

CHAPTER IV

RESULTS AND DISCUSSION

4.1 MEA-based CO₂ Capture Process

4.1.1 Process Description and Optimization

In this study, flue gas from 180 MW_e coal fired power plant with flue gas flow rate of 32 ton/hr, and a compositions of 84 % N₂, 12 % CO₂, and 4 % H₂O in standard volume which is equivalent to 77.93 % N₂, 13.14 % CO₂, and 8.92 % H₂O in mole% as shown in Table 4.1 (Khonkaen *et al.*, 2014) was simulated in this study. The MEA-based process was designed for 90 % CO₂ capture efficiency and CO₂ product of 98 % by weight from the flue gas by varying the MEA solution from 15 to 30 wt. % and lean loading from 0.15 – 0.3 mol CO₂/mol MEA. The flue gas at high temperature from coal-fired power plant was cooled down to 46.1 °C at slightly above atmospheric pressure (115.1 kPa) in the scrubbing section using cooling water before entering the absorber. Then the scrubbed flue gas with CO₂ counter-currently contacts lean MEA (30 wt. %) with CO₂ loading of 0.2 mole CO₂/mole MEA (135.8 kPa and 35 °C) to capture CO₂ out of the flue gas. For the absorber column, the equilibrium stages of the absorber were set as 25 stages to achieve a rich amine loading of 0.36 mole CO₂/mole MEA and 90 % recovery (Khonkaen *et al.*, 2014). The rich MEA solution was pumped and heated up to around 239.2 kPa and 89 °C in the cross heat exchanger, respectively before entering the stripper. At 2.36 atm the reboiler temperature was 116.4 °C, and the heat from reboiler was used to regenerate the amine. Over 98.2 wt. % of CO₂ purity was stripped out at the stripper top, while the regenerated MEA went out at the bottom of the stripper. The condenser and reboiler temperatures were (25 and 116.4) °C, respectively. MEA solution was recycled back to absorber section in order to minimize MEA usage. MEA solution and make-up water were used to maintain the concentration and CO₂ lean loading of MEA solution.

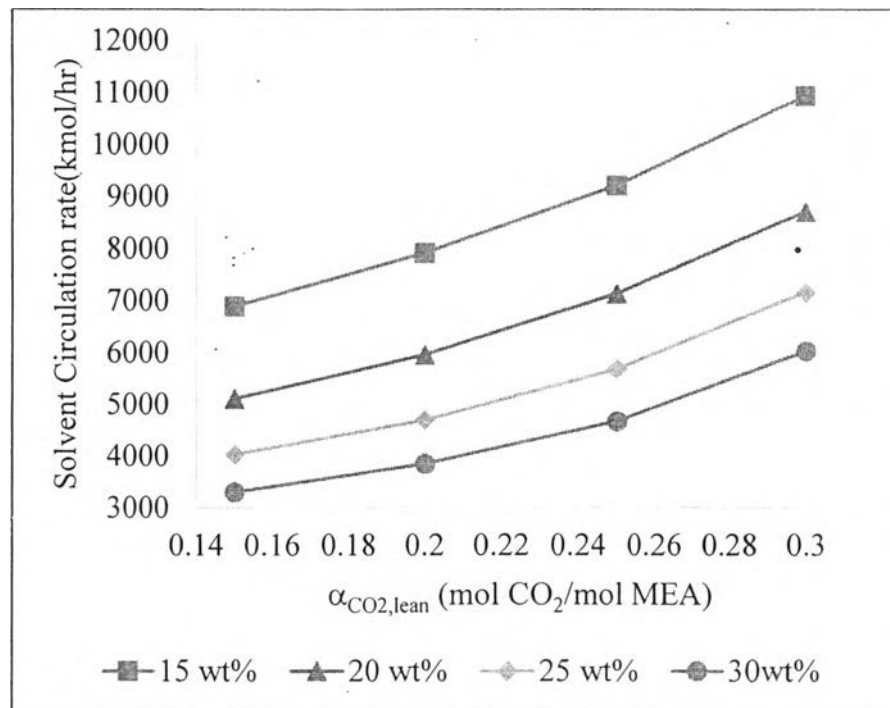


Figure 4.1 Influence of MEA concentration and lean loading on the circulation rate usage in LEANIN steam.

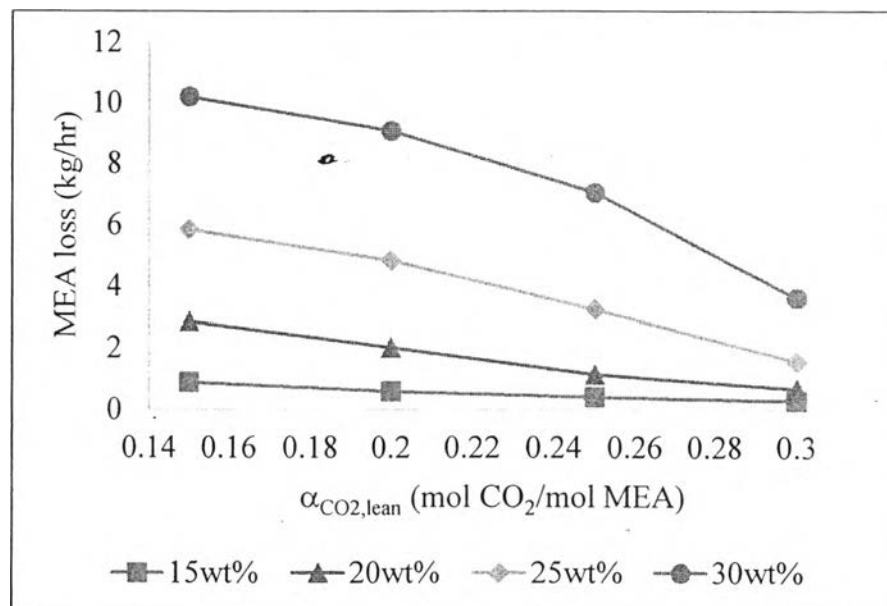


Figure 4.2 Influence of MEA concentration and lean loading on MEA loss in VENT GAS stream.

The result in Figure 4.1 showed that more concentration usage and less lean loading usage in lean MEA stream required less circulation rate in order to achieve 90 % CO₂ capture efficiency in the absorber section. On the other hand, high amount of MEA in the lean stream which is high concentration and low lean loading, caused significant amount of MEA loss in the vented gas stream as shown in Figure 4.2. The optimal condition must be considered before running the full plant. Regarding the optimization of CO₂ absorption section, 30 wt. % of MEA concentration and 0.2 lean loading were used to capture CO₂ from the flue gas. A simplified flow sheet development (absorber/stripper configuration) was shown in Figure 4.3.

Table 4.1 Flue gas composition from post-combustion

Temperature (°C)	46.1
Pressure (kPa)	115.1
Vapor fraction	1.0
Composition (%mol)	
N ₂	77.93
CO ₂	13.14
H ₂ O	8.92

The crucial parameter which affects the energy performance of MEA-based system, was CO₂ loading. Loading was an important parameter referring to mole of CO₂ carrying species over mole of MEA carrying species as displayed in Equation 4.1.

$$\alpha_{CO_2} = \frac{[CO_2] + [HCO_3^-] + [CO_3^{2-}] + [MEACOO^-]}{[MEA] + [MEA^+] + [MEACOO^-]} \quad (4.1)$$

4.1.2 Process Heat Integration

MEA-based CO₂ capture was optimized by GAMS program with stage-wise model (Yee and Grossmann, 1990) to generate HEN for the based-case process. GAMS program was modeled by using constant heat capacity. There was one

hot process stream; H1 and one cold process stream; C1 from the MEA-based scrubbing system (based-case which was the basic process without applying process integration), as shown in Figure 4.3, consuming heating and cooling duties of 9837.2 and 7154.5 kW, respectively. Heating and cooling duties were accounted from overall duties of the system including the reboiler heat duty and heater. 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 4.4 with exchanger of H1-C1 match and heating and cooling duty savings of 6386.4 and 3702.9 kW, respectively. This conceptual process design with process heat integration, shown in Figure 4.4, was validated by Aspen Plus simulator to ensure the feasibility of the process. The result showed that the relative error between conceptual process and validated process were very small.

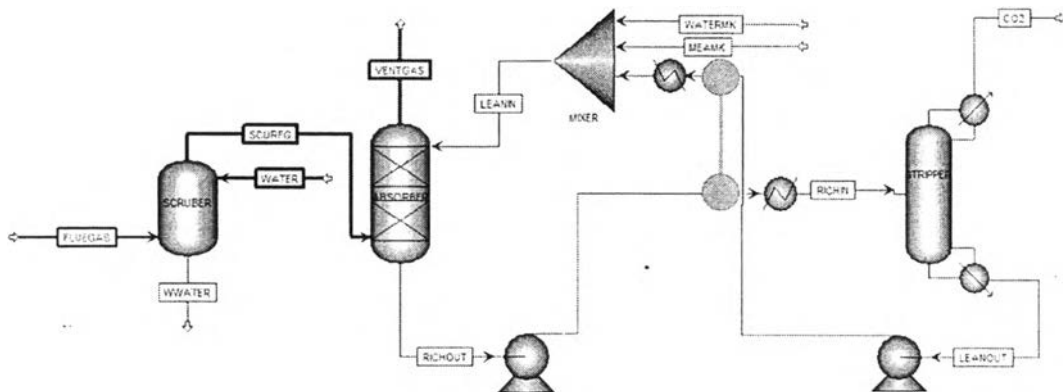


Figure 4.3 Validated process flow diagram of improved MEA-based scrubbing system (Aspen plus) with process heat integration.

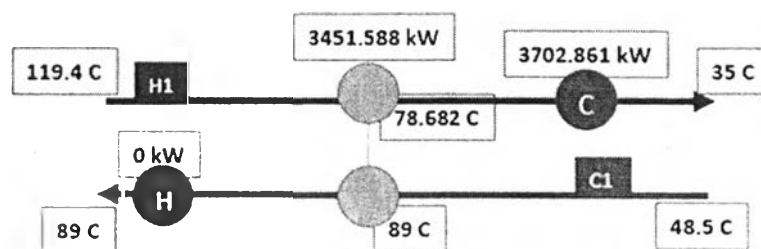


Figure 4.4 MEA based conceptual process integration from GAMS.

The validated result showed that energy requirement of the overall system was reduced around 40.6% compared to the MEA-based process without process integration. In addition, the savings in hot and cold utilities were 35.1% and 48.2%, respectively. Furthermore, regeneration energy of the stripper was 3963.8 kJ/kg CO₂. The stream summary of MEA-based process for capturing CO₂ from the flue gas was shown in Table 4.2.

