CHEMICAL ENGINEERING TRANSACTIONS
VOL. 43, 2015
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-34-1; **ISSN** 2283-9216
DOI: 10.3303/CET1543250

Process Heat Integration of 1-Ethyl-3-Metylimidazolium Acetate for Carbon-Dioxide Capture

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A carbon dioxide (CO_2) capture process simulation was developed for treating flue gas from a power plant with heat integration. This process required high energy usage. It is possible to reduce energy requirements by many ways, such as mixing or changing the absorbents. Alternatively, heat integration is an alternative methodology used to minimize energy requirements. Our work was focused on the simulation and optimization of CO_2 capture process in a 180 Mwe coal-fired power plant using an ionic liquid, 1-Ethyl-3-methylimidazolium Acetate (EmimAc). The challenge in process design, energy integration and utility design is to achieve the same CO_2 recovery efficiency. This work, starting from an ionic liquid (EmimAc) configuration proposed by Khonkaen et al. (2014), illustrates the simulation and solution method used to implement the process heat optimization with respect to the energy consumption and capital investment cost. First, basic monoethanolamine (MEA) and EmimAc based processes were simulated with the optimization method without heat integration. Then process heat integration was applied to improve both processes by minimizing the energy usage in the system. The preliminary result showed that the designed simulated process of IL using EmimAc provided better result in term of energy requirement than conventional monoethanolamine

1. Introduction

The effects of global warming on our planet continue to be a serious concern due to the increasing rate of greenhouse gas emissions. A major greenhouse gas that contributes to global warming effect is CO_2. Many new technologies have been proposed to solve this issue. CO_2 capture technologies can be classified as post-combustion capture (PCC), pre-combustion capture or oxy-fuel combustion capture processes. The most mature technology for CO_2 capture from flue gas in coal-fired power plant is based on PCC. Post-combustion capture with chemical absorption has been considered as a promising way for capturing large amounts of CO_2 emissions from many industries including coal-fired power plants. Currently, commercially available chemical absorption technologies for PCC are mainly based on amines, more particularly MEA. MEA-based system has been considered as the most feasible technology to capture CO_2 from post-combustion flue gas due to its maturity, stable operation, good reactivity, high absorption capacity and the low cost of MEA. However, the limitation of MEA process was the corrosion due to loaded MEA solutions, high losses of solvent and degradation of MEA. Taking into account these limitations, the MEA concentration is usually limited to 30 wt. % of MEA solution or less. Moreover, the capture of CO_2 with MEA involves a chemical reaction with a large enthalpy of absorption (-88.91 kJ/mole CO_2). Consequently, a large amount of heat is required to dissociate the chemical bonding between MEA and CO_2 in the regeneration section. Retrofitting this unit to an existing power plant, would lower the energy output of the plant by approximately 25-40 %. Accordingly, the price of electricity would increase more than 35 %, which does not comply to the target of the Department of Energy of 90 % of CO_2 removal from post-combustion flue gas with no more than a 35 % increase in the cost of electricity (Khonkaen et al., 2014). The high cost of CO_2 removal of MEA-scrubbing process (50 to 150 \$/t CO_2) also causes this process to be unattractive for large scale operation. Many studies were devoted to find another solvent to use in replacement to MEA. Ionic liquids has been considered as one of the most promising green

Please cite this article as: Jongpitisub A., Siemanond K., Henni A., 2015, Process heat integration of 1-ethyl-3-methylimidazolium acetate for carbon-dioxide capture, Chemical Engineering Transactions, 43, 1495-1500 DOI: 10.3303/CET1543250

