Minimization of Energy Consumption for Amine Based CO₂ Capture Process by Process Modification

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Abstract

The high energy penalty in amine-based post-combustion CO₂ capture process is hampering its industrial scale application. An advanced process is designed by intensive heat integration within the conventional process to reduce the stripper duty. The study presents the technical feasibility for stripper duty reduction by intensive heat integration in CO₂ capture process. A rigorous rate-based model has been used in Aspen Plus® to simulate conventional and advanced process for a 300 MW coal-based power plant. Several design and operational parameters like split ratio, stripper inter-heater location and flowrate were studied to find the optimum values. The results show that advanced configuration with heat integration can reduces the stripper heat by 14%.

1. Introduction

With the fast-paced economic development in today's world, the demand of energy has increased manifolds. The increase in the combustion of fossil fuels to produce energy is increasing the problem of Global Warming by releasing a huge amount of greenhouse gasses into atmosphere. A lot of work is being done to reduce the emission of CO₂ from power plants. Many different techniques are available for capturing CO₂ from the flue gas of power plants including absorption, adsorption, cryogenic separation, chemical looping combustion, and membrane separation [1]. Post combustion capture by absorption is the most mature and reliable technology among all the available CO₂ sequestration processes that can be easily retrofitted into an existed facility. However, a major drawback associated with absorption process is the high energy penalty for solvent regeneration [2].

An effective and easy way of reducing the regeneration energy is the improvement in process configuration that can be done by retrofitting in an existing power plant. Dmartiz et al [3], Erik et al [4], and Amrollahi et al [5] simulated many different configurations using process simulators like Aspen Plus® to compare the energy requirement of the process. They all concluded that process modifications have potential to improve the energy efficiency of the CO₂ capture process by reducing the regeneration energy requirement. Commonwealth Scientific and Industrial Research Organization (CSIRO) tested rich split modification on a pilot plant and reported a reduction of 7% in regeneration energy and 60% in condenser duty [6]. Danish Oil and Natural Gas (DONG) Energy reported that regeneration energy can be reduced by 7% by implementing stripper intercooling modification on a pilot plant [7]. A combination of different modifications in a single flowsheet is likely to reduce regeneration energy requirement more

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Table 1. Reaction Kinetics

Reaction	Type	k	E (cal/mol)
$CO_2 + OH^- \leftrightarrow HCO_3^-$	Kinetic	4.32e+13	13249
$HCO_3^- \leftrightarrow CO_2 + OH^-$	Kinetic	2.38e+17	29451
$MEA + CO_2 + H_2O \leftrightarrow MEACOO^- + H_3O^+$	Kinetic	9.77e+10	9855.8
$MEACOO^- + H_3O^+ \leftrightarrow MEA + CO_2 + H_2O$	Kinetic	3.23e+19	156554
$H_2O + MEAH^+ \leftrightarrow MEA + H_3O^+$	Equilibrium	-	-
$2H_2O \leftrightarrow H_3O^+ + OH^-$	Equilibrium	-	-
$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+$	Equilibrium	-