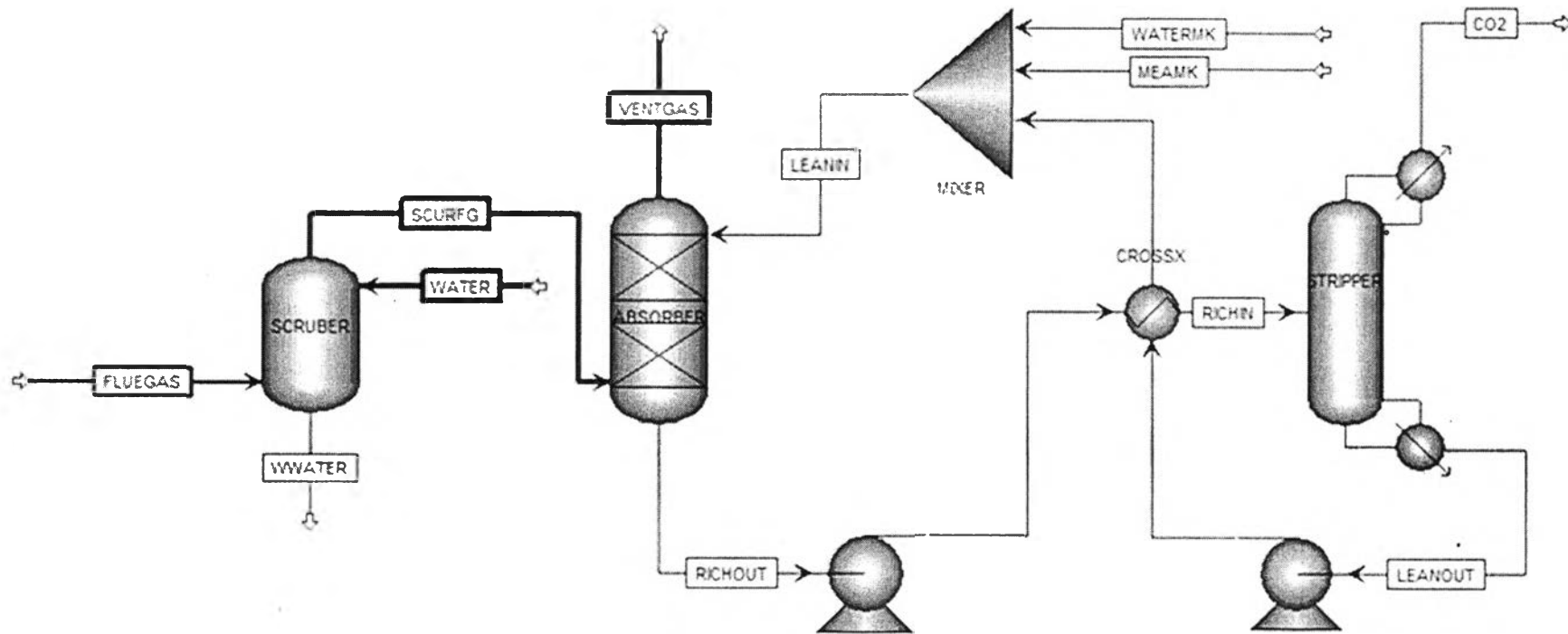


Figure 4.5 Simplified process flow diagram of MEA-based scrubbing system (Aspen plus).

Table 4.2a Stream summary of MEA-based CO₂ capture process

	Units	FLUEGAS	WATER	WWATER	SCURFG	LEANIN	VENTGAS
Phase:		Vapor	Liquid	Liquid	Vapor	Liquid	Vapor
Temperature	°C	142.000	30.000	46.100	46.100	35.000	64.823
Pressure	ATM	11	1.272	1.136	1.136	1.340	1
Vapor Fraction		1.000	0.000	0.000	1.000	0.000	1.000
Liquid Fraction		0.000	1.000	1.000	0.000	1.000	0.000
Solid Fraction		0.000	0.000	0.000	0.000	0.000	0.000
Mole Flow	KMOL/HR	1044.899	100.713	32.926	1112.685	3763.633	1119.820
Mass Flow	KG/HR	31297.870	1814.373	593.232	32519.010	90980.230	29230.710
Volume Flow	CUM/HR	3230.949	1.822	0.599	25621.790	93.325	31021.520
Enthalpy Flow	GCAL/HR	-14.685	-6.871	-2.237	-19.319	-265.357	-14.807
Component Mole Flow							
MEA	KMOL/HR	0.000	0.000	0.000	0.000	268.868	0.149
CO ₂	KMOL/HR	146.286	0.000	0.002	146.284	0.000	14.597
N ₂	KMOL/HR	867.266	0.000	0.000	867.266	0.000	867.256
H ₂ O	KMOL/HR	31.347	100.713	32.924	99.136	3314.035	237.819
MEA ⁺	KMOL/HR	0.000	0.000	0.000	0.000	91.343	0.000
H ₃ O ⁺	KMOL/HR	0.000	0.000	0.000	0.000	0.000	0.000
OH ⁻	KMOL/HR	0.000	0.000	0.000	0.000	0.019	0.000
MEACOO ⁻	KMOL/HR	0.000	0.000	0.000	0.000	86.620	0.000
HCO ₃ ⁻	KMOL/HR	0.000	0.000	0.000	0.000	0.791	0.000
CO ₃ ²⁻	KMOL/HR	0.000	0.000	0.000	0.000	1.957	0.000

Table 4.2b Stream summary of MEA-based CO₂ capture process

	Units	RICHOUT	S4	RICHIN	CO2	LEANOUT	S1
Phase:		Liquid	Liquid	Mixed	Vapor	Liquid	Liquid
Temperature	°C	48.415	48.460	89.000	24.996	119.398	119.390
Pressure	ATM	1	2.36	2.36	1.7	1.7	1.34
Vapor Fraction		0.000	0.000	0.001	1.000	0.000	0.000
Liquid Fraction		1.000	1.000	0.999	0.000	1.000	1.000
Solid Fraction		0.000	0.000	0.000	0.000	0.000	0.000
Mole Flow	KMOL/HR	3624.922	3624.923	3629.930	134.207	3622.365	3622.365
Mass Flow	KG/HR	94268.540	94268.540	94268.540	5840.859	88427.680	88427.680
Volume Flow	CUM/HR	100.417	100.415	143.808	1906.252	97.031	97.030
Enthalpy Flow	GCAL/HR	-269.868	-269.864	-266.895	-12.532	-249.569	-249.570
Component Mole Flow							
MEA	KMOL/HR	24.061	24.070	36.760	0.000	270.907	270.906
CO ₂	KMOL/HR	0.111	0.112	5.119	131.681	0.080	0.080
N ₂	KMOL/HR	0.010	0.010	0.010	0.010	0.000	0.000
H ₂ O	KMOL/HR	3157.351	3157.345	3155.635	2.516	3172.552	3172.552
MEA ⁺	KMOL/HR	222.445	222.442	216.469	0.000	89.516	89.516
H ₃ O ⁺	KMOL/HR	0.000	0.000	0.000	0.000	0.000	0.000
OH ⁻	KMOL/HR	0.001	0.001	0.001	0.000	0.017	0.017
MEACOO ⁻	KMOL/HR	200.176	200.170	193.452	0.000	86.259	86.259
HCO ₃ ⁻	KMOL/HR	19.267	19.274	21.950	0.000	2.828	2.828
CO ₃ ²⁻	KMOL/HR	1.501	1.499	0.533	0.000	0.206	0.206

Table 4.2c Stream summary of MEA-based CO₂ capture process

	Units	WATERMK	MEAMK	S5	RLEANIN
Phase:		Liquid	Liquid	Mixed	Liquid
Temperature	°C	35.000	35.000	112.026	35.000
Pressure	ATM	1.34	1.34	1.34	1.34
Vapor Fraction		0.000	0.000	0.009	0.000
Liquid Fraction		1.000	1.000	0.991	1.000
Solid Fraction		0.000	0.000	0.000	0.000
Mole Flow	KMOL/HR	142.914	0.149	3764.399	3763.544
Mass Flow	KG/HR	2574.629	9.076	90978.910	90978.910
Volume Flow	CUM/HR	2.590	0.009	885.571	93.324
Enthalpy Flow	GCAL/HR	-9.737	-0.010	-259.219	-265.352
Component Mole Flow					
MEA	KMOL/HR	0.000	0.149	272.407	268.856
CO ₂	KMOL/HR	0.000	0.000	0.855	0.000
N ₂	KMOL/HR	0.000	0.000	0.000	0.000
H ₂ O	KMOL/HR	142.914	0.000	3313.805	3313.947
MEA ⁺	KMOL/HR	0.000	0.000	88.794	91.349
H ₃ O ⁺	KMOL/HR	0.000	0.000	0.000	0.000
OH ⁻	KMOL/HR	0.000	0.000	0.018	0.019
MEACOO ⁻	KMOL/HR	0.000	0.000	85.629	86.626
HCO ₃ ⁻	KMOL/HR	0.000	0.000	2.633	0.791
CO ₃ ²⁻	KMOL/HR	0.000	0.000	0.257	1.957

4.1.3 Key Process Simulation Specifications

A summary of integrated process simulation inputs are displayed in Table 4.3.

Table 4.3a MEA-based CO₂ capture plant key process simulation specifications

FLUEGAS (Post-Combustion Flue Gas Stream)	Temperature (°C)	142
	Pressure (atm)	11
	Molar Flow (kmol/hr)	1044.9
	Composition (mole fraction)	
	N ₂	0.83
	CO ₂	0.14
	H ₂ O	0.03
	MEA	-
S3 (Flue Gas Stream from Scrubber)	Temperature (°C)	46.1
	Pressure (atm)	1.136
	Molar Flow (kmol/hr)	1112.69
	Composition (mole fraction)	
	N ₂	0.79
	CO ₂	0.12
	H ₂ O	0.09
LEANMEA (Lean Amine Stream)	Temperature (°C)	35
	Pressure (atm)	1.34
	Molar Flow (kmol/hr)	3763.6
	Composition (mole fraction)	
	CO ₂	2.2552E-08
	H ₂ O	0.880542
	MEA	0.0714384
	MEA ⁺	0.0242698
	H ₃ O ⁺	3.3217E-12
	MEACOO ⁻	0.230148

Table 4.3b MEA-based CO₂ capture plant key process simulation specifications

Absorber	Number of Stages	25
	Pressure (atm)	1
	CO ₂ Removal (%)	90.02
	Rich Amine Loading	0.49
Rich Amine Pump	Outlet Pressure (atm)	2.36
Stripper Pre-heater	Temperature (°C)	89
	Pressure (atm)	2.36
Stripper	Number of Stages	25
	Pressure (atm)	1.7
	Reboiler Temperature (°C)	119.4
	Lean Amine Loading	0.2
CO ₂ (CO ₂ Outlet Stream)	Temperature (°C)	25
	Pressure (atm)	1.7
	Molar Flow (kmol/hr)	134.207
	Composition (mole fraction)	
	N ₂	7.52643E-12
	CO ₂	0.981177
	H ₂ O	0.0187473
MEA	4.4372E-12	
Condenser	Temperature (°C)	25

Table 4.3c MEA-based CO₂ capture plant key process simulation specifications

Lean Amine Pump	Outlet Pressure (atm)	1.34
MEAMK (MEA Makeup Stream)	Temperature (°C)	35
	Pressure (atm)	1.34
	Molar Flow (kmol/hr)	0.148583
	Composition (mole fraction)	
	MEA	1
H2OMK (Water Makeup Stream)	Temperature (°C)	35
	Pressure (atm)	1.34
	Molar Flow (kmol/hr)	142.914
	Composition (mole fraction)	
	H ₂ O	1
Lean Amine Cooler	Outlet Temperature (°C)	35

4.1.4 Economic Evaluation

The economic evaluation of the process indicated the feasibility of the process design. In this study, the economics of the MEA process were divided into two parts including the capital investment and the annual costs of the plant. The purchased equipment cost was mainly performed on a commercial package in Aspen Plus v.8.6. The capital investment and operating costs were estimated using basic utility costs reported by Hassan et al. (2007). The important assumptions and specification used in carrying out the economic evaluation of MEA based CO₂ capture process were given below:

- Currency description: US dollars (\$)
- Operating hours per year: 8000
- Interest rate: 7 percent per Year
- Labor cost: \$ 20/hr/operator
- Supervisor cost \$ 35/hr/supervisor
- Electricity cost: \$ 0.06/kWh
- Steam cost: \$ 9.18/ton

- Cooling water cost: \$ 0.015/m³
- MEA cost: \$ 1.44/kg
- Operating charges: 25 percent of Operating labor costs
- Plant overhead cost: 50 percent of Operating labor and Maintenance costs
- General and administrative expenses: 8 percent of subtotal operating costs
- Working capital: 5 percent of Total capital investment
- Construction material for absorber and regenerator are stainless steel 304 in order to prevent the corrosion
- Industrial water price (OECD): \$ 0.00035/kg

4.1.4.1 Purchased Equipment Cost

The standard model or process equipment would be mapped and sized in Aspen plus economic software (Aspen plus v.8.6). The cost of each project equipment was estimated in order to evaluate the total cost of the entire capture plant. The detail data about purchased equipment costs was taken into account and then the basic economic factors based on Hassan et al. (2007) were used to estimate the capital investment and annual operating costs. The purchased equipment cost of MEA process with process integration was shown in Table 4.4.

