

On the use of Ionic Liquids for CO₂ Capturing

Emad Ali, Inas Alnashef, Abdelhamid Ajbar, Mohamed Hadjkali, and Sarwono Mulyono

Abstract—In this work, ionic liquids (ILs) for CO₂ capturing in typical absorption/stripper process are considered. The use of ionic liquids is considered to be cost-effective because it requires less energy for solvent recovery compared to other conventional processes. A mathematical model is developed for the process based on Peng-Robinson (PR) equation of state (EoS) which is validated with experimental data for various solutions involving CO₂. The model is utilized to study the sorbent and energy demand for three types of ILs at specific CO₂ capturing rates. The energy demand is manifested by the vapor-liquid equilibrium temperature necessary to remove the captured CO₂ from the used solvent in the regeneration step. It is found that higher recovery temperature is required for solvents with higher solubility coefficient. For all ILs, the temperature requirement is less than that required by the typical monoethanolamine (MEA) solvent. The effect of the CO₂ loading in the sorbent stream on the process performance is also examined.

Keywords—Ionic liquid, CO₂ capturing, CO₂ solubility, Vapor-liquid equilibrium.

I. INTRODUCTION

IT is widely acceptable that global warming is occurring. Many scientists believe that the major cause is the emission of greenhouse gases (GHGs), as carbon dioxide (CO₂), nitrous oxide and methane, into the atmosphere. Among these GHGs, CO₂ is the largest contributor in regard to its amount present in the atmosphere contributing to about 60% of global warming effects [1]. CO₂ capture and sequestration from fossil-fueled power plants is drawing increasing attention as a potential method for controlling greenhouse gases emissions. Among different developed methods, post-combustion capture has the advantage that it can be applied to retrofit the existing power plants. The most mature technology for CO₂ post-combustion is amine-based absorption due to its high affinity to CO₂ [2-7]. However, solvent recovery for reuse becomes very expensive in terms of energy requirements [8-9]. It is of benefit to find alternative solvents that compromise high affinity for CO₂ with ease of solvent regeneration and reuse. The search could be impossible because the number of candidate solvents and solvent blends is very large.

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The amine-based absorption belongs to the chemical separation methods which demand intensive energy use to break the chemical bonds between the absorbents and the absorbed CO₂ in the regeneration step. On the other hand, Ionic Liquids have several advantages. One of which is low energy demand to extract the absorbed CO₂ from ILs in the regeneration step. This is attributed to a physical absorption mechanism [10]. In this work, CO₂ capture using conventional ionic liquids is studied. Specifically, numerical simulation will be used to model CO₂-capture process using ILs. It is believed that the IL will be easier to recover at low energy requirement compared to the amine-based methods. Solubility of CO₂ in specific ILs is determined using the homogeneous approach based on the PR EoS. Using the developed model, parametric estimation study will be performed to compare the energy requirements for the process through investigating the effects of stripper operating temperature, CO₂ removal percentage, the CO₂ lean solvent loading and the rich solvent loading. The thermodynamic model, which is the core of the process, is used to estimate the equilibrium constant and vapor-liquid equilibrium necessary to carry out the parametric study.

PR EoS is used by several researchers to estimate the vapor-liquid equilibrium (VLE) [11]. This equation is suitable to handle systems containing hydrocarbons, water, air and combustion gases, the typical components in a natural gas based power plant. Other applications to mixtures containing CO₂ are reported. Harvey [12] used the PR EoS for VLE calculation for water with synthesis gas mixtures. Tombokan [13] reported successful application for polar systems, systems containing gases (CO₂, CH₄ and C₂H₆) with n-alkanes, sterols and vitamins in CO₂. Greer [14] also utilized PR EoS to estimate the VLE for CO₂-MEA mixtures in order to design the CO₂ absorber column. Similar effort is also reported by Lars [15].

