, BTEX incineration energy and amine losses, were studied. The optimal operating point corresponding to the lowest energy requirement was identified and the separate contribution of each process parameter was estimated. The study showed that the optimal amine mass fraction is influenced by the presence of BTEX and that it shifts from 0.5 if BTEX are not present in the sour feed gas to 0.45 if their incineration is taken into account.

Keywords: Natural gas, CO_2 capture, BTEX, MDEA/DEA,

1. Introduction

Due to the increasing world population and rapidly growing emerging economies, the global primary energy use is expected to increase by 1.5 % per annum on average between 2012 and 2035 [1]. Nowadays, fossil fuels account for 83% of global energy consumption. This tendency is forecasted to continue. Even after two decades, fossils are foreseen to contribute by 80% in the world energy mix by 2030. Natural gas, more specifically, has low CO_2 emissions per kilowatt of energy produced. It has been so far an economically and environmentally valuable "bridge fuel". This global market is expected to grow by 60% until 2035 [2, 3].

In order to satisfy such rapidly growing appetite for fossil fuels, natural gas (NG) industry will have to face a lot of challenges. Oil and gas companies, which have always preferably produced oil and gas from the easiest reservoirs, will inevitably have to develop more complex sour hydrocarbon projects. About 26.9% of the world's natural gas reservoirs have CO_2 content higher than 10% [4].

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The presence of volatile contaminants such as Benzene, Toluene, E-Benzene and Xylene, which are present in unconventional reservoirs, may add an even more stringent constraint. Improving the efficiency of acid gas capture processes is therefore believed to play a decisive role in securing a sustainable natural gas supply.

CO_2 capture can be done through chemical absorption, membranes, cryogenic distillation, adsorption, pressure swing adsorption (PSA) [5]. Chemical absorption is the most advanced technique in the power sector [6] and is well established for acid gas removal in NG [5]. However, this process is still facing some serious drawbacks related mainly to the high capital expenditures and operational costs [7]. The first arises from the use of stainless steel equipment considering the corrosiveness of aqueous CO_2 as well as some of the species being carried in the process, whereas the operational costs are mainly induced by the high energy requirement of solvent regeneration [7].

Monoethanolamine (MEA) solutions, the most studied solvent for CO_2 capture is known for its fast absorption of CO_2. However, that solution can present corrosion issues and requires high amount of energy for its regeneration [8]. Other solvents with improved characteristics have emerged as potential substitutes of MEA; yet, each solvent has its own limitations: DEA (diethanolamine) and DIPA (diisopropylamine), for instance, are less corrosive and allow a higher loading but react with CO_2 at moderate rates. MDEA (methyldiethanolamine) demonstrates an insignificant degradation rate and a low regeneration energy but also a slow reaction with CO_2. The use of solvent blends is a practical solution to take benefit from the most suitable characteristics of each solvent and presents therefore an interesting route for improving the efficiency of the capture process [8, 9].

Many studies evaluated and compared the performances of the different solvents and solvent blends. For example, at laboratory scale, Kim et al. [10] compared the solubility and the heat of reaction of MDEA, TEA (triethanolamine), DEA and AMP (2-amino-2-methylpropanol). Gao et al. [11] investigated the absorption/regeneration of CO_2 in blends of MEA with tertiary amines, such as MDEA, used as regeneration promoters. Benamor et al. [12] focused on the MDEA/DEA solubility, while Adeosum et al. [8] studied the rate and capacity of several aqueous blends of MEA, DEA, MDEA, AMP and PZ.

The performances of amines at process scale have been studied extensively in the literature through modelling and simulation. Abkhiz et al. [8] studied the circulation rate, the sulfur recovery rate and the energy demand of a refinery gas sweetening using DEA, MDEA and their mixtures. Al-Lagtah et al. [14] used AspenHysys to optimize the operating conditions of MDEA in a natural gas sweetening with OPEX minimization as an objective function. Similarly, Nuchitprasittichai et al. [15] used AspenHysys to study the optimal MDEA/DEA concentration to reduce the OPEX of CO_2 capture from power plant. Léonard et al. [16] and Garcia et al. [17] used AspenPlus to investigate the effect of process conditions on the solvent degradation and on the performance of several capture pilots, respectively. BTEX are present in the NG and are known for their strong affinity to amine solutions. Consequently, they can be drifted along to the regeneration section where they might be flared to the atmosphere. Many papers were dedicated to investigating the solubility of these compounds in amine solutions [18]. Yet, only few papers tried to elucidate the impact of their presence on the optimal operating conditions of the process.