Table 4.4 Summary of equipment cost estimation of MEA-based process (Aspen Plus)

Equipment	Type	Unit	Size Parameter	Size Unit	Cost(2013)	CEPCI	Cost(2014)	
CROSSX	Cross Exchanger	CROSSX	1,576	Ft ²	41,900	1.022	42,822	
COOLER	Cooler	COOLER	1,966	Ft ²	49,600	1.022	50,691	
LEANPUMP	Centrifugal	LEANPUMP	Head = 4.2	m	12,600	1.022	12,877	
RICHPUMP	Centrifugal	RICHPUMP	Head = 15	m	10,400	1.022	10,629	
ABSORBER	Packed	ABSORBER	Dia/H = 10,55.5	Ft.	989,900	1.022	1,011,678	
WATER SCURBBER	Horizontal Vessel	SCRUBER	Dia/H =7,12	Ft.	74,700	1.022	76,343	
STRIPPER	Packed	STRIPPER	Dia/H = 6,52	Ft.	343,800	1.022	351,364	
Total Purchased Equipment Cost (\$)								1,556,404

4.1.4.2 Capital Investment Cost

The summary of capital cost for MEA based CO₂ capture was shown in Table 4.5.

Table 4.5 Total capital investment cost of MEA-based process

Total Capital Investment			
1	Fixed Capital Investment		10,779,997
2	Working Capital		539,000
		Total TCI	11,075,338
Direct		Factor	Dollars (\$)
	Purchased Equipment Cost		1,556,404
	Purchased Equipment Installation	0.55	856,022
	Instrumentation and Controls (Installed)	1	1,556,404
	Piping (Installed)	1	1,556,404
	Electrical installations	0.15	233,461
	Yard Improvement	0.2	311,281
	Service Facilities (Installed)	0.8	1,245,123
	Land	0.08	124,512
		Total	7,439,611
Indirect	Engineering and Supervision	0.08	595,169
	Construction Expenses	0.1	743,961
	Contractor's Fees	0.08	595,169
	Contingency	0.15	1,406,087
		Total	3,340,386
Working Capital		0.05	539,000
	Total Capital Investment (\$)	Total	11,318,996

4.1.4.3 Annual Operating Cost

Raw material including MEA make up, water make up, and water for scrubbing section were discussed in this section. Moreover, utilities requirement for CO₂ capture system were clarified in Table 4.6. In last section, annual operating cost was estimated by many factors shown in Table 4.7.

Table 4.6 Utilities consumption summary of MEA based process

Parameters	Amount	Cost per year (\$)
Raw material		
Make up MEA (kg/yr)	72,608	104,556
Make up water (kg/yr)	20,597,032	7,209
Water for Scrubbing section (kg/yr)	14,514,960	5,080
Total		116,845
Utility		
Cooling water (m ³ /yr)	2,798,207	41,973
Heating stream (kg/yr)	88,907	816,163
Electricity (kWh)	89.713	43,062
Total		901,198

Table 4.7 Annual operating cost for MEA based process

Parameters	Cost per year (\$)
Raw material cost	116,845
Utility cost	901,198
Operating labor cost	640,000
Operating supervision cost	280,000
Maintenance and repair cost	400,000
Operating supplies and laboratory charge	230,000
Total Direct Production Cost	2,568,043
Plant overhead cost	660,000
General and administrative cost	258,243
Total Annual Cost	3,486,286

The annual cost of the integrated process was reduced by 13% and as a result of the savings in utility usage in the system of close to 34 %. The capital cost of integrated process reduced by 0.6 % compared to the process without heat integration. The overall results illustrated that the optimization of the based-case process and process integration application were beneficial in terms of savings in energy requirement and operating expenses of the process compared with basic process.

4.2 Aqueous Ammonia Based CO₂ Capture Process

4.2.1 Process Description and Optimization

In this study, the Redlich–Kwong equation of state and the Electrolyte-NRTL (Non-Random Two Liquid) model were used to compute the properties of the vapour phase and liquid phase, respectively. Flue gas from a 180 MW_e coal burning power plant with a flow rate of 32 ton/hr, and a composition of 84 % N₂, 12 % CO₂, and 4 % H₂O in standard volume which is equivalent to 77.93 % N₂, 13.14 % CO₂, and 8.92 % H₂O in mole% (Khonkaen et al., 2014) was simulated in this study. The flow sheet development was divided into two parts including the CO₂ capture system and the ammonia abatement system. CO₂ capture system was designed to 90 % CO₂ capture efficiency from the flue gas. The flow sheet was optimized by varying the concentration of ammonia solution in a range between 2 to 8 wt. % and CO₂ lean loading of ammonia solution from 0.20 to 0.35 mole CO₂/mole NH₃. Then, 98 % by weight of CO₂ purity entering storage section was specified by varying the reflux ratio (mass), distillation rate and liquid holdup in the stripping section. The ammonia abatement system was used to recycle the volatized ammonia and also minimize ammonia vent to the atmosphere due to restriction of environmental standards. Vented ammonia flow rate was kept below 2 kg/hr based on ammonia emission standards (Zhang and Guo, 2013). This limitation was set as the target of the absorber in the ammonia abatement system and achieved by varying the aqueous ammonia concentration at the high loading. Obviously, a sequential optimization was observed (Zhang and Guo, 2013).

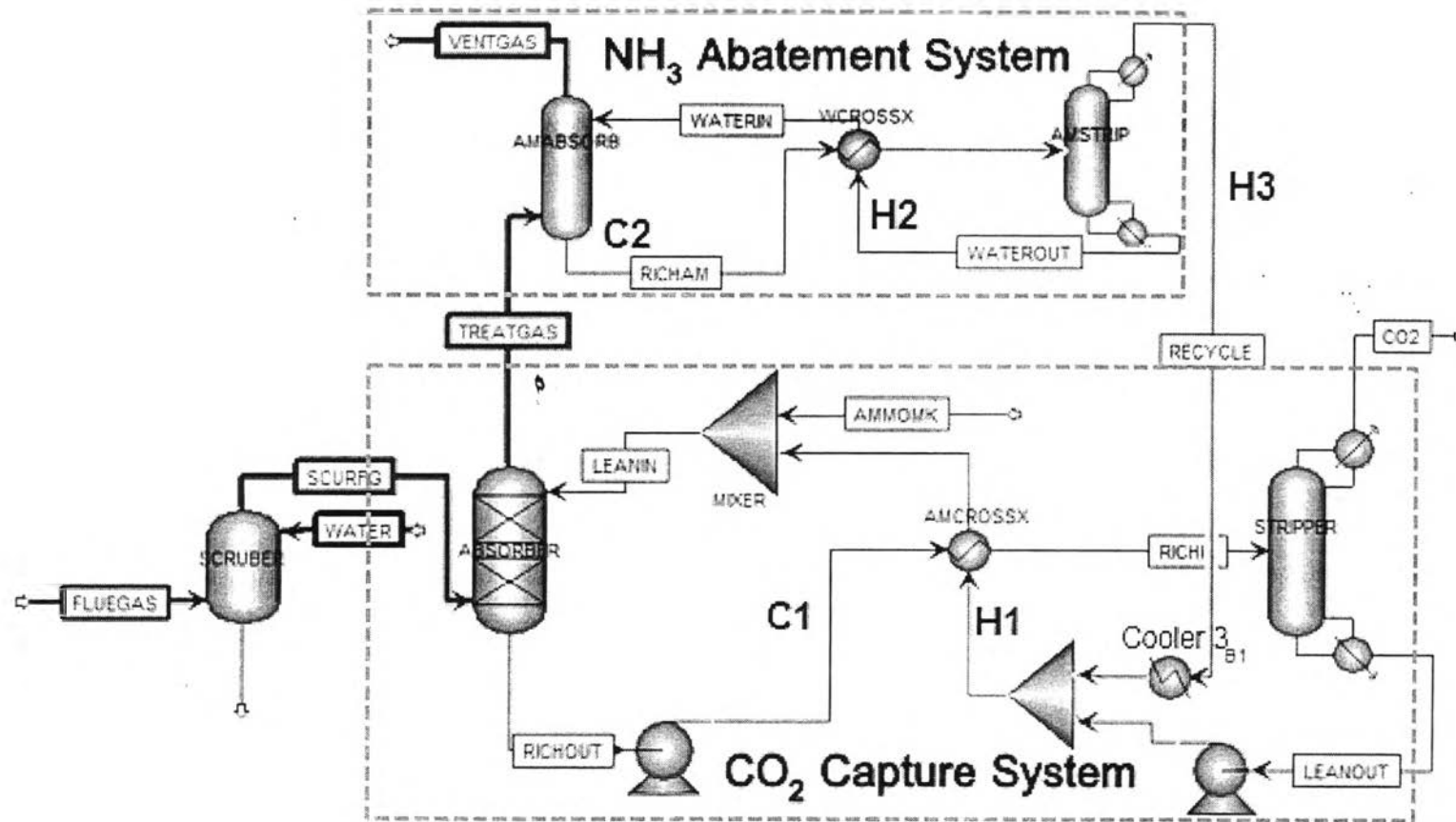


Figure 4.6 Simplified process flow diagram of aqueous ammonia-based scrubbing system.

4.2.1.1 Carbon-Dioxide Capture System

A simplified process flow diagram of CO₂ capture system was shown in Figure 4.6. At first, flue gas at high temperature from coal-fired power plant was cooled down to 46.1 °C with a pressure near atmospheric pressure (115.1 kPa) in the scrubbing section by cooling water before entering to the absorber. Then, the flue gas with CO₂ contacted the aqueous ammonia solution as counter-current flow to separate CO₂ from the flue gas stream. In the absorber column section, the equivalent equilibrium stages of the absorber were set at 20 stages.