II. ABSORBER MODEL

Schematic description of the CO₂ capturing process is depicted in Fig. 1. The process consists of an absorber followed by a stripper. In the absorber, the lean sorbent is fed to extract the CO₂ in the Flue gas. The contaminated Sorbent is then sent to the stripper for regeneration where the exact amount of CO₂ captured is assumed to be released in the top product. The regenerated solvent is recycled back to the absorber. In this work the stripper is treated as a simple flash drum where it is assumed that the required amount of CO₂ to be released occurs at a specific VLE condition. The flue gas is mainly air with some amount of CO₂ and Water vapor. It is assumed that only CO₂ is miscible in the solvent and that transfer of liquid species to the gas phase is negligible. The

CO₂ transfer to the liquid phase is only due to physical absorption, no chemical reaction occurs.

The absorber is a multistage countercurrent column as shown in Fig. 2. Assuming steady state and adiabatic conditions, the typical component balance for stage *i* is given as follows:

$$G_{i+1} y_{i+1} + L_{i-1} x_{i-1} = G_i y_i + L_i x_i \quad (1)$$

In terms of inert free flow rates, which is valid since only CO₂ is transferring:

$$G \frac{y_{i+1}}{1-y_{i+1}} + L \frac{x_{i-1}}{1-x_{i-1}} = G \frac{y_i}{1-y_i} + L \frac{x_i}{1-x_i} \quad (2)$$

The equilibrium line:

$$y_i = m x_i \quad (3)$$

The gas feed conditions are well defined. Specifically, the feed flow rate is 12000 mol/h, with 5% CO₂, 1% water vapor and the rest is air. Therefore, given the CO₂ removal efficiency, assuming that only CO₂ is absorbed by the liquid phase, the gas outlet condition can be exactly determined using the overall mass and component balances. Since the component mole fraction in the gas phase is related to the liquid phase via Eq. (3), the remaining unknown variables are the liquid phase mole fractions and the solvent flow, *L*. In this case, the number of unknown variables is *N*+2. Because *N* component balance equations can be written, two additional given relations must be defined. The equilibrium constant, *m* in (3) will be determined via VLE analysis as described in the next section.

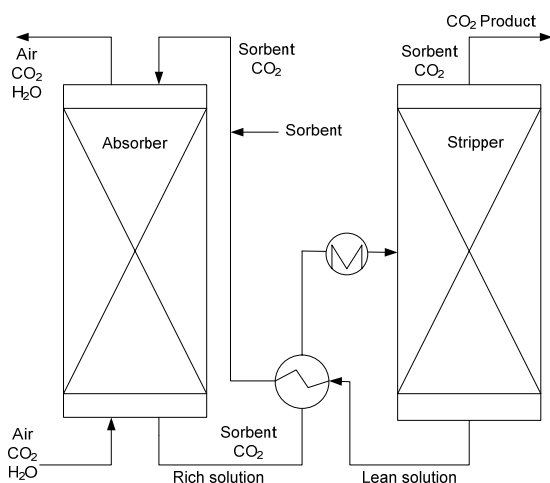


Fig. 1 Schematic of the CO₂ capturing Process

III. THERMODYNAMIC MODEL

CO₂ can be physically absorbed in a solvent according to Henry's law and hence more applicable to gases with high partial pressure of acid gas. The solvent regeneration step is relatively simple for physical absorption as it is carried out by pressure let down. Usually solubility of gases in liquids is determined by Henry's law, some correlation for estimating the CO₂ solubility in MEA, water and other liquids exist in the literature. For the ILs used in this work, the solubility of CO₂ in these liquids will be determined by the VLE analysis based on PR EoS defined as follows [16,17]:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \quad (4)$$

where *a*, and *b* are function of the critical properties of the chemical species. The properties of CO₂ and ionic liquids required for the calculation is listed in Table I. Data for CO₂ are taken from the ASPEN database while for ionic liquids, the estimated pseudo-critical properties are taken from the work of Valderrama et al [18] who have developed a group contribution method to obtain these properties.