In this paper, the use of an MDEA/DEA blend as a CO_2 capture solvent in NG production was studied taking into account the presence of BTEX. The impact of solvent concentration on the reboiler energy, pumping energy and energy required for BTEX incineration were studied. Finally, the resulting energy cost of the process was estimated at several solvent concentrations and the optimal concentration was hence identified.

2. Methodology and modeling framework

An industrial acid gas removal unit was simulated using AspenHysys V9. The model is equilibrium based, the pressure drop in the columns as well as the tray efficiencies were estimated using the built-in tray sizing utility. Also, an additional incineration unit was simulated as an equilibrium reactor where the fuel gas is burnt so that the adiabatic flame temperature reaches 800°C, the auto dissociation temperature of BTEX.

In the simulated case, 5 MMSCM (million standard cubic meters) of natural gas enters the absorption tower at 80 bars and 55°C, and with an initial CO_2 content of 7%. The sweet gas leaves at 2% CO_2, whereas the bottom stream is sent to regeneration after being depressurized in order to lower its boiling point.
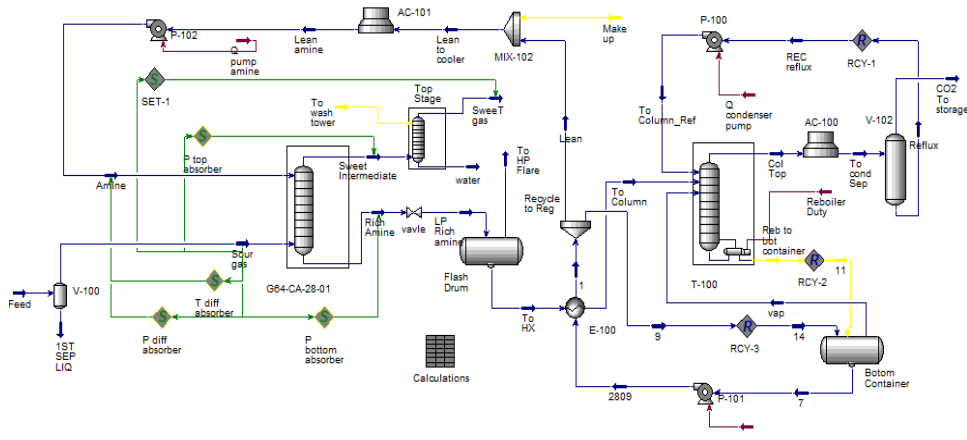
Figure 1 Flowsheet of the natural gas sweetening plant

The Lean/Rich exchanger is designed to recover a part of the regeneration energy to preheat the distillation feed, which enters the regeneration column at 100°C at a pressure of 190 kPa. AspenHysys provides several fluid packages for estimating thermodynamic properties of amine systems, namely the Kent & Eisenberg and the Li & Mather. The first is an empirical model whereas the latter is a rigorous one, the major distinction between the both lies in the way of handling liquid phase non-ideality [7]. Kent-Eisenberg model is a simple correlation which lumps all the non-idealities into certain selected equilibrium constants, namely amine protonation and carbamate formation. Although it was first developed for single amine solvents, this model is easily extended to amine mixtures. Despite its wide acceptance and popular use, the simplified treatment of phase non-ideality may reduce its credibility beyond the regression area [12]. However, the Li-Mather model is a rigorous one. The non-idealities of the liquid phase are taken into account through the activity coefficient, which is represented by the Pitzer correlation.

The thermodynamic package was selected by comparing the predictions of CO_2 output in the sweet gas to the measured value. We have found that the model of Li-Mather was able to predict the CO_2 content in the sweet stream with an error of 2.52% whereas the error of the model of Kent-Eisenberg was at 90%. The Li-Mather gives more accurate predictions for the MDEA/DEA blend, which is confirmed in literature [14, 15].

Firstly, the predictions of the simulation were found to be very close to averaged measurements over one day of operation of a CO_2 capture plant located in Algeria as shown in Table 1. The temperature profiles in both columns as well as the composition of the sweet gas were retrieved with a relative Error not exceeding 5%. The estimation of the liquid outlet from the absorption showed a relative deviation slightly above 5%, potentially due to the fluctuations caused by the constant change in liquid level in the flash drum.

Secondly, the validated model was used to investigate the effect of solvent composition on different process variables. The mass ratio between MDEA/DEA was kept constant at 48/2. The total amine mass fraction was varied between 0.2 and 0.5.