Table 4.8 The parameters of the DZ-II-750Y structure packing (Haroun et al., 2012)

Specific surface area (m ² /m ³)	Void fraction (%)	Pressure drop (kPa/m)	Density (kg/m ³)	Liquid loading (m ³ /(m ² h))
750	87	0.46-0.66	210	0.2-20

The packing type was chosen as DZ-II-750Y for economic evaluation, one of the CY structured packings, which has high mass transfer efficiency (Haroun et al., 2012; Zhao et al., 2011) shown in Table 4.8.

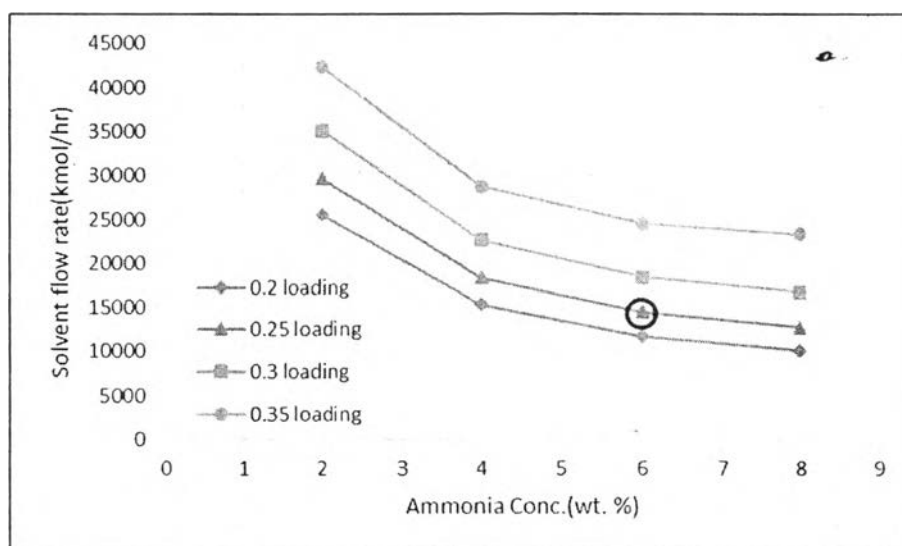


Figure 4.7 Effect of ammonia concentration and CO₂ loading on LEANIN stream to solvent flow rate in LEANIN stream.

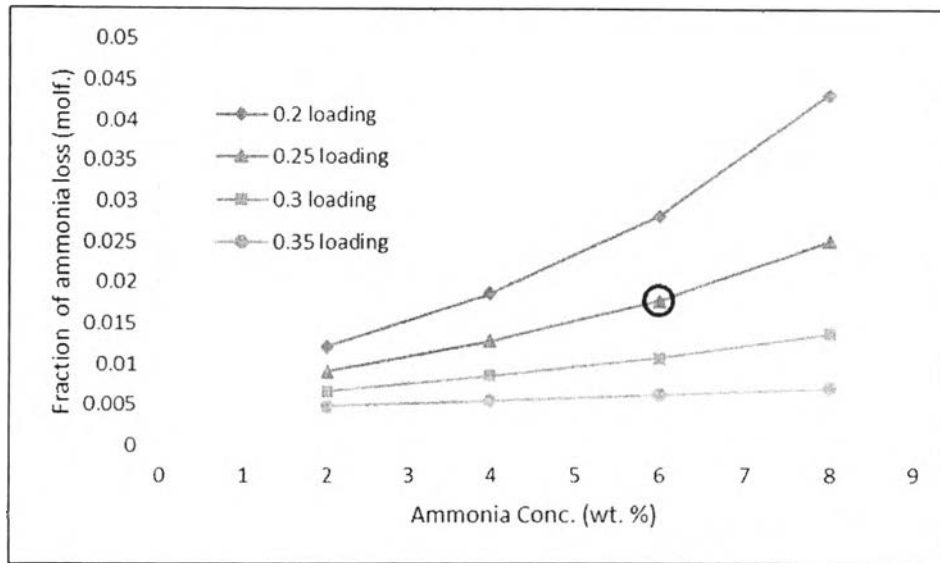


Figure 4.8 Effect of ammonia concentration and CO₂ loading on LEANIN stream to fraction of ammonia loss in TREATGAS stream.

It is well known that the annual cost is mainly due to the energy requirement from the regeneration of the solvent and utilities. Therefore, optimization of the solvent usage was adopted to find minimum-energy-usage condition for CO₂ capture process. Solvent circulation rate and fraction of ammonia loss (TREATGAS) were effectively related to the overall energy requirement of the system as shown in Figures 4.7 and 4.8. Solvent circulation rate and the fraction of ammonia loss were optimized by varying the ammonia concentration and CO₂ loading based on 90% CO₂ capture efficiency. The result showed more ammonia concentration in the solvent circulation, and this caused more fraction of ammonia loss in TREATGAS stream resulting in more energy requirement in the ammonia abatement system. Increasing the ammonia concentration led to a decrease in the required solvent flow rate. The crucial parameter which affected the energy performance of ammonia-based system was the loading. Loading refers to the moles of CO₂ carrying species over the moles of NH₃ carrying species as specified in Equation 4.2.

$$\text{Loading} = \frac{[\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{NH}_2\text{COO}^-]}{[\text{NH}_3] + [\text{NH}_4^+] + [\text{NH}_2\text{COO}^-]} \quad (4.2)$$

In case of increasing loading in the LEANIN stream, the fraction loss of ammonia decreased while the solvent flow rate decreased because of reduction in term of ammonia species and the availability to capture CO₂ from the flue gas. The optimal concentration of ammonia solution and CO₂ lean loading at 111 kPa and 25 °C were 6 wt. % and 0.25 mole CO₂/mole NH₃, respectively. The optimal condition resulted in a solvent flow rate and ammonia loss equal to 14666 kmol/hr and 16.75 kmol/hr, respectively. Rich CO₂ ammonia solution had a loading of approximately 0.36 mole CO₂/mole NH₃ left from the bottom of the absorber to the stripping section for regeneration. The rich CO₂ ammonia solution was pumped and heated up at around 120 kPa and 60 °C, respectively, before entering to the stripper. Heat from the reboiler was used to dissociate the chemical bonds of the formed carbamates and other compounds between ammonia and CO₂. Then, over 98 wt. % of CO₂ purity was stripped out at the top and the regenerated ammonia that exited from the bottom of the stripper. The condenser and reboiler temperatures were simulated at 25 °C and 89 °C, respectively. Ammonia solution was mostly recycled back to the absorber section in order to minimize the ammonia usage. Ammonia solution and make-up water were used to maintain the concentration and CO₂ lean loading of the aqueous ammonia solution.

4.2.1.1 Ammonia Abatement System

Process flow diagram of ammonia abatement system is shown in Figure 4.5. This system consists of an absorber to remove ammonia from the treated flue gas (TREATGAS stream) by using water, and a stripper to recover ammonia from the used absorbent (RICHAM stream). The TREATGAS stream is the flue gas with some ammonia contamination, leaves the absorber in CO₂ capture system and is then treated by counter-current flowing water stream with low-ammonia concentration and high CO₂ loading. The number of equivalent equilibrium stages of the absorber of this abatement system was set at 15 stages. The WATERIN stream at ambient condition with the flow rate, ammonia concentration and CO₂ loading of 832 kmol/hr, 9 ppm (by mass) and 1.2 mole CO₂/mole NH₃, respectively, were used to capture volatilized ammonia in TREAT GAS stream from the CO₂ capture system. The flow rate of the treated flue gas (VENTGAS stream) in this abatement system was around 1.7 kg/hr which was acceptable for environmental emission standards (Zhang and Guo, 2013).

The used absorbent stream with rich ammonia (RICHAM stream) from the bottom of the absorber was regenerated in the stripping section. After regeneration, the stream with rich ammonia (RECYCLE stream) from the top of stripper of the abatement system was recycled to the absorber of CO₂ capture system to save ammonia usage in the overall process. The regenerated absorbent stream with lean ammonia (WATEROUT stream) from the stripper of the abatement system was regenerated and sent to the ammonia absorber to minimize water usage in ammonia abatement system. The most important operating conditions of the main streams are shown in Table 4.9.

Table 4.9 Optimal operating parameters of main streams in overall CO₂ capture process

Streams	Optimal Operating Conditions
FLUEGAS	3.2 x 10 ⁵ kg/hr, at 46.1°C and 1.136 atm
LEANIN	2.70 x 10 ⁵ kg/hr, 6 wt. % NH ₃ and 0.25 CO ₂ loading at 25 °C and 1.1 atm
TREATGAS	2.6 x 10 ⁴ kg/hr, at 29 °C and 1 atm
VENTGAS	2.6 x 10 ⁴ kg/hr at 32 °C and 1 atm
CO ₂	6 x 10 ³ kg/hr, 98 wt. % CO ₂ at 25 °C and 1 atm

4.2.2 Process Heat Integration

In the scratch process has three hot process streams from the scratch; H1, H2 and H3, and two cold process streams; C1 and C2, from the simplified CO₂ capture process, as shown in Figure 4.6, consumed heating and cooling duties of 24567 and 25284 kW, respectively. Heat integration was applied the same method with MEA based process by GAMS program using the stage-wise model (Yee and Grossmann, 1990). The result from the GAMS model was the conceptual HEN design as shown in Figure 4.9 with two exchangers for H1-C1 and H2-C2 matches and heating and cooling duty savings of 9987 and 10705 kW, respectively. This conceptual process design with process heat integration, shown in Figure 4.9, was validated by Aspen Plus (Figure 4.10) simulator to ensure the feasibility of the process. The results showed

that the relative error between the conceptual process and the validated process was very small.

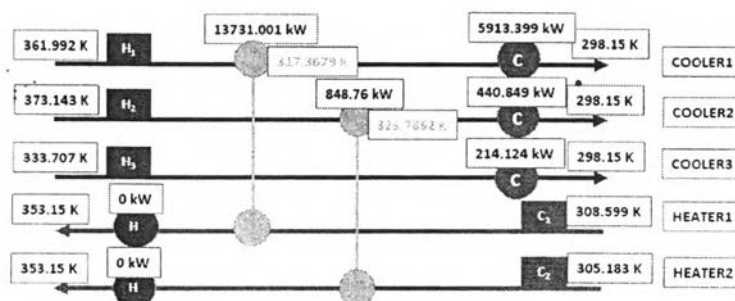


Figure 4.9 Aqueous ammonia based conceptual process integration from GAMS.

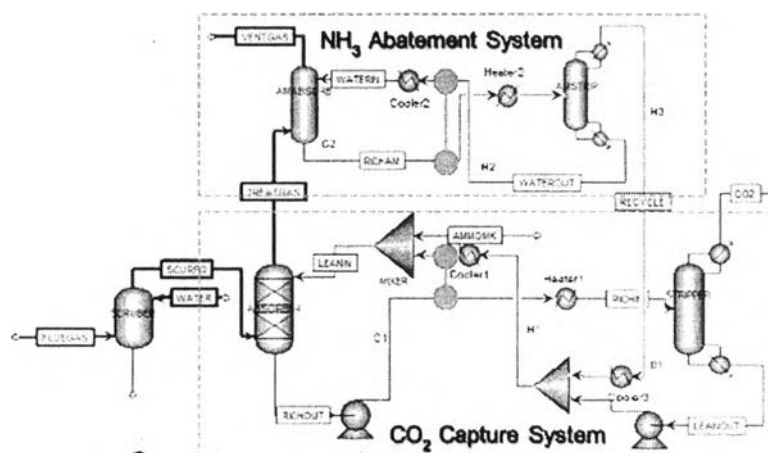


Figure 4.10 Validated process flow diagram of improved aqueous ammonia-based scrubbing system (Aspen plus) with process heat integration.