TABLE I
THE PHYSICAL PROPERTIES OF CO₂ & ILS

Component	T _c (K)	P _c (atm)	W
1-butyl-3-methylimidazolium tetrafluoroborate (IL1)	632.3	20.4	0.8489
hexyl-(2-hydroxyethyl)-dimethylammonium bromide (IL2)	776.6	21.7	0.9601
1,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide (IL3)	1235.7	36.8	0.1418
CO ₂	304.2	73.8	0.411

This can be rearranged into a cubic equation and solved numerically at fixed temperature and pressure to obtain the molar volume. The compressibility factor, $Z=Pv/RT$ can then be computed. The latter is used to compute the following component fugacity for each phase [16]:

$$\phi_i = \exp \left[(Z-1) \frac{B_i}{B} - \ln(Z-B) - \frac{A}{2\sqrt{2}B} \left(\frac{2\sum_j y_j A_{ij}}{A} - \frac{B_i}{B} \right) \right] \ln \left(\frac{Z+(1+\sqrt{2})B}{Z-(1-\sqrt{2})B} \right) \quad (5)$$

where $A = \frac{aP}{(RT)^2}$, $B = \frac{bP}{RT}$

The following mixing rules are required to calculate *A* and *B* (from *a* and *b*) and extend the application field of equation of state to mixtures:

$$A = \sum_{i=1}^{nc} \sum_{j=1}^{nc} y_i y_j \sqrt{A_i A_j} (1 - k_{ij}), \quad B = \sum_{i=1}^{nc} y_i B_i \quad (6)$$

This is a classical mixing rule of the Van der Waals type where k_{ij} is the binary interaction parameter fitted on the basis of experimental liquid-vapor equilibrium data. After solving the above equation (5), the largest root of the cubic equation will be used to compute the vapor phase fugacity, while the smallest for the liquid phase fugacity. The VLE is obtained using the homogeneous approach (ϕ - ϕ method) based on the calculated fugacities for each component in both liquid and vapor phases using the PR cubic EoS as follows:

$$\hat{f}_i^L = \hat{f}_i^V, \quad i = 1, \dots, nc \quad (7)$$

where

$$\hat{f}_i^L = x_i \phi_i^L P, \quad \hat{f}_i^V = y_i \phi_i^V P \quad (8)$$

The VLE calculation in this case is an iterative procedure where the liquid and vapor mole fraction are determined at fixed Temperature and pressure such that the condition in (7) in addition to the following conditions:

$$\sum_{i=1}^{nc} x_i = 1, \quad \sum_{i=1}^{nc} y_i = 1 \quad (9)$$

are satisfied. Once the VLE is satisfied, the CO₂ solubility in the specific IL is taken as its mole fraction in the liquid phase, i.e. x_{CO_2} . The mixing rules used in (5) includes the binary interaction parameters to account for mismatch between the experimental values and the model predictions. This parameter is set to zero in this work. It will be optimized in later work when our lab tests are concluded. The entire VLE calculation is carried out in MATLAB software.

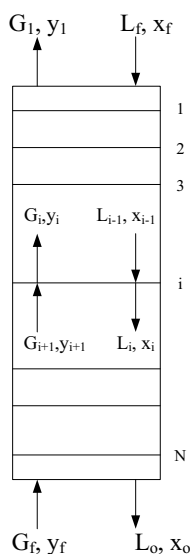


Fig. 2 The absorber Column

The PR thermodynamic model is well tested with extensive experimental data and had been used successfully in VLE representation of many other aqueous systems [19]. Therefore, it will be utilized to determine the CO₂ solubility necessary to solve the absorber model and to estimate the VLE temperature necessary to recover the captured CO₂ from the rich sorbent.