For an amine mass fraction ranging from 0.2 to 0.5, the amine circulation rate was adjusted so that the sweet gas CO_2 content meets the pipeline transport specification, which is 2% ±0.01%. At the regeneration section, the CO_2 loading of the lean amine was set at 0.01 and the bottom temperature was adjusted accordingly.

Thirdly, the incinerator was simulated as a conversion reactor. Air was provided in 10% excess and a full conversion was assumed. The light hydrocarbons absorbed by the amine solution and vented at the top of the regeneration unit were used as a first source for the incineration. A second source was provided to the reactor, and was adjusted so that the temperature inside the reactor reaches the BTEX auto-dissociation threshold: 800°C.

AspenHysys v9 was automated via Microsoft-Excel to simplify the data introduction and monitoring. After the convergence of each run, results were collected and used for further economic evaluation. Fuel gas price was estimated at 3$/MMBTU. In order to estimate the pumping energy, an 80% pumping efficiency and a 50% conversion efficiency from natural gas into electricity were assumed [19]. The energy cost included the reboiler energy, the incineration energy, the light hydrocarbon losses and the pumping energy.

Table 1 Comparison between model predictions and plant data

		Absorber/Regenerator			Sweet gas composition, Mole %			
		Sim.	plant	Relative Error%	Comp.	Sim.	plant	Relative Error%
T 3rd stage absorber	°C	59.18	58.2 ±0,8	1,59	CO_2	1.93	1.98	2.53
T 4th stage absorber	°C	60.16	60.5 ±1	0,66	Methane	82.2	85.69	4.05
T Bottom absorber	°C	78.23	79.9 ±1,5	2,15	Ethane	6.72	6.62	1.51
Liquid Flow absorber	m^3/h	305.2	288.5 ±20	5,82	Propane	2.27	2.23	1.68
T Top regenerator	°C	86.3	90.9 ±7	5,10				
T Bottom regenerator	°C	126.1	127.5 ±1	1,13				
Liquid Flow regenerator	m^3/h	760.1	755.2 ±3	0,64				

3. Results and discussions

The influence of solvent amine fraction on the required flow rate, reboiler energy, hydrocarbon losses, and incineration energy was studied through a sensitivity analysis performed with AspenHysys v9.
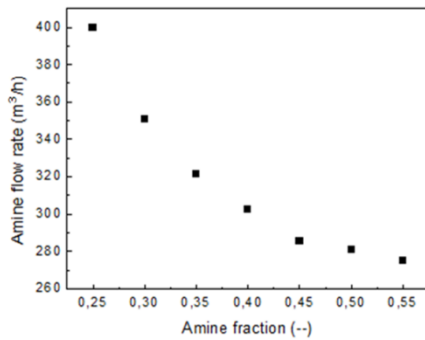

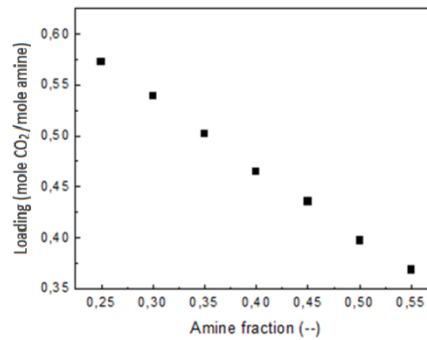Figure 2 Required solvent flowrate at different amine mass fraction

Figure 3 Rich amine loading as a function of lean amine mass fraction
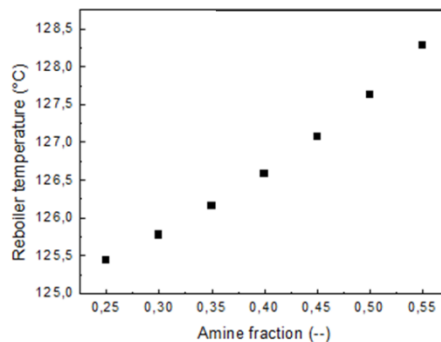

Figure 4 Reboiler temperature at different amine mass fraction

The required solvent flow to reach the transport condition was found to range from 377 to 278 m3/h, as shown in figure 2. The resulting loading at the bottom of the absorption column varied from 0.57 to 0.38 (Figure 3).

Figure 4 depicts the resulting variation in reboiler temperature, which, depending on the solvent type, may have an influence on the rate of degradation. Yet, we chose to neglect that aspect since tertiary amines were reported to have good resistance to thermal degradation [14].