solvents due to the advantages of high CO_2 solubility, non-volatility, high thermal stability, and tunability of structure and properties. Furthermore, ionic liquid (IL) has been of interest as a potential solvent for green CO_2 capture technology with the benefit of less energy usage and cost reduction. One promising ionic liquid, EmimAc, was studied due to its ability to effectively capture CO_2 (chemical absorption behaviour) with lower energy consumption compared to MEA-based process. In this study, flow sheets of both scrubbing processes (MEA and IL) for post-combustion CO_2 capture from 180 Mw_e coal-fired power plant were simulated and optimized using a commercial simulation program (Aspen Plus®). Both processes were improved by process heat integration using GAMS. The conceptual design by GAMS was validated in Aspen Plus to ensure the feasibility of the design. Then, the energy consumptions of both processes were compared. To ascertain the potential of economic benefits of the IL-based process, the investment cost is calculated and compared to the MEA-based process. Results show lower energy requirement of IL-based process by 13.5 % compared to MEA-based process, but the investment cost of IL-based process was twice as much as one of MEA-based process.

2. MEA-based Scrubbing System

In this study, a flue gas from 180 MWe coal burning power plant with flue gas flow rate of 32 ton/hr, and gas composition of 84 % N_2, 12 % CO_2, and 4 % water vapour in standard volume (Khonkaen et al., 2014) was simulated in this flow sheet development. The MEA-based process was designed to capture CO_2 about 90 % by weight with 98 % purity of CO_2 from the flue gas using 30 wt. % MEA solution. Simplified flow sheet development (absorber/stripper configuration) was shown in Figure 1. The flue gas at high temperature from coal-fired power plant was cooled at a pressure near atmospheric pressure (115.1 kPa) in the scrubbing section by cooling with water before entering the absorber. Then, the scrubbed flue gas with CO_2 contacted the lean MEA (30 wt. %) with CO_2 loading of 0.2 mole CO_2/mole MEA (135.8 kPa and 308 K) in a countercurrent flow to separate CO_2 from the flue gas. For the absorber column, the number of equilibrium stages of the absorber was set at 25 stages to achieve a rich amine loading of 0.36 mole CO_2/mole MEA and 90 % recovery. Vented gas from the top of absorber contained CO_2 less than 0.02 vol % which met the environmental emission standards. Rich CO_2 in MEA solution was pumped and heated up to 239.2 kPa and 389.4 K, respectively, before entering the stripper. Heat from reboiler was used to dissociate the chemical bond of carbamate formation and other compounds between MEA and CO_2. Then, over 98.2 wt. % of CO_2 purity was stripped out at the top and regenerated MEA exited at the bottom of the stripper. The condenser and reboiler temperatures were 25 ºC and 116 ºC**,** respectively. MEA solution was recycled back to absorber section in order to minimize MEA usage. MEA and water make-ups were used to maintain the concentration and CO_2 lean loading of MEA solution.

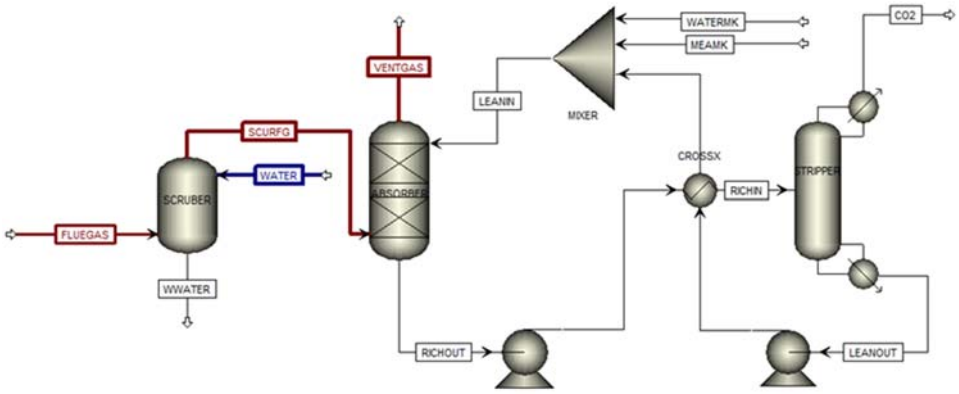

Figure 1: Simplified process flow diagram of MEA-based scrubbing system (Aspen plus).