IV. STRIPPER MODEL

The PR equation of state is further utilized in this work to carry out flash calculation for the flash drum which is assumed to represent the stripper unit. The flash calculation involves determining the vessel temperature and the corresponding equilibrium liquid and vapor composition at fixed pressure and given feed conditions. In the addition, the calculation will determine the portion of the feed that vaporized. This is another numerical iteration that involves satisfying the conditions set by (7) and (8) in addition to the following famous Rachford and Rice equation:

$$\sum_{i=1}^{nc} \frac{z_i (K_i - 1)}{1 + \lambda (K_i - 1)} = 0 \quad (10)$$

where z_i is the mole fraction of the stripper feed, $K_i = y_i/x_i$ is the equilibrium constant, and λ is the ratio of the produced vapor to the feed. To ensure that the amount of CO₂ extracted in the flash drum equal exactly the amount captured in the absorber column, the following constraint is also added to the flash calculations:

$$\lambda F y_{CO_2} - CO_{cap} = 0 \quad (11)$$

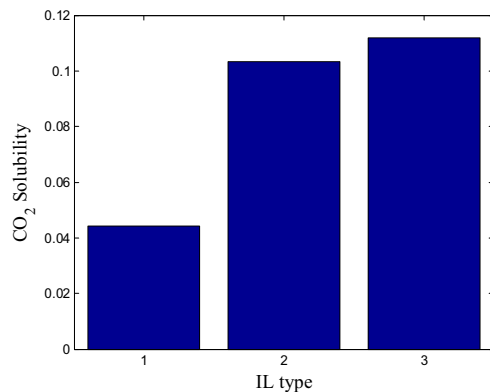


Fig. 3 Solubility of CO₂ in three different ILs at 1 atm and 40 °C

where F is the molar flow rate of the flash feed (rich solution), y_{CO_2} is the mole fraction of CO₂ in the vapor flow rate (CO₂ product), and the CO_{cap} is the amount of CO₂ captured in the absorber column. The purpose of the flash calculation is to determine the energy requirement for regenerating the solvent in terms of the flashing temperature. Therefore, the temperature will be a measure of the cost effectiveness of the IL used for CO₂ capturing. It should be noted that the energy requirement for regeneration is based only on overcoming the physical absorption, i.e. to vaporize specific amount of the

CO₂ in the rich solution. This means that the energy required to overcome the chemical reaction, if any, is not considered. The entire numerical calculations are carried out using MATLAB software.

V. RESULTS AND DISCUSSION

Fig. 3 shows the solubility of CO₂ in three types of Ionic liquids at 40 °C and 1 atm. The solubility for each case is obtained by solving the VLE problem (4-8) using PR EoS at the specified temperature and pressure. In each case, the solution is considered as binary system involving the specific IL and CO₂. The solubility is then taken as the mole fraction of CO₂ in the liquid phase.

These IL's has different levels for CO₂ solubility; consequently they will have different effect on the CO₂ capturing process. It is believed that higher solubility will demand less Sorbent flow rate. However, the energy required to extract the CO₂ from the rich sorbent in the desorption column will be higher. The effect of these types of ILs on the capturing process will be examined for the CO₂ loading in the absorber column.

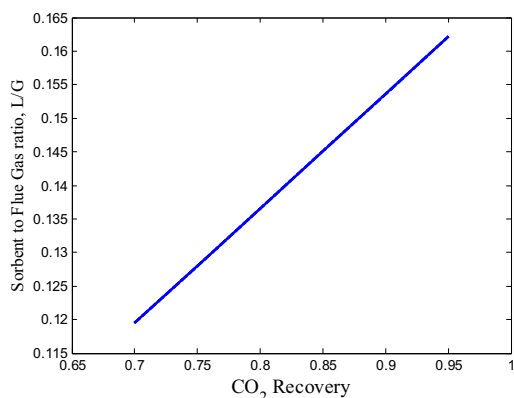


Fig. 4 Effect of CO₂ recovery rate on the solvent demand at X_o = 0.01 and X_f = 0.3