The validated result showed that the energy requirement of the overall system was reduced by 58.1% compared to the ammonia-based process without process integration. The saving in hot and cold utilities were 59.3% and 57.7%, respectively. Furthermore, the overall energy used in regeneration of both CO₂ capture system and NH₃ abatement system was 8601 kJ/kg CO₂ which was a bit higher than the value reported as 8472 kJ/kg CO₂ by Zhang and Guo (2013) for a 550 MW plant size.

Table 4.10a Stream summary of aqueous ammonia based CO₂ capture process

	Units	AMMKI	CO2	CRECYCAM	ELEANIN	EWATER	FLUEGAS
Phase:		VAPOR	VAPOR	MIXED	LIQUID	LIQUID	MIXED
Temperature	°C	25	25	25	25	25	46.1
Pressure	ATM	1.095	1.000	1.000	1.095	1.000	1.136
Vapor Frac		1.000	1.000	0.384	0.000	0.000	1.000
Liquid Frac		0.000	0.000	0.616	1.000	1.000	0.000
Solid Frac		0.000	0.000	0.000	0.000	0.000	0.000
Enthalpy	CAL/SEC	-25269.39	-3582300.00	-259620.00	-268790000.00	-15795000.00	-5365200.00
Total Flow	KMOL/HR	8.289	142.000	19.832	14471.970	832.920	1112.813
Total Flow	KG/HR	141.158	6053.697	524.527	270255.000	15005.640	32521.320
Total Flow	L/MIN	3060.467	57579.660	3091.412	4585.593	250.800	427111.000
Mole Flow							
H ₂ O	KMOL/HR	0.000	3.545	3.134	13437.470	832.903	99.263
NH ₃	KMOL/HR	8.289	3.780	8.324	517.720	0.000	0.000
CO ₂	KMOL/HR	0.000	134.577	0.005	0.001	0.002	146.284
H ₃ O ⁺	KMOL/HR	0.000	0.000	0.000	0.000	0.000	0.000
OH ⁻	KMOL/HR	0.000	0.000	0.000	0.048	0.000	0.000
NH ₄ ⁺	KMOL/HR	0.000	0.000	4.193	278.711	0.007	0.000
NH ₂ COO ⁻	KMOL/HR	0.000	0.000	4.137	155.698	0.000	0.000
HCO ₃ ⁻	KMOL/HR	0.000	0.000	0.007	41.692	0.007	0.000
CO ₃ ²⁻	KMOL/HR	0.000	0.000	0.024	40.637	0.000	0.000
N ₂	KMOL/HR	0.000	0.098	0.008	0.000	0.000	867.266
NH ₄ HCO ₃ S	KMOL/HR	0.000	0.000	0.000	0.000	0.000	0.000

Table 4.10b Stream summary of aqueous ammonia based CO₂ capture process

	Units	TREATGAS	H2OMK2	LEANAM	LEANOUT	RAMIN	RECYCAM
Phase:		VAPOR	LIQUID	LIQUID	LIQUID	MIXED	VAPOR
Temperature	°C	28.8	25	100	89	80	60.6
Pressure	ATM	1.000	1.000	1.000	1.000	1.184	1.000
Vapor Frac		1.000	0.000	0.000	0.000	0.000	1.000
Liquid Frac		0.000	1.000	1.000	1.000	1.000	0.000
Solid Frac		0.000	0.000	0.000	0.000	0.000	0.000
Enthalpy	CAL/SEC	-987710.00	-216000.00	-15271000.00	-265050000.00	-15625000.00	-208470.00
Total Flow	KMOL/HR	933.558	11.390	821.527	14512.360	841.362	24.000
Total Flow	KG/HR	25851.460	205.201	14800.040	270871.000	15324.570	524.527
Total Flow	L/MIN	385211.000	3.430	257.446	4739.570	266.375	10892.860
Mole Flow							
H ₂ O	KMOL/HR	35.020	11.390	821.519	13433.050	821.638	3.166
NH ₃	KMOL/HR	16.769	0.000	0.006	604.847	11.223	16.653
CO ₂	KMOL/HR	14.601	0.000	0.000	0.234	0.008	4.173
H ₃ O ⁺	KMOL/HR	0.000	0.000	0.000	0.000	0.000	0.000
OH ⁻	KMOL/HR	0.000	0.000	0.001	0.042	0.002	0.000
NH ₄ ⁺	KMOL/HR	0.000	0.000	0.001	239.290	4.317	0.000
NH ₂ COO ⁻	KMOL/HR	0.000	0.000	0.000	87.443	1.119	0.000
HCO ₃ ⁻	KMOL/HR	0.000	0.000	0.000	143.107	2.897	0.000
CO ₃ ²⁻	KMOL/HR	0.000	0.000	0.000	4.349	0.149	0.000
N ₂	KMOL/HR	867.168	0.000	0.000	0.000	0.008	0.008
NH ₄ HCO ₃ S	KMOL/HR	0.000	0.000	0.000	0.000	0.000	0.000

Table 4.10c Stream summary of aqueous ammonia based CO₂ capture process

	Units	RICHAM	RICHIN	RICHOUT	RLEANIN	RWATER	SI
Phase:		LIQUID	MIXED	LIQUID	LIQUID	LIQUID	LIQUID
Temperature	°C	31.9	80	35.9	25	25	89
Pressure	ATM	1.000	1.184	1.000	1.000	1.000	1.095
Vapor Frac		0.000	0.000	0.000	0.000	0.000	0.000
Liquid Frac		1.000	1.000	1.000	1.000	1.000	1.000
Solid Frac		0.000	0.000	0.000	0.000	0.000	0.000
Enthalpy	CAL/SEC	-15828000.000	-269890000.000	-273170000.000	-270030000.000	-15795000.000	-265050000.000
Total Flow	KMOL/HR	841.359	14520.170	14519.960	14540.240	832.917	14512.300
Total Flow	KG/HR	15324.570	276924.000	276924.000	271536.000	15005.250	270871.000
Total Flow	L/MIN	259.629	4811.864	4787.519	4608.358	250.798	4758.852
Mole Flow							
H ₂ O	KMOL/HR	824.556	13337.440	13497.880	13500.830	832.909	13450.100
NH ₃	KMOL/HR	8.418	437.922	274.079	520.402	0.005	588.338
CO ₂	KMOL/HR	0.005	0.627	0.417	0.001	0.000	0.175
H ₃ O ⁺	KMOL/HR	0.000	0.000	0.000	0.000	0.000	0.000
OH ⁻	KMOL/HR	0.001	0.015	0.006	0.048	0.001	0.039
NH ₄ ⁺	KMOL/HR	4.202	374.990	378.194	279.649	0.001	238.689
NH ₂ COO ⁻	KMOL/HR	4.040	122.448	283.087	156.469	0.000	104.552
HCO ₃ ⁻	KMOL/HR	0.096	240.742	77.313	42.539	0.000	126.713
CO ₃ ²⁻	KMOL/HR	0.033	5.893	8.894	40.296	0.000	3.692
N ₂	KMOL/HR	0.008	0.098	0.098	0.008	0.000	0.000
NH ₄ HCO ₃ S	KMOL/HR	0.000	0.000	0.000	0.000	0.000	0.000

Table 4.10d Stream summary of aqueous ammonia based CO₂ capture process

	Units	S2	S3	S4	S5	S6	VENTGAS
Phase:		LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	VAPOR
Temperature	°C	25	100	32	35.5	25	31.8
Pressure	ATM	1.095	1.000	1.184	1.184	1.000	1.000
Vapor Frac		0.000	0.000	0.000	0.000	0.000	1.000
Liquid Frac		1.000	1.000	1.000	1.000	1.000	0.000
Solid Frac		0.000	0.000	0.000	0.000	0.000	0.000
Enthalpy	CAL/SEC	-269750000.00	-15271000.00	-15828000.00	-273170000.00	-15579000.00	-954890.00
Total Flow	KMOL/HR	14512.120	821.527	841.354	14519.580	821.527	920.958
Total Flow	KG/HR	270871.000	14800.040	15324.570	276924.000	14800.040	25532.530
Total Flow	L/MIN	4591.777	257.446	256.682	4663.783	247.368	383836.000
Mole Flow							
H ₂ O	KMOL/HR	13497.220	821.519	822.268	13396.220	821.519	43.244
NH ₃	KMOL/HR	503.828	0.006	9.883	355.824	0.005	0.117
CO ₂	KMOL/HR	0.001	0.000	0.000	0.033	0.000	10.437
H ₃ O ⁺	KMOL/HR	0.000	0.000	0.000	0.000	0.000	0.000
OH ⁻	KMOL/HR	0.046	0.001	0.002	0.011	0.001	0.000
NH ₄ ⁺	KMOL/HR	275.892	0.001	5.021	397.712	0.001	0.000
NH ₂ COO ⁻	KMOL/HR	151.859	0.000	1.756	181.823	0.000	0.000
HCO ₃ ⁻	KMOL/HR	42.559	0.000	1.571	159.830	0.000	0.000
CO ₃ ²⁻	KMOL/HR	40.714	0.000	0.846	28.024	0.000	0.000
N ₂	KMOL/HR	0.000	0.000	0.008	0.098	0.000	867.160
NH ₄ HCO ₃ S	KMOL/HR	0.000	0.000	0.000	0.000	0.000	0.000

4.2.2 Key Process Simulation Specifications

A summary of simulation inputs are displayed in Table 4.11.