The crucial parameter which affected the energy performance of MEA-based system is loading. Loading is an important parameter referring to mole of CO_2 carrying species over mole of MEA carrying species as displayed in Equation 1. The MEA-based system is optimized to minimize energy consumption of overall CO_2 capture system by varying MEA mass flow rate, MEA loading and MEA concentration to meet the same target of 90 % CO_2 recovery. In this study, optimal MEA mass flow rate, loading of the solution and concentration of MEA solution that minimize the energy consumption were 91 ton/hr, 0.2 mole CO_2/mole MEA and 30 wt. %, respectively.

$$Loading = \frac{[CO_2]+[HCO_3^-]+[CO_3^{2-}]+[MEACOO^-]}{[MEA]+ [MEA^+]+ [MEACOO^-]} \quad (1)$$

3. IL-based Scrubbing System

ILs have been considered as alternative solvents for capturing huge amount CO_2. ILs are salts in liquid state with a melting point below 100 ºC. ILs can be possibly tuned to have special properties by adjusting the cation and anion in their molecules for many applications especially absorbent for CO_2 capture process. Most of ILs acted as physical absorbents (conventional ILs) that is not appropriate to capture CO_2 at low partial pressure from post-combustion. To overcome this problem, many researchers have modified the structure of ILs by adding amine functional groups in ILs which greatly improve CO_2 absorption capacity. It is well known that the addition of an amine group in the IL structure caused a higher energy of reaction on this type of ILs. For example, the enthalpy of reaction with CO_2 of trihexyl(tetradecyl)phosphonium prolinate ([P66614][Pro]) is at -80 kJ/mole that is nearly that of MEA at -85 kJ/mol. Moreover, this type of IL suffers from other another drawback such as high viscosity. All of these drawbacks do not make this type of ILs the best solvents as alternative solvents for replacing MEA. One promising IL, EmimAc, shows an unusual phase behavior different from the other conventional ILs. Shiflett and Yokozeli (2009) reported that at low CO_2 fraction (less than 20 mole %), the binary system of CO_2 and EmimAc has very low vapor pressure, reflecting the strongly (chemically) absorbed CO_2 into EmimAc and with the benefit of low enthalpy of absorption (-38 kJ/mol CO_2). After doing the simulation using Aspen Plus, the property parameters of selected components will be automatically retrieved. Since the database of Aspen Plus, for now, do not provide any pure component data for EmimAc, the direct input information and data regression mode in Aspen Plus are essentially employed. For the critical properties of ILs, the group contribution method, “modified Lyndersen-Joback-Reid” method is used to estimate the critical properties of IL (Valderama et al., 2007), since the ILs start to decompose at a temperature near their normal boiling point.

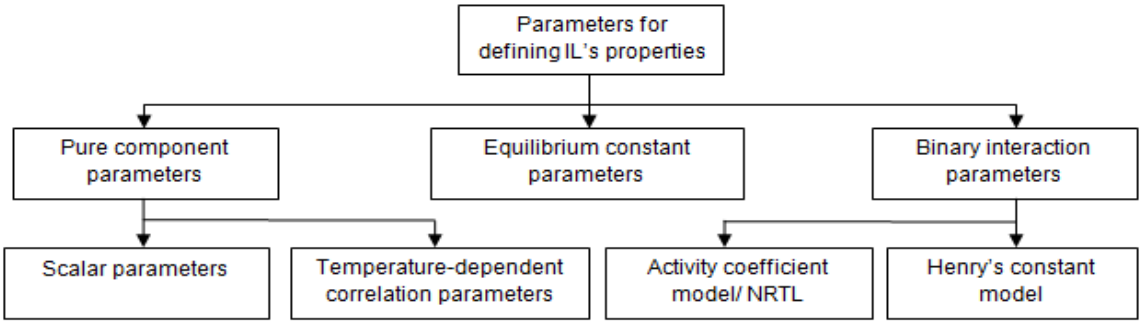

Figure 2: Flowchart of defining ionic liquid into Aspen Plus (Khonkaen, et al., 2014).