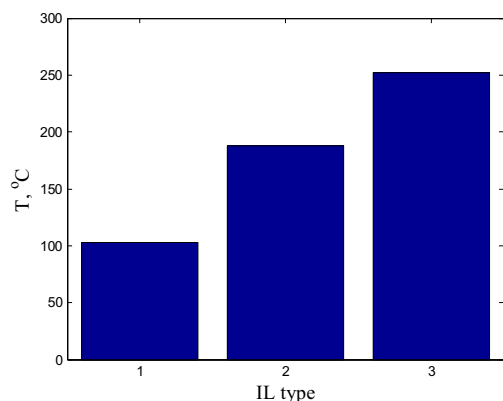


Fig. 5 Temperature requirement for CO₂ regeneration in the stripper at X_o = 0.01 and X_f = 0.3

To solve the absorber mass balance equations, two degrees of freedom should be specified. In this case, we choose to fix

the CO₂ mole fraction in the absorber feed (lean sorbent influent), X_f and the CO₂ mole fraction in the absorber outlet stream (rich sorbent effluent), X_o. Specifically X_o = 0.3 and X_f = 0.01 is employed. For different values of the CO₂ removal efficiency, the model equation is solved and the sorbent flow rate is determined as shown in Fig. 4 as a ratio to the flue gas flow. Apparently, the sorbent requirement increases linearly with the CO₂ recovery rate. Interestingly, all types of ILs had exactly the same sorbent flow rate. When the liquid end-conditions of the absorber column are fixed, the sorbent requirement becomes independent of the IL physical properties. Hence, the solvent requirement is controlled by the CO₂ removal rate and the magnitude of the end conditions. In order to differentiate between the ILs, the energy requirements to release CO₂ from the rich sorbent are investigated. The energy will be manifested by the VLE temperature necessary to release *only* the captured amount of CO₂. Solving the desorption problem defined by (4-10) gives the results shown in Fig. 5. In the calculation, the stripper pressure is taken to be 1 atm and the feed composition equals that of the absorber outlet (rich solution). It can be seen that the separation temperature is proportional to the IL solubility factor. The IL with higher solubility factor requires more energy to release the captured CO₂. Hence, IL 1 is preferable in this case.

Since the end conditions are set arbitrary, it is interesting to study their effect on the process performance. First we examine varying the value of the lean sorbent loading, X_f at fixed X_o = 0.3. The result for IL 1 at three CO₂ recovery rates is depicted in Fig. 6. It is obvious that the sorbent supply increases with increasing X_f. Exactly the same performance is observed for the other types of ILs because the sorbent supply is independent of the physical properties as mentioned earlier. The increase in sorbent requirement has its effect on the VLE temperature necessary to emit the captured CO₂ from the solution. This is evident from Fig. 7 which indicates that the temperature decreases as X_f grows. As the solvent flow increase at fixed X_o, the CO₂ content in the rich sorbent grows up. Therefore, removing a small amount of the CO₂ content equivalent to the captured amount becomes easier and can occur at a low temperature.

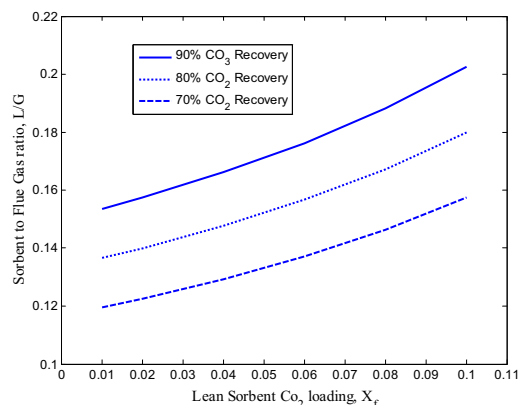


Fig. 6 Effect of lean CO₂ loading on the solvent demand for IL1 at X_o = 0.3

Secondly we examine the effect of varying X_0 at fixed X_f . Specifically, the CO_2 mole fraction in the rich sorbent is varied between 0.13 and 0.39 at fixed X_f of 0.1. The influence of this experiment on the sorbent requirements for IL1 is demonstrated in Fig. 8. It is evident that the solvent flow rate grows up exponentially at lower values of X_0 . The result is identical for the other ILs. Interestingly, the growing demand for the sorbent is not associated with higher heating needs, which is not shown here for brevity. The growth in Solvent flow occur at lower values of X_0 where the CO_2 content remains within certain values that do not call for elevated separation temperature.