Table 4.11a Aqueous ammonia based CO₂ capture plant key process simulation specifications

FLUEGAS (Post-combustion Flue Gas Stream)	Temperature (°C)	142
	Pressure (atm)	11
	Molar Flow (kmol/hr)	1044.9
	Composition (mole fraction)	
	N ₂	0.83
	CO ₂	0.14
	H ₂ O	0.03
	NH ₃	-
SCURFG (Flue Gas Stream from Scrubber)	Temperature (°C)	46.1
	Pressure (atm)	1.136
	Molar Flow (kmol/hr)	1112.8
	Composition (mole fraction)	
	N ₂	0.78
	CO ₂	0.13
	H ₂ O	0.09
LEANIN (Lean Ammonia Stream)	Temperature (°C)	25
	Pressure (atm)	1.095
	Molar Flow (kmol/hr)	14235.86
	Ammonia Concentration (wt. %)	6
	CO ₂ loading (mole CO ₂ / mole NH ₃)	0.25
RICHOUT (Rich Ammonia Stream)	Temperature (°C)	36
	Pressure (atm)	1
	CO ₂ loading (mole CO ₂ / mole NH ₃)	0.4

Table 4.11b Aqueous ammonia based CO₂ capture plant key process simulation specifications

TREATGAS (Treat gas steam from CO ₂ absorber)	Temperature (°C)	29
	Pressure (atm)	1
	Mass Flow (kg/hr)	25851
	Composition (mass fraction)	
	N ₂	0.94
	CO ₂	0.03
	H ₂ O	0.02
	NH ₃	0.01
ABSORBER (CO ₂ Abated Absorber)	Number of Stages	20
	Pressure (atm)	1
	CO ₂ Removal (%)	90.02
	Rich Amine Loading	0.4
Rich Amine Pump	Outlet Pressure (atm)	1.18
Stripper Pre-heater	Temperature (°C)	80
	Pressure (atm)	1.18
STRIPPER (CO ₂ Abated Stripper)	Number of Stages	25
	Pressure (atm)	1
	Reboiler Temperature (°C)	89
	Lean Amine Loading	0.25
	Condenser Temperature (°C)	25
CO ₂ (CO ₂ Outlet Stream)	Temperature (°C)	25
	Pressure (atm)	1
	Molar Flow (kmol/hr)	142
	Composition (mole fraction)	
	N ₂	trace
	CO ₂	0.98
	H ₂ O	0.01
	MEA	0.01

Table 4.11c Aqueous ammonia based CO₂ capture plant key process simulation specifications

WATERIN (Lean Water Stream)	Temperature (°C)	25
	Pressure (atm)	1
	CO ₂ loading	1.2
	Molar Flow (kmol/hr)	833
	Composition (mole fraction)	
	N ₂	trace
	CO ₂	trace
	H ₂ O	1
	NH ₃	trace
VENTGAS (Vent gas Stream in ammonia abatement system)	Temperature (°C)	31.8
	Pressure (atm)	1
	Molar Flow (kmol/hr)	921
	Composition (mole fraction)	
	N ₂	0.94
	NH ₃	trace
	CO ₂	0.01
	H ₂ O	0.05
RICHAM (Rich Water Stream)	Temperature (°C)	32
	Pressure (atm)	1
	Molar Flow (kmol/hr)	841
AMABSORB (Ammonia Abated Absorber)	Number of Stages	15
	Pressure (atm)	1

Table 4.11d Aqueous ammonia based CO₂ capture plant key process simulation specifications

AMSTRIP (Ammonia Abated Stripper)	Number of Stages	15
	Pressure (atm)	1
	Reboiler Temperature (°C)	100
	Condenser Temperature (°C)	25
	Lean Amine Loading	1.2
WRP (Water Rich Pump)	Outlet Pressure (atm)	1.18
WCROSSX (Stripper Pre-heater)	Temperature (°C)	80
	Pressure (atm)	1.184
RECYCLE (Recycled NH₃ Stream)	Temperature (°C)	61
	Pressure (atm)	1
	Molar Flow (kmol/hr)	24
	Composition (mole fraction)	
	N ₂	trace
	CO ₂	0.17
	H ₂ O	0.13
NH ₃	0.69	

4.2.4 Economic Evaluation

The economic evaluation of aqueous ammonia process was estimated by the same methodology with MEA based process. The additional assumptions and specification used in carrying out the economic evaluation of aqueous ammonia based CO₂ capture process were given below:

- Ammonia cost: \$ 0.456/kg (ICIS)

4.1.4.1 *Purchased Equipment Cost*

The purchased equipment cost of MEA process with process integration was shown in Table 4.12.

Table 4.12 Summary of equipment cost estimation of aqueous ammonia-based process (Aspen Plus)

Equipment	Type	Unit	Size Parameter	Size Unit	Cost(2013)	CEPCI	Cost(2014)
WATER SCURBBER	Horizontal Vessel	SCRUBER	Dia/H =7,12	Ft.	74,700	1.022	76,343
CO ₂ ABSORBER	Packed	ABSORBER	Dia/H = 10,40.5	Ft.	801,600	1.022	819,235
CO ₂ RICH PUMP	Centrifugal	CO2RP	Head = 2	m	15,300	1.022	15,637
CO ₂ CROSSX	Cross Exchanger	AMCROSSX	19,636	Ft ²	359,700	1.022	367,613
CO ₂ STRIPPER	Packed	STRIPPER	Dia/H = 9,44.5	Ft	871,800	1.022	890,980
CO ₂ LEANPUMP	Centrifugal	CO2LP	Head = 1	m	15,200	1.022	15,534
CO ₂ PRE-COOLER	Cooler	CO2CR	72,811	Ft ²	1,299,700	1.022	1,328,293
NH ₃ ABSORBER	Packed	AMABSORB	Dia/H = 7.5,34	Ft	342,900	1.022	350,444
NH ₃ RICH PUMP	Centrifugal	AMRP	Head = 2	m	5,700	1.022	5,825
NH ₃ CROSSX	Cross Exchanger	WCROSSX	556	Ft ²	22,800	1.022	23,302
NH ₃ STRIPPER	Packed	AMSTRIP	Dia/H = 3.5,31.5	Ft.	224,500	1.022	229,439
NH ₃ LEANPUMP	Centrifugal	AMLP	Head = 1	m	6,900	1.022	7,052
AMMONIA PRE-COOLER	Cooler	AMCR	2,270	Ft ²	57,700	1.022	58,969
RECYCLED PRE-COOLER	Cooler	RECCR	420	Ft ²	19,600	1.022	20,031
Total purchased equipment cost (\$)							4,208,698

4.1.4.2 Capital Investment Cost

The summary of capital cost for aqueous ammonia based CO₂ capture was shown in Table 4.13.

Table 4.13 Total capital investment cost of aqueous ammonia-based process

Total Capital Investment			
1	Fixed Capital Investment		29,150,368
2	Working Capital		1,457,518
		Total TCI	29,949,010
Direct		Factor	Dollars (\$)
	Purchased Equipment Cost		4,208,698
	Purchased Equipment Installation	0.55	2,314,784
	Instrumentation and Controls (Installed)	1	4,208,698
	Piping (Installed)	1	4,208,698
	Electrical installations	0.15	631,305
	Yard Improvement	0.2	841,740
	Service Facilities (Installed)	0.8	3,366,958
	Land	0.08	336,696
		Total	20,117,576
Indirect	Engineering and Supervision	0.08	1,609,406
	Construction Expenses	0.1	2,011,758
	Contractor's Fees	0.08	1,609,406
	Contingency	0.15	3,802,222
		Total	5,230,570
Working Capital		0.05	1,457,518
	Total Capital Investment (\$)	Total	30,607,887

4.1.4.3 Annual Operating Cost

Raw material including ammonia make up, water make up, and water for scrubbing section were discussed in this section. Moreover, utilities requirement for CO₂ capture system were clarified in Table 4.14. In last section, annual operating cost was estimated by many factor showed in Table 4.15.

The result showed that the annual cost of the integrated process was reduced by 26.5% and resulted from savings in utility usage in the system of close to 58 %. The capital cost of integrated process increased by 39 % compared to the process without heat integration. The overall results illustrated that the optimization of the based-case process and process integration application were beneficial in terms of savings in energy requirement and operating expenses of the process compared with basic process.

Table 4.14 Utilities consumption summary of aqueous ammonia based process

Parameters	Amount	Cost per year (\$)
Raw material		
Make up ammonia (kg/yr)	1,129,264	514,944
Make up water (kg/yr)	1,641,608	575
Water for Scrubbing section (kg/yr)	14,514,960	5,080
Total		520,599
Utility		
Cooling water (m ³ /yr)	7,716,850	115,753
Heating steam (kg/yr)	172,002	1,578,980
Electricity (kWh)	305.774	146,772
Total		1,841,505

Table 4.15 Annual operating cost for aqueous ammonia based process

Parameters	Cost per year (\$)
Raw material cost	520,599
Utility cost	1,841,505
Operating labor cost	640,000
Operating supervision cost	280,000
Maintenance and repair cost	400,000
Operating supplies and laboratory charge	230,000
Total Direct Production Cost	3,912,104
Plant overhead cost	660,000
General and administrative cost	365,768
Total Annual Cost	4,937,873

4.3 Ionic Liquid EmimAc based CO₂ Capture Process (Khonkaen et al., 2014)

4.3.1 Process Description and Optimization

IL's has been considered as alternative solvent for capturing huge amount CO₂. IL's are salts in liquid state which is melting point generally below 100 °C. ILs can be possibly tuned to have special properties by adjusting the cation and anion in their molecules for many applications especially absorbent for CO₂ capture process. Most of IL's act as physical absorbent (conventional ILs) that is not appropriate to capture CO₂ at low partial pressure from post-combustion. To overcome this problem, many researchers have modified the structure of IL's by adding amine functional group in ILs which greatly improves CO₂ absorption capacity. In addition, the presence of amine group in the IL structure causes high enthalpy of reaction on this type of ILs. For example, the enthalpy of reaction with CO₂ of trihexyl(tetradecyl)phosphonium proline ([P66614][Pro]) is at -80 kJ/mole that is nearly one of MEA at -85 kJ/mol. Moreover, this type of IL suffers from other drawback which is high viscosity. All of drawbacks make this type of IL not possibly to replace MEA. One promising IL; EmimAc, shows an unusual phase behavior

different from the other conventional ILs. Shiflett and Yokozeli (2009) reported that at low CO₂ fraction (less than 20 mole %), the binary system of CO₂ and EmimAc has very low vapor pressure, reflecting the strongly (chemically) absorbed CO₂ into EmimAc and with the benefit of low enthalpy of absorption (-38 kJ/mol CO₂). After doing the simulation using Aspen Plus, the property parameters of selected components will be automatically retrieved. Since the databases of Aspen Plus 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 IL's, the group contribution method, "modified Lyndersen-Joback-Reid" method is used to estimate the critical properties of IL (J.O. Valderama et al., 2007), since the IL's start to decompose at the temperature near their normal boiling point.

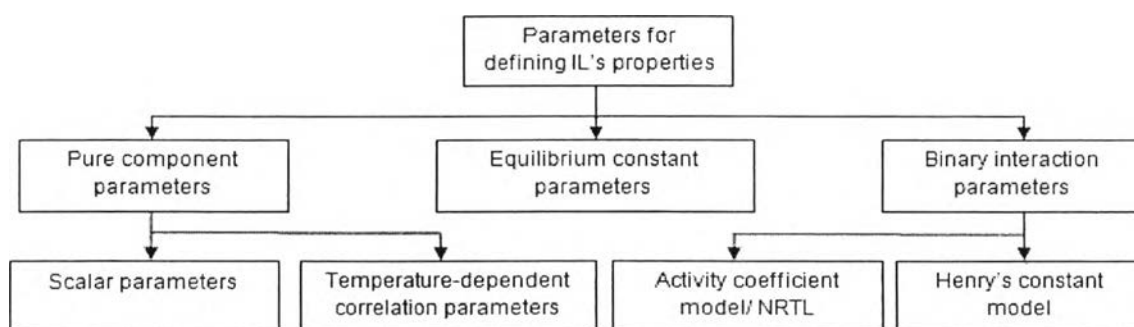


Figure 4.11 Flowchart of defining ionic liquid into Aspen Plus (Khonkaen, *et al.*, 2014).

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 (MUVDP), liquid vapour pressure (MUVDP) and liquid surface tension (SIGDIP); are regressed based on the reported properties of EmimAc available in the literature. The IL-based system involves the mixture system, which is composed of the solubility of gases in IL (N₂ and CO₂ in EmimAc) and solubility of liquid in liquid (EmimAc in water). The binary interaction parameters of

Non-Random Two Liquid (NRTL) are used to calculate the activity coefficient of the binary system (EmimAc + water) and Henry's constant model is 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 are taken from the regression of the experimental data (PTX-diagram) reported in the literature. The reaction data of EmimAc with CO_2 are taken from the literature for equilibrium calculation. Based on all of these parameters, a process simulation of IL EmimAc can be carried out to meet the same target of MEA-based system.