For the temperature-dependent properties, the temperature-dependent correlation parameters of nine property models including, ideal gas heat capacity (CPIG), heat of vaporization (DHVLDP), liquid density (DNLDIP), liquid thermal conductivity (KLDIP), vapour thermal conductivity (KVDIP), liquid viscosity (MULDIP), vapour viscosity (MUVDIP), liquid vapour pressure (MUVDIP) and liquid surface tension (SIGDIP) were regressed based on the reported properties of EmimAc available in the literature. The IL-based system involved a mixture system, which is composed of the solubility of gases in IL (N_2 and CO_2 in EmimAc) and solubility of liquid in liquid (EmimAc in water). The binary interaction parameters of Non-Random Two Liquid (NRTL) were used to calculate the activity coefficient of the binary system (EmimAc + water) and Henry’s constant model was used to calculate the Henry’s constant of N_2 and CO_2 in EmimAc. Both binary interaction parameters and parameters of Henry’s constant model were taken from the regression of the experimental data (PTX-diagram) reported in the literature. The reaction data of EmimAc with CO_2 were taken from the literature for the equilibrium calculation. Based on all of these parameters, a process simulation of IL EmimAc was carried out to meet the same target as that used for the MEA-based system.

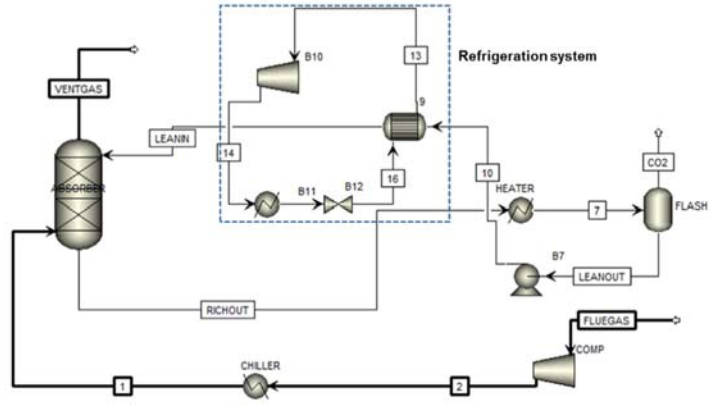

Figure 3: Simplified process flow diagram of IL-based scrubbing system (Aspen plus).

The flow diagram of IL process is shown in Figure 3. Due to the low capacity, the absorber was operated under a pressure of 618 kPa to improve the solubility of CO_2. The absorber pressure and IL flow rate were optimized to minimize the energy requirement and meet the same target as the MEA process. CO_2 is chemically absorbed by EmimAc. The regeneration process is different from MEA where a flash technique was applied instead of stripper column (Aspen plus RCSTR). IL-rich solution was regenerated by decreasing the pressure to the atmospheric pressure and increasing temperature to 80 ºC. IL-lean solution is pumped and cooled down to -2 ºC using a refrigeration unit and then recycled back to the top of the absorber.

4. Process Heat Integration

Process heat integration is an important tool to reduce energy usage in the designed process by applying HEN. In this study, heat integration of both flow sheet development, MEA-based and IL-based processes, were optimized by GAMS program with stage-wise model (Yee and Grossmann, 1990), as shown in Figure 4, to generate HEN for the based-case process. GAMS program was modeled by using constant heat capacity. In order to ensure the data from GAMS, the validation between conceptual design (constant heat capacity) by GAMS and actual design (variable heat capacity) were needed.