The interesting result is that the temperature requirement for all types of IL remains at the most below 100 °C. For CO_2 capturing using MEA, it is reported that the temperature requirement reaches 120 °C when the stripper is operating at 1 atm [5-7,20].

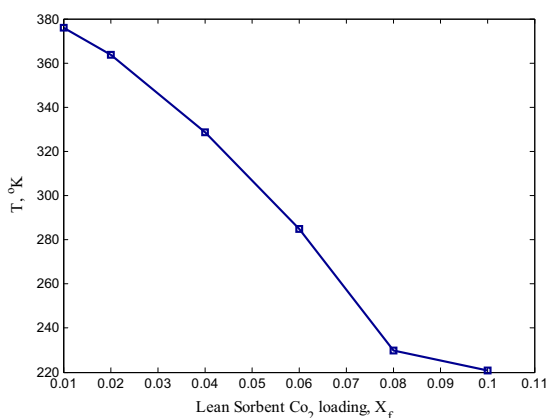


Fig. 7 Effect of the lean CO_2 loading on the energy demand for IL1 at $X_0 = 0.3$

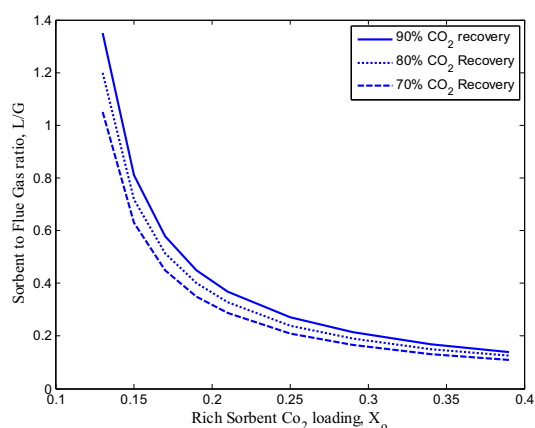


Fig. 8 Effect of the rich CO_2 loading on the solvent demand for IL1 at $X_f = 0.1$

VI. CONCLUSIONS

CO_2 capturing is becoming increasingly demanding with the expansion of the industrial activities around the world. This work is an attempt to study the use of ILs in the typical CO_2 capturing process. The recovery operation is modeled based

on the well-known PR EoS. Parametric investigation is carried out using the developed model to determine the solvent and energy demands to recover specific amount of CO_2 from the flue gas using these ILs. The energy demand is represented by the VLE temperature necessary to emit the captured CO_2 from the spent solvent. The equilibrium temperature is used to control the CO_2 recovery because the stripper pressure is kept as low as 1 atm. It is found that energy requirement for ILs is less than that demanded by the amine-based processes. Furthermore, the energy demand decrease with increasing the CO_2 loading in the lean sorbent while it is marginally affected by the CO_2 loading of the rich sorbent. On the other hand, the solvent demand grows with the lean CO_2 loading and vice versa.