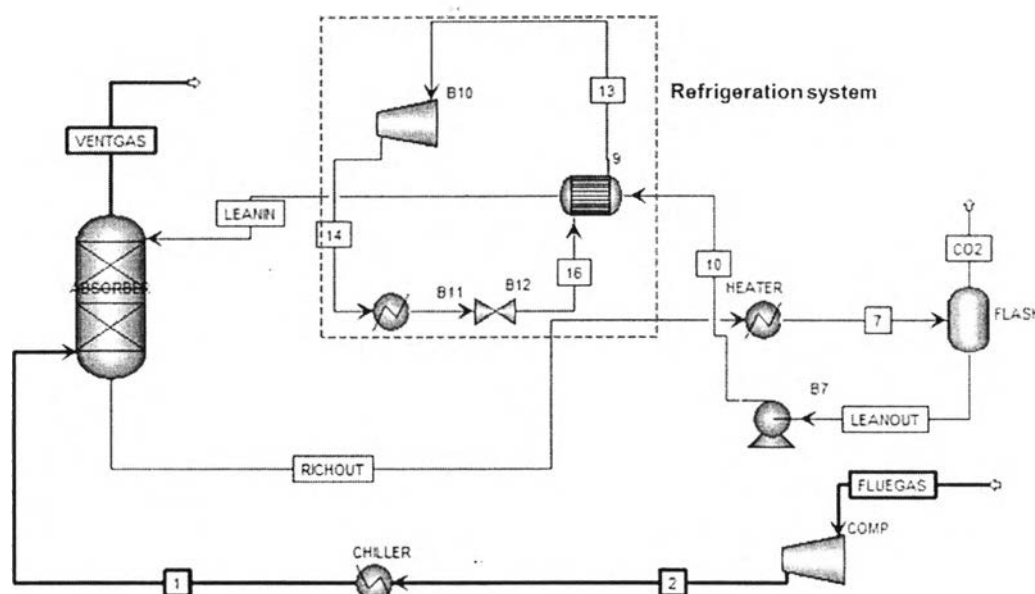


Figure 4.12 Simplified process flow diagram of IL-based scrubbing system (Aspen plus).

The flow diagram of IL process was shown in Figure 4.12. Due to the low capacity, the absorber was operated under pressure at 6.1 atm 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 with MEA process. CO_2 is chemically absorbed by EmimAc. Regeneration process is different from MEA where flash technique is applied instead of stripper column (Aspen plus RCSTR). IL-rich solution is regenerated by decreasing the pressure to the atmospheric pressure and

increasing temperature to 80 °C. IL-lean solution is pumped and cooled down to -2 °C using refrigeration and then recycled back to the top of the absorber.

4.3.2 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) 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 4.13 with two exchangers for H1-C1 and H2-C1 matches and heating and cooling duty savings of 0 and 7824.2 kW, respectively. In this system it suffered from large energy used of flue gas compressor about 4452.5 kW which was taken into account in hot utility stream. This conceptual process design with process heat integration, shown in Figure 4.13, was validated by Aspen Plus (Figure 4.14) simulator to ensure the feasibility of the process. The result showed that the relative error between conceptual process and validated process were very small.

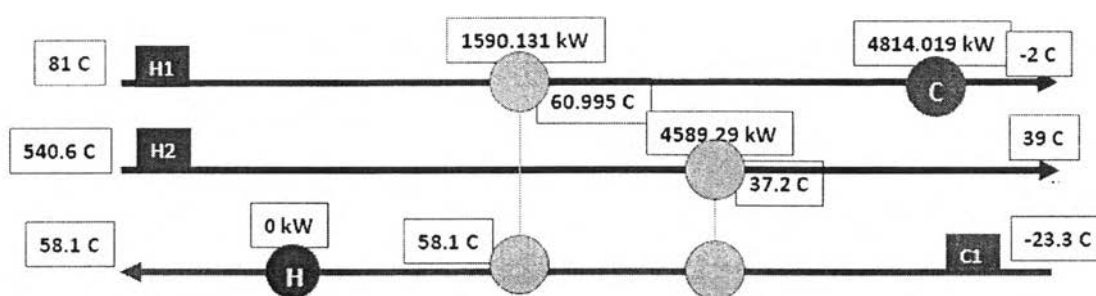


Figure 4.13 MEA based conceptual process integration from GAMS.

The validated result showed that energy requirement of the overall system was reduced around 50.03% compared to the IL-based process without process integration. And the saving in hot and cold utilities were 58.1% and 44.1%, respectively.

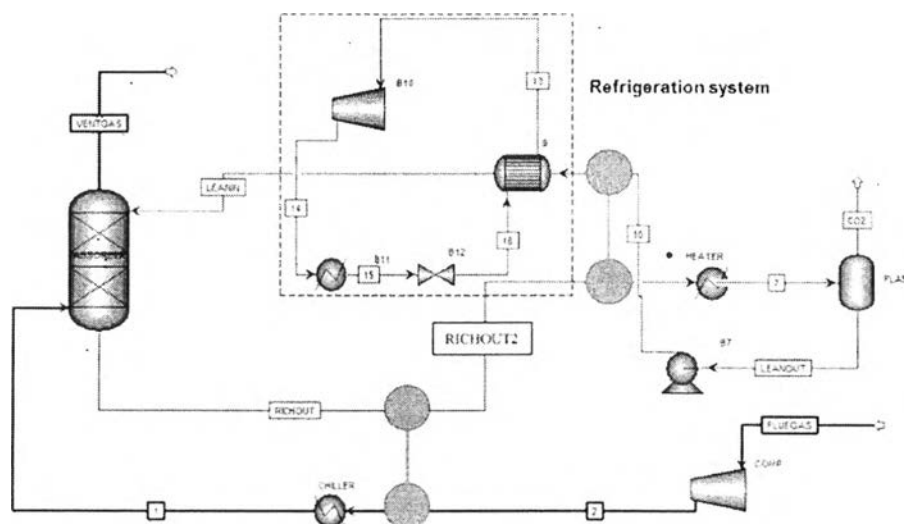


Figure 4.14 Validated process flow diagram of improved IL-based scrubbing system (Aspen plus) with process heat integration.

Table 4.16a Stream summary of IL based CO₂ capture process

	Units	LEANIN	VENTGAS	RICHOUT	FLUEGAS	2	1	RICHOUT2	CO2
Temperature	°C	-2	7.4	-23.3	142	540.6	39	38	80.8
Pressure bar	ATM	7.8	6.1	6.1	1	7.8	7.8	6.1	1
Vapor Frac		0	1	0	1	1	1	0.001	1
Mole Flow	KMOL/HR	700.1	880.468	663.786	1013.526	1013.526	1013.526	663.786	133.228
Mass Flow	KG/HR	172712	24898.84	178545.2	30732.01	30732.01	30732.01	178545.17	5836.421
Volume Flow	CUM/HR	263.633	3311.969	249.288	34532.38	8693.956	3311.624	252.418	3857.02
Enthalpy	GCAL/HR	-141.759	-1.496	-153.925	-12.877	-9.717	-13.663	-149.979	-12.313
Mole Flow									
N2	KMOL/HR	0.005	865.823	1.448	867.266	867.266	867.266	1.448	1.446
O2	KMOL/HR	0	0	0	0	0	0	0	0
CO	KMOL/HR	0	0	0	0	0	0	0	0
CO2	KMOL/HR	4.149	14.63	2.939	146.26	146.26	146.26	2.939	131.636
CH4	KMOL/HR	0	0	0	0	0	0	0	0
H2O	KMOL/HR	0.554	0.014	0.539	0	0	0	0.539	0.146
BMIMAC	KMOL/HR	517.049	trace	347.677	0	0	0	347.677	trace
BMIMCO2	KMOL/HR	10.218	trace	127.66	0	0	0	127.66	trace
BMIM2CO2	KMOL/HR	64.187	trace	58.454	0	0	0	58.454	trace
BMIM3CO2	KMOL/HR	103.937	trace	125.07	0	0	0	125.07	trace
DICHL-01	KMOL/HR	0	0	0	0	0	0	0	0

Table 4.16b Stream summary of IL based CO₂ capture process

	Units	LEANOUT	10	LEANOUT2	7	16	13	14	15
Temperature	°C	80.8	81	61.2	58.1	-30.4	45.4	137.5	16
Pressure bar	ATM	1	7.8	7.8	6.1	0.98	0.98	5.71	5.71
Vapor Frac		0	0	0	0.001	0.252	1	1	0
Mole Flow	KMOL/HR	699.975	699.975	699.975	663.786	851.52	851.52	851.52	851.52
Mass Flow	KG/HR	172708.7	172708.7	172708.72	178545.2	102960	102960	102960	102960
Volume Flow	CUM/HR	265.956	265.942	265.359	253.478	4279.904	22430.56	4798.038	72.52
Enthalpy	GCAL/HR	-136.299	-136.243	-137.61	-148.612	-103.844	-99.705	-98.291	-103.843
Mole Flow									
N2	KMOL/HR	0.002	0.002	0.002	1.448	0	0	0	0
O2	KMOL/HR	0	0	0	0	0	0	0	0
CO	KMOL/HR	0	0	0	0	0	0	0	0
CO2	KMOL/HR	4.178	4.178	4.178	2.939	0	0	0	0
CH4	KMOL/HR	0	0	0	0	0	0	0	0
H2O	KMOL/HR	0.393	0.393	0.393	0.539	0	0	0	0
BMIMAC	KMOL/HR	517.094	517.094	517.094	347.677	0	0	0	0
BMIMCO2	KMOL/HR	10.116	10.116	10.116	127.66	0	0	0	0
BMIM2CO2	KMOL/HR	64.334	64.334	64.334	58.454	0	0	0	0
BMIM3CO2	KMOL/HR	103.859	103.859	103.859	125.07	0	0	0	0
DICHL-01	KMOL/HR	0	0	0	0	851.52	851.52	851.52	851.52

4.3.3 Key Process Simulation Specifications

A summary of simulation inputs are displayed in Table 4.17.