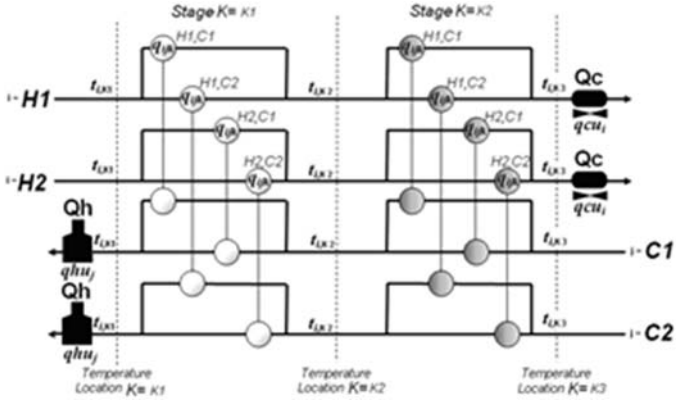

Figure 4: Stage-wise model for HEN (Yee and Grossmann, 1990).

4.1 MEA-based Process Heat Integration

There was one hot process stream; H1 and one cold process stream; C1 from the MEA-based scrubbing system (based-case which was the scratch process without applying process integration), as shown in Figure 1, consuming heating and cooling duties of 9837.2 and 7154.5 kW, respectively. Heating and cooling duties were accounted from the overall duties of the system including the reboiler heat duty and heater. Then, heat integration was initiated using the GAMS program to generate HEN on the based-case process. The result from GAMS model was the conceptual HEN design as shown in Figure 5a with exchangers H1-C1 match and heating and cooling duty savings of 6386 and 3703 kW, respectively. This conceptual process design with process heat integration, shown in Figure 5a, was validated in Aspen Plus (Figure 5b) simulator to ensure the feasibility of

the process. The result showed that the relative error between conceptual process and validated process were very small.

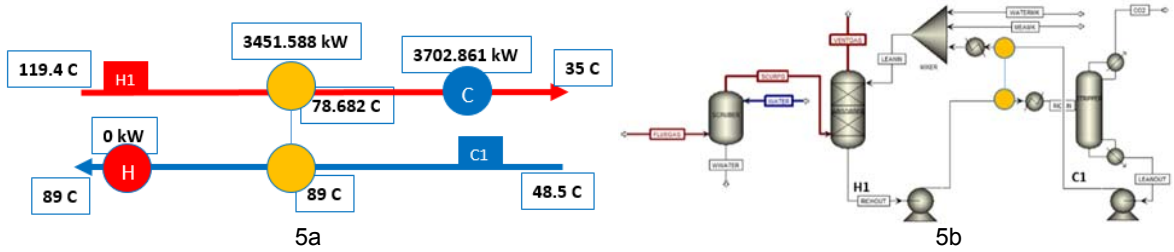

Figure 5a and 5b: Conceptual process integration from GAMS and validated process flow diagram of improved MEA-based scrubbing system (Aspen plus) with process heat integration.

The validated result showed that energy requirement of the overall system was reduced around 41 % compared to the MEA-based process without process integration. And the saving in hot and cold utilities were 35 % and 48 %, respectively. Furthermore, regeneration energy of the stripper was 3963.8 kJ/kg CO_2.

4.2 IL-based Process Heat Integration

In the system has two hot process streams; H1 and H2 and one cold process streams; C1 from IL-based scrubbing system (based-case), as shown in Figure 3, consuming heating and cooling duties of 6176.7 and 14003.6 kW, respectively. Then, heat integration was applied by GAMS program to generate HEN on the based-case process. The result from GAMS model was the conceptual HEN design as shown in Figure 5a with two exchangers (H1-C1 and H2-C1) matching lead to heating and cooling duty savings of 0 and 7824.2 kW, respectively. This system suffered from the large energy used in the flue gas compressor of about 4452 kW which was taken into account in the hot utility stream. This conceptual process design with process heat integration, shown in Figure 6a, was validated by Aspen Plus (Figure 6b) to ensure the feasibility of the process. The result showed that the relative error between conceptual process and validated process were very small.