REFERENCES

- [1] A. Yamasaki, "An Overview of CO_2 Mitigation Options for Global Warming – Emphasizing CO_2 Sequestration Options." *Journal of Chemical Engineering of Japan*, 36(4): 2003, 361-375.
- [2] S. M. Cohen, H. L. Chalmers, M. E. Webber and C. W. King, "Comparing post-combustion CO_2 capture operation at retrofitted coal-fired power plants in the Texas and Great Britain electric grids", *Environmental Research Letter*, 6, 2011, 1-14.
- [3] C. B. Tarun, E. Croiset, P. L. Douglas, M. Gupta, M. H. M. Chowdhury, "Techno-economic study of CO_2 capture from natural gas based hydrogen plants", *Inter j of greenhouse gas control* 1, 2007, 55–61.
- [4] N. Dave, T. Do, G. Puxty, R. Rowland, P.H.M. Feron and M. I. Attalla, " CO_2 capture by aqueous amines and aqueous ammonia– A Comparison", *Energy Procedia*, 1, 2009, 949–954.
- [5] N. Rodriguez, S. Mussati, N. Scenna, "Optimization of Post-Combustion CO_2 Process Using DEA-MDEA Mixtures", *Chemical Engineering Research and Design*, 89, 2011, 1763-1773.
- [6] M. Mofarhi, Y. Khojasteh, H. Khaledi, A. Farahnak, "Design of CO_2 Absorption Plant for Recovery of CO_2 for Flue Gases of Gas Turbine", *Energy*, 33, 2008, 1311-1319.
- [7] M. Abu-Zahra, L H Schneides, J P Niederer, P H Feron, G F Versteeg, " CO_2 Capture from power plants Part I, parametric study of the technical performance based on monoethanolamine", *Int. j of green house gas control*, 1, 2007, 37-46.
- [8] M. K. Hanne and G. T. Rochelle, "Effects of the temperature bulge in CO_2 absorption from flue gas by aqueous monoethanolamine", *Industrial Engineering Chemistry Research*, 47, 2008, 867-875.
- [9] B. R. Anand, E. S. Rubin, D. W. Keith, and M. G. Morgan, "Evaluation of potential cost reductions from improved amine-based CO_2 capture systems", *Energy Policy*, 34, 2006, 3765-3772.
- [10] J. Huang, and T. Ruther, "Why are Ionic Liquids Attractive for CO_2 Absorption? An Overview", *Aust J of Chemistry*, 62, 2006, 298-308.
- [11] D. Peng, D.B. Robinson, "A New Two-Constant Equation of State", *Industrial Engineering Chemistry Fundamental*, 15(1), 1876, 59-64.
- [12] A. H. Harvey, "Application of Molecular Modeling to Vapor-Liquid Equilibrium of Water with Synthesis Gas", *15th Inter Conference on the Properties of Water and Steam*, Berlin, Sep 8–11, 2008.
- [13] X. C. Tombokan, "Ternary Phase Equilibrium of the Sclareol-Ethyl Lactate- CO_2 System and its Application in the Extraction and Isolation of Sclareol from Clary Sage", PhD dissertation 2008, North Carolina State University, USA.
- [14] T. Greer, "Modeling and Simulation of Post Combustion CO_2 Capturing", Msc thesis 2008, Telemark University College, Norway.
- [15] E. O. Lars, "Aspen HYSYS Simulation of CO_2 Removal by Amine Absorption from a Gas Based Power Plant", *The 48th Scandinavian Conference on Simulation and Modeling*, Göteborg, Oct 30-31st, 2007.
- [16] S. L. Sandler, *Chemical and Engineering Thermodynamics*, 3rd Edition. John Wiley and sons INC., 1999.
- [17] Z. Nasri and H. Binous, "Applications of the Peng-Robinson Equation of State using MATLAB", *Chem Eng Education*, 43(2), 2009, 1-10.
- [18] J.O. Valderrama, L.A.; Forero, R.E. Rojas, "Critical Properties and Normal Boiling Temperature of Ionic Liquids. Update and a New Consistency Test." *Ind. Eng. Chem. Res.*, 51 (22), 2012 7838–7844.

- [19] J. Yim, H. N. Song, B. Lee, J. S. Lim; "High-pressure phase behavior of binary mixtures containing ionic liquid [HMP][Tf₂N], [OMP][Tf₂N] and carbon dioxide", *Fluid Phase Equilibrium*, 308, 2011, 147– 152.
- [20] T. Greer, A. Bedelbayev, J. Igreja, J. Gomrz, B. Lie, "A dynamic model for the de-absorption of carbon dioxide from monoethanolamine solution", *The 49th Scandinavian Conference on Simulation and Modeling* (SIMS2008), Oslo University college, Oct 7-8, 2008.