Hydrocarbon losses are another important parameter that affects the environment and the operation expenses of a carbon capture unit. It was found that hydrocarbon losses, represented by BTEX and volatile organic compounds (VOC) emissions, are strongly influenced by the solvent composition. Figure 5 shows the evolution of BTEX emissions from the plant as a function of amine concentration, whereas Figure 6 represents the light hydrocarbon losses.

The amount of hydrocarbon losses depends on the solvent flow rate. As discussed earlier, if the amine concentration in the solvent increases, the required flow rate decreases. Consequently, based on the Henry's law, more hydrocarbons are physically absorbed into the amine solution.
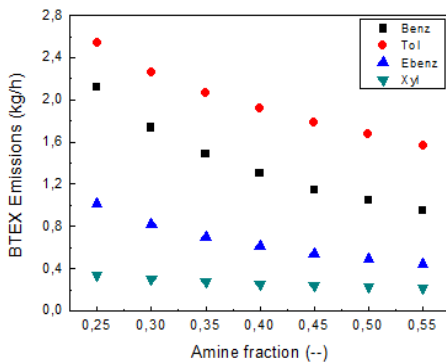

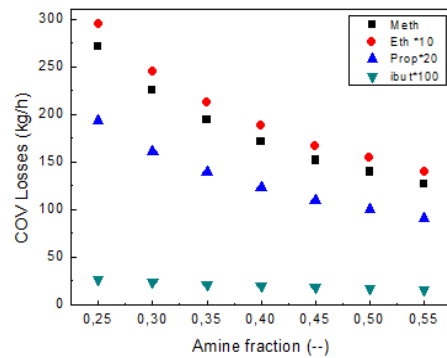Figure 5 BTEX emissions as a function of amine mass fraction

Figure 6 Light hydrocarbon emissions for different amine mass fractions

The amine concentration in the solvent was found to have an impact on the amine evaporative loss. According to Henry law, the partial pressure of amines in the sweet natural gas stream is higher as higher is the amine content in the solvent solution (Figure 7).
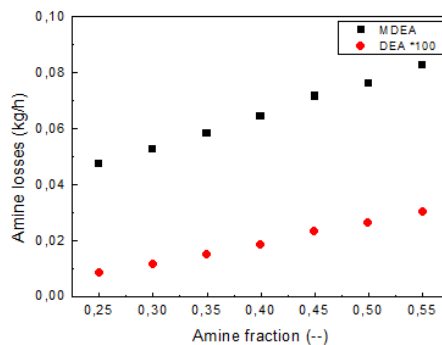

Figure 7 Solvent losses at different amine mass fraction

Figure 8-a shows that as the solvent composition increases, the reboiler energy decreases until it is balanced by the energy required to increase the reboiler temperature. The pumping energy, represented in figure 8-b, was slightly influenced by the change in solvent composition.

The increase of solvent concentration induced a subsequent increase of the additional energy required for the incineration of the BTEX, as shown in Figure 8-b. At low amine fraction (lower than 20% wt.), the absorbed light hydrocarbons contributed to the combustion and therefore less additional energy was needed. Yet, as we go to higher amine concentration, the hydrocarbon losses decreased and more fuel was hence required to get the incinerator to its set point.

In order to identify the optimal amine mass fraction, a sensitivity analysis on the total energy required was done (Figure 8-c). The total energy is defined as the sum of reboiler energy, pumping energy and the energy required for BTEX incineration.

Figure 8-d shows the evolution of energy cost with amine mass fraction for two scenarios: in the BTEX-free scenario the incineration of BTEX is not taken into account. The energy cost includes pumping, regeneration energy and energy content of the hydrocarbon losses. In the BTEX scenario, the presence of the incineration unit is taken into account and its energy is included in the energy cost.

It was found that the optimal amine mass fraction shifted from 0.5 for the BTEX-free scenario to 0.45 for the BTEX scenario. The energy costs were estimated at 11.25 and 12.93 \$/ton CO_2 captured respectively.