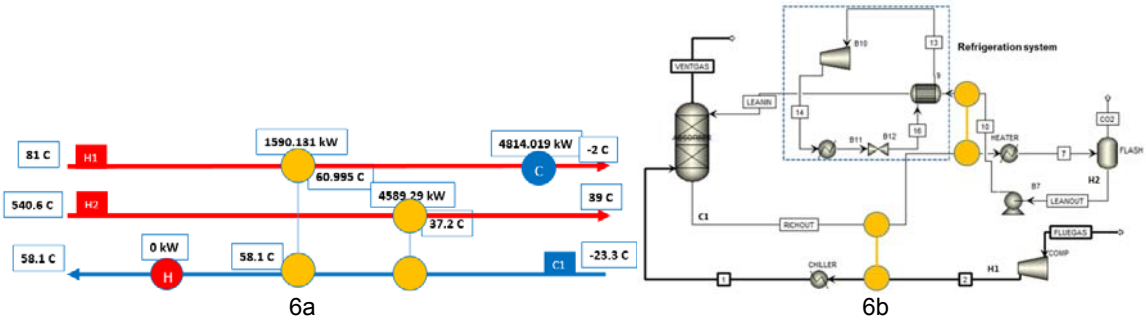

Figure 6a and 6b: Conceptual process integration from GAMS and validated process flow diagram of improved MEA-based scrubbing system (Aspen Plus) with process heat integration.

The validated result showed that energy requirement of the overall system was reduced around 50% compared to the MEA-based process without process integration, and the saving in hot and cold utilities were 58% and 44%, respectively. This type of heat integration is taken into account in the optimisation of CO_2 capture plants.

5. Economic Evaluation

The overall result illustrated that the optimization of the based-case process (without heat integration usually used in the process) and process integration application were beneficial in savings in energy requirement and capital investment cost of the process. In this last section, comparison of energy requirement and capital investment cost between MEA-based and IL-based processes were investigated, as shown in Table 1.

Table 1: Scrubbing performance and cost of MEA and IL-based process

		MEA	IL
CO_2	Capture (tons/years)	50,758	50,749
	Recovery (%)	90.03	90.01
	Purity (%)	98.18	99.26
Energy	Steam (kg/s)	6,380.9	0
	Electricity (kW)	5.5	4,518
	Total (kW)	6,386	4,518
	Total Capital investment ($)	11,075,337	25,729,487

The results show that the energy requirement of MEA and IL-based processes are 6,386 kW and 4,518 kW, respectively. This indicates that IL-based process has lower energy consumption by 29 %. To ascertain the economic benefit, capital cost is figured out using the percentage of delivered equipment cost method. In this method, the cost of equipment has been calculated from a commercial package in Aspen Plus. The capital investment cost was estimated based on basic costs of utilities published by Hassan et al. (2007). The additional equipment for IL-based process including compressor and refrigeration systems, are calculated as a ready to install package (56 % of total investment). IL-based process showed higher capital investment cost was twice that for MEA-based process. The long-term economic evaluation is necessary to obtain the feasibility of the IL-based system.

6. Conclusion

This study focused on the comparison of energy requirement and capital investment cost between conventional MEA and IL-based process using an IL (EmimAc) for CO_2 capture before and after process heat integration by HEN, based on the flue gas from a 180 MWe coal burning power plant. The conceptual HEN design by GAMS model was validated using Aspen Plus simulator. The results in process heat integration show conventional MEA and IL-based using EmimAc lower energy requirement compared to process without heat integration by 31 % and 58 %, respectively. After applying process heat integration, the results show lower energy requirement of IL-based process than that for of MEA-based process by 29 %. The capital investment cost of IL-based process using EmimAc double that of conventional MEA. The initial study of IL-based process shows its potential to replace conventional MEA-based process in term of energy requirement of the system. However, further experimental pilot plant studies for ionic liquids are recommended to futher ascertain their abilities to replace amine based processes.

Acknowledgement

Petroleum and Petrochemical College, Chulalongkorn University, PETROMAT and Thai Government budget funding for financial support.

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