Table 4.17a IL based CO₂ capture plant key process simulation specifications

FLUEGAS (Post-combustion Flue Gas Stream)	Temperature (°C)	142
	Pressure (atm)	0.987
	Molar Flow (kmol/hr)	1013.526
	Composition (mole fraction)	
	N ₂	0.855692
	CO ₂	0.144308
	H ₂ O	-
COMP (Flue Gas Compressor)	Discharge Pressure (atm)	7.8
CHILLER (Flue Gas Cooler)	Outlet Temperature (°C)	39
ABSORBER	Number of Stages	20
	Pressure (atm)	6.1
	CO ₂ Removal (%)	90
LEANIN (Absorbent Inlet Stream)	Temperature (°C)	-2.0
	Pressure (atm)	7.8
	Molar Flow (kmol/hr)	700.1
	Composition (mole fraction)	
	N ₂	trace
	CO ₂	0.006
	H ₂ O	trace
	BMIMAC	0.74
	BMIMCO ₂	0.015
	BMIM ₂ CO ₂	0.092
BMIM ₃ CO ₂	0.148	

Table 4.17b IL-based CO₂ capture plant key process simulation specifications

HEATER (Flash Pre-heater)	Temperature (°C)	58.1
	Pressure (atm)	6.1
Flash (RCSTR)	Temperature (°C)	81
	Pressure (atm)	1
Flash Pump	Outlet Pressure (atm)	7.8
9 (Coolant Heat Exchanger)	Hot Side Outlet Temperature (°C)	-2
	Cold Side Outlet Temperature (°C)	-30.4
	Temperature Approach (°C)	5
B10 (Coolant Compressor)	Discharge Pressure (atm)	5.71
B11 (Coolant Cooler)	Outlet Temperature (°C)	16
B10 (Coolant Valve)	Outlet Pressure (atm)	0.97
VENTGAS (Vent Gas from Absorber)	Temperature (°C)	7.4
	Pressure (atm)	6.1
	Molar Flow (kmol/hr)	880.468
	Composition (mole fraction)	
	N ₂	0.98
	CO ₂	0.02
	H ₂ O	trace
	EMIMAC (Total)	trace
CO ₂ (Stored CO ₂ Stream)	Temperature (°C)	80.8
	Pressure (atm)	1
	Molar Flow (kmol/hr)	133
	Composition (mole fraction)	
	N ₂	0.01
	CO ₂	0.99
	H ₂ O	trace
	EMIMAC (Total)	trace

Table 4.17c IL-based CO₂ capture plant key process simulation specifications

1 (Scrubbed Flue Gas Stream)	Temperature (°C)	39
	Pressure (atm)	7.8
	Molar Flow (kmol/hr) •	1014
	Composition (mole fraction)	
	N ₂	0.86
	CO ₂	0.14
16 (Coolant Usage Stream)	Temperature (°C)	-30.4
	Pressure (atm)	1
	Molar Flow (kmol/hr)	852
	Vapor Fraction	0.252
	Composition (mole fraction)	
	DICHL-01 (Diethylene Glycol)	1

4.3.4 Economic Evaluation

The economic evaluation of aqueous ammonia process was estimated by the same methodology with IL based process. The additional assumptions and specification used in carrying out the economic evaluation of aqueous ammonia based CO₂ capture process were given below:

- EmimAc cost: 10 time that of MEA cost (Khonkaen *et al.*, 2014)
- Ready installed package for refrigeration system (Khonkaen *et al.*, 2014)

4.1.4.1 *Purchased Equipment Cost*

The purchased equipment cost of IL process with process integration was shown in Table 4.18.

Table 4.18 Summary of equipment cost estimation of IL-based process (Aspen Plus)

Equipment	Type	Unit	Size Parameter	Size Unit	Cost(2013)	CEPCI	Cost(2014)
FLUEGAS COMPRESSOR	Centrifugal	COMP	4928	HP	2,727,900	1.022	2,787,913
CROSSX1	Cross Exchanger	CROSSX1	276	Ft ²	23,500	1.022	24,017
ABSORBER	Packed	ABSORBER	Dia/H = 8,74	Ft	544,500	1.022	556,479
CROSSX2	Cross Exchanger	CROSSX2	874	Ft ²	27,500	1.022	28,105
FLASH RCSTR	Flash	FLASH	Dia/H = 3.5,15	Ft	120,100	1.022	122,742
LEANPUMP	Centrifugal	B7	Head = 108	m	54,800	1.022	56,006
CROSSX3	Cross Exchanger	CROSSX3	1353	Ft ²	39,600	1.022	40,471
Ready installed package							
COOLANT COMPRESSOR	Centrifugal	B10	2206	HP	1,791,900	1.022	1,831,322
COOLANT COOLER	Cooler	B11	1179	Ft ²	34,500	1.022	35,259
Total purchased equipment cost (\$)							3,615,734

4.1.4.2 Capital Investment Cost

The summary of capital cost for IL based CO₂ capture was shown in Table 4.19.

Table 4.19 Total capital investment cost of IL-based process

Total Capital Investment			
1	Fixed Capital Investment		25,902,574
2	Working Capital		1,295,129
		Total TCI	25,729,487
Direct		Factor	Dollars (\$)
	Purchased Equipment Cost		3,615,734
	Purchased Equipment Installation	0.55	1,988,654
	Instrumentation and Controls (Installed)	1	3,615,734
	Piping (Installed)	1	3,615,734
	Electrical installations	0.15	542,360
	Yard Improvement	0.2	723,147
	Service Facilities (Installed)	0.8	2,892,587
	Land	0.08	289,259
		Total	17,876,172
Indirect	Engineering and Supervision	0.08	1,430,094
	Construction Expenses	0.1	1,787,617
	Contractor's Fees	0.08	1,430,094
	Contingency	0.15	3,378,597
		Total	25,902,574
Working Capital		0.05	1,295,129
	Total Capital Investment (\$)	Total	27,197,703

4.1.4.3 Annual Operating Cost

Raw material including ammonia make up, water make up, and water for scrubbing section were discussed in this section. Moreover, utilities requirement for CO₂ capture system were clarified in Table 4.20. In last section, annual operating cost was estimated by many factor showed in Table 4.21.

Table 4.20 Utilities consumption summary of IL based process

Utility	Amount	Cost per year (\$)
Electricity (kWh)	3,852	1,848,815
Total		1,848,815

Table 4.21 Annual operating cost for IL based process

Parameters	Cost per year (\$)
Raw material cost	0
Utility cost	1,848,815
Operating labor cost	640,000
Operating supervision cost	280,000
Maintenance and repair cost	400,000
Operating supplies and laboratory charge	230,000
Total Direct Production Cost	3,398,815
Plant overhead cost	660,000
General and administrative cost	324,705
Total Annual Cost	4,383,520

The annual cost of the integrated process was reduced by 18% and resulted from savings in utility usage in the system of close to 32 %. The capital cost of integrated process increased by 8 % compared to the process without heat integration. The overall results illustrated that the optimization of the based-case process and process integration application were beneficial in terms of savings in

energy requirement and operating expenses of the process compared with basic process.

4.4 Comparative Investment Evaluation

4.4.1 Energy Requirement

Energy consumptions in each capture processes mainly consisted of hot utilities, cold utilities, and electricity. However, these kind of energy were depended on absorbent, conditions, and process component usage in the system. In Figure 4.15 Amine systems including MEA based and aqueous ammonia based consumed huge energy in both hot and cold utilities. Heating steam and cooling water was necessary for amine systems in order to regenerate the absorbent in stripping section. On the other hand, IL based mostly consumed in electricity for pressurize section (Compressor unit). In term of energy consumption, EmimAc was the lowest energy usage compared to MEA and aqueous ammonia processes. Aqueous ammonia was the highest energy usage but regeneration temperature was around 80 °C which low grade thermal energy can be supplied.

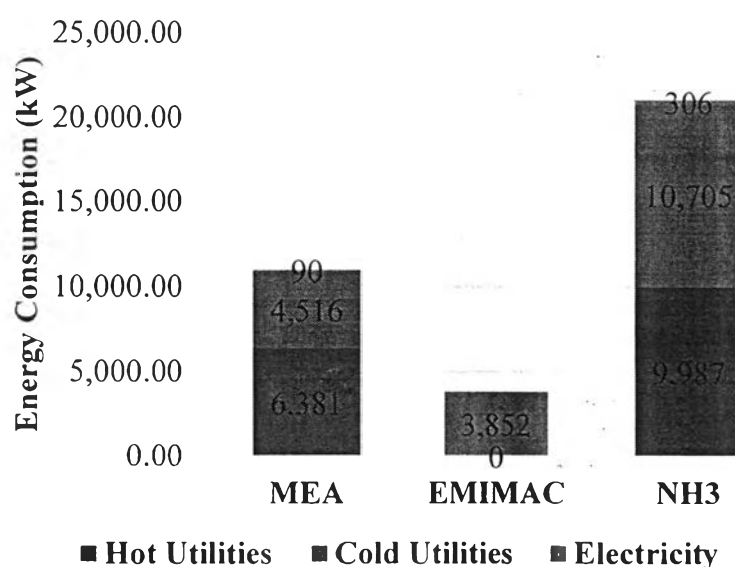


Figure 4.15 Energy consumption among absorbents for CO₂ capture process.

4.4.2 Investment Cost

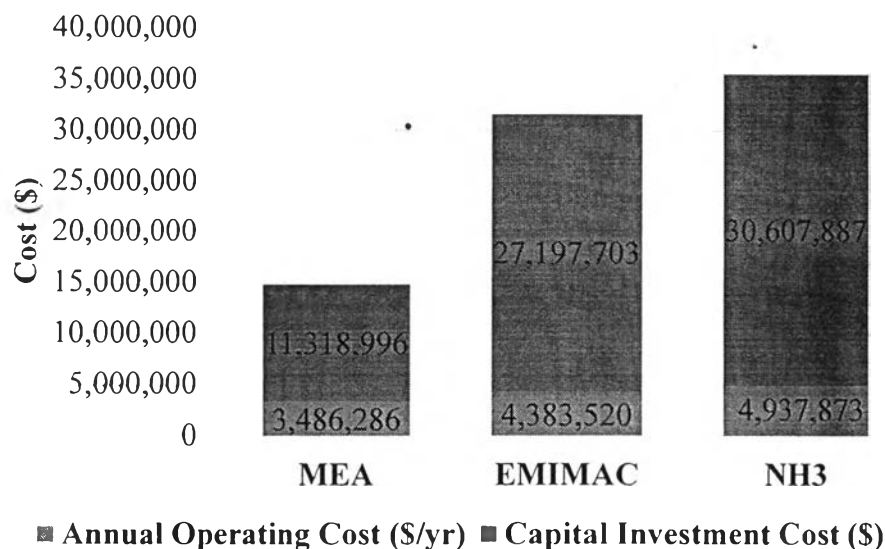


Figure 4.16 Capital investment and annual operating costs.

The feasibility of each capture processes was estimated based on many factors as mention in section 5.5. This study mainly focused on capital investment and annual operating costs. The comparison of investment cost among three processes was shown in Figure 4.16. It indicated that annual operating costs among three processes were not different, but the capital investment cost was significantly different. The capital investment of each processes depended on equipment type number of equipment. IL-based (EmimAc) process, compressor was 80 percent of the total equipment cost which was 2.8 MM\$. While, ammonia-based had two loop designs including CO₂ capture process and ammonia abatement process. Ammonia process had quite high equipment cost on absorber and stripper section which was 70 percent of the total equipment cost. MEA-based process was the simple process capture which only used one loop for operation and did not have expensive equipment like IL-based. Eventually, these kind of processes had many advantages and disadvantages. They may depend on the situation faced such as corrosive and space limitations. In this study, some assumption was made in the same range but in the real-life many needed parameters must be taken into account.

Table 4.22 shown pros and cons for CO₂ capturing by MEA, aqueous ammonia and IL (EmimAc) processes.

Table 4.22 Pros and Cons for CO₂ capturing by absorbents

Absorbents	Pros	Cons
MEA (30 wt%)	- Simple process	- Corrosive problem - High regeneration temperature
Ammonia (6 wt%)	- Less corrosion - Low regeneration temperature	- Complex process
EmimAc	- Expensive unit operation	- Need refrigeration system