Finally, Figure 9 shows the composition of energy penalty for the BTEX-free and BTEX cases at their optimum amine concentrations calculated previously. Evaporative amine losses were included in order to show their economic magnitude compared to the other process variables.
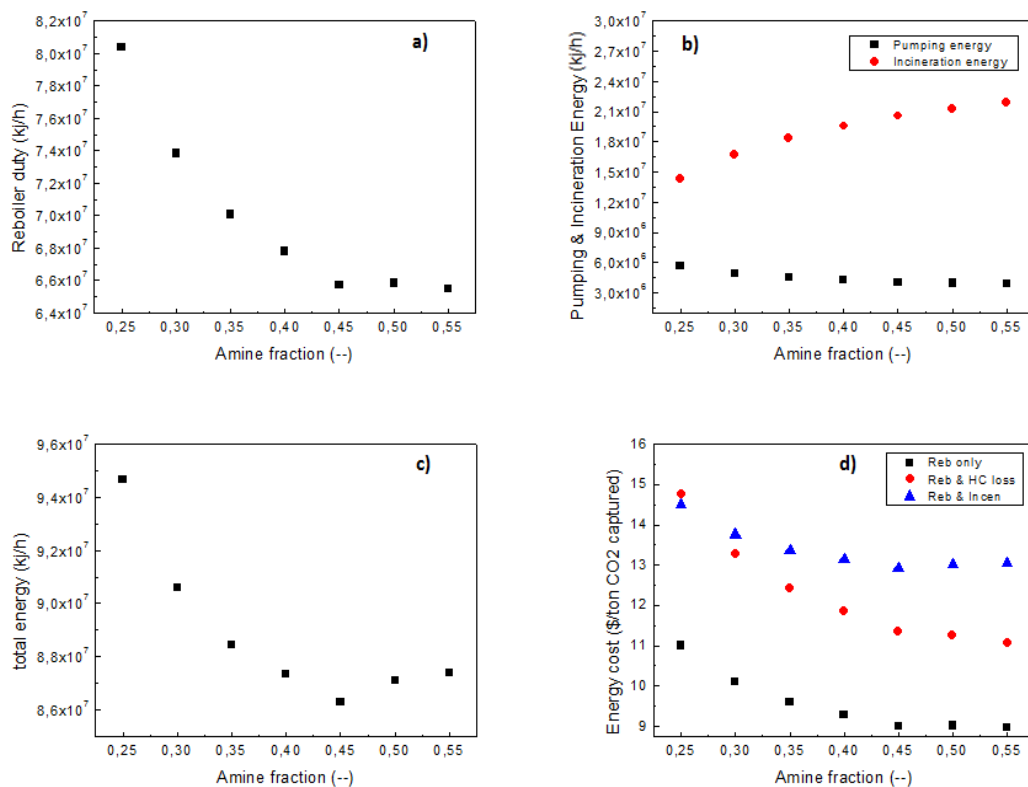

Figure 8 Energy demand as a function of amine mass fraction, a) Reboiler Energy, b) Pumping and incineration Energy, c) total energy based on natural gas consumption, d) Energy cost per ton of CO_2 captured
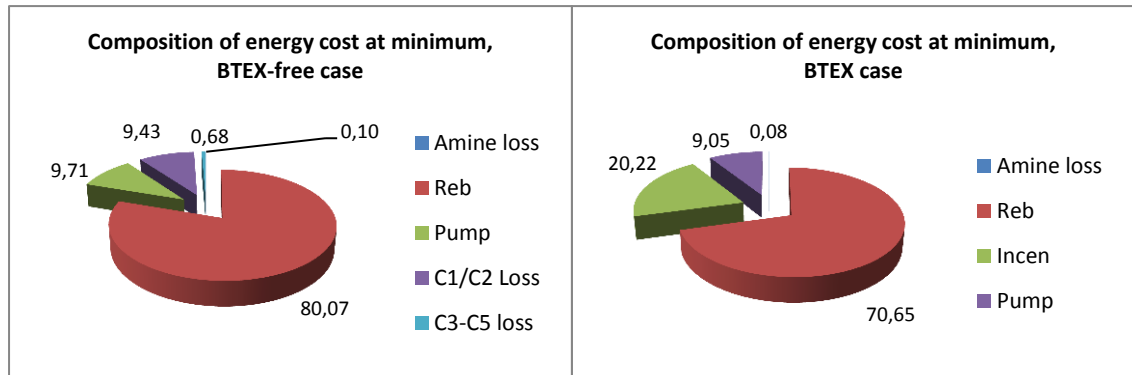
Figure 9 Costs resulting from energy expenses and amine losses, left) BTEX-Free scenario, right) BTEX Incineration scenario

4. Conclusion

In this work, we have investigated the influence of the solvent concentration on the energy demand of an MDEA/DEA based natural gas sweetening unit under environmental and technical constraints regarding the CO_2 content in sweet gas and the emissions of BTEX. A process model constructed in AspenHysys V9 and validated against plant data was used for the study. The amine concentration was found to be a key parameter that has a significant impact on the design and operations of the process.

In the conventional case, it is always more profitable to work in higher amine concentration, since it reduces the regeneration energy and rich solvent as well as the flow rate of solvent and hence the pumping energy. Yet, the optimal concentration was found to shift from 0.5 for the conventional case where the BTEX emission is not taken into account, to 0.45 if an incineration unit is put in place to control the emissions. The minimal energy costs were estimated at 11.25 and 12.93 \$/ton CO_2 captured respectively.

The presence of BTEX in sour gas units entails an additional energy requirement to the absorption process. Addressing this aspect in the early stages of the design might achieve considerable energy and economic savings.

References

[1] BP p.l.c, (2016) BP Energy Outlook, London, United Kingdom, June 2016
[2] K. Costello, Why natural gas has an uncertain future", The Electricity Journal, 2017, 30: 18-22
[3] IEA (2012) World Energy outlook, 2012
[4] D. Foo, R. Ooi, R. Tan, J. Lee, "Process integration approaches to optimal planning of unconventional gas field development", Chemical Engineering Science, 2016, 150: 85-93
[5] IEAGHG (2017) CO_2 Capture in Natural Gas Production by adsorption Processes for CO_2 storage, EOR and EFR (2017/04)
[6] IEAGHG (2014) Assessment of emerging CO_2 capture technologies and their potential to reduce costs (2014/TR4)
[7] A. Muhammad, Y. GadelHak, "Simulation based improvement techniques for acid gases sweetening by chemical absorption: A review", International Journal of Greenhouse Gas Control, 2015, 37: 481-491.
[8] V. Abkhiz, I. Haydari, "Comparison of amine solutions performance for gas sweetening", Asia Pac. J. of Chem. Engineering, 2014, 9: 656-662.
[9] M. Garcia, H.K. Knuutila, S. Gu, "Determination of Kinetics of CO_2 Absorption in Unloaded and Loaded DEEA+MAPA Blend", Energy Procedia, 2017, 114, 1772-1784
[10] Y. Kim, J. Lim, S. Jeong, Y Yoon, S. Bae, S.Nam, "Comparison of Carbon Dioxide Absorption in Aqueous MEA, DEA, TEA, and AMP Solutions", Bull. Korean Chem. Soc. 2013, 783-787
[11] H. Gao, Z. Wu, H. Liu, X. Luo, Z. Liang, "Experimental Studies on the Effect of Tertiary Amine Promoters in Aqueous Monoethanolamine (MEA) Solutions on the Absorption/Stripping Performances in Post-combustion CO2 Capture", Energy Fuels, 2017, 31: 13883-13891.
[12] A. Benamor, K. Aroua, "Modeling of CO_2 solubility and carbamate concentration in DEA, MDEA and their mixtures using the Deshmukh– Mather model", Fluid Phase Equilibria, 2005, 231, 150-162.
[13] A. Adeosun, N. El-Hadri, E. Goetheer, M. AbuZahra, "Absorption of CO_2 by Amine Blends Solution: An Experimental Evaluation", International Journal Of Engineering And Science, 2013, 3: 12-23.

[14] N. Al-Lagtah, S. Al-Habsi, S. Onaizia, "Optimization and performance improvement of Lekhwair natural gas sweetening plant using Aspen HYSYS", Journal of Natural Gas Science and Engineering, 2015, 26: 367-381.

[15] A. Nuchitprasittichai, S. Cremaschi, "Optimization of CO2 Capture Process with Aqueous Amines", Eng. Chem. Res., 2013, 52: 236–243.

[16] G. Léonard, B. Mogador, S. Belletantea, G. Heyen," Dynamic modelling and control of a pilot plant for post-combustion CO2 capture", Computer Aided Chemical Engineering, 2013, 32: 451-456

[17] M.Garcia, H.K. Knuutila, S. Gu, "ASPEN PLUS simulation model for CO_2 removal with MEA: Validation of desorption model with experimental data". Journal of Environmental Chemical Engineering, 2017, 5(5): 4693–4701.

[18] A.Valtz, M. Hegarty, D. Richon, "Experimental determination of the solubility of aromatic compounds in aqueous solutions of various amines", Fluid Phase Equilibria, 2003, 15: 257-276.

[19] R. Kannan, K. Leong, R. Osman, H. Ho, C. Tso, "Gas fired combined cycle plant in Singapore: energy use, GWP and cost—a life cycle approach", Energy Conversion and Management, 2005. 46: 2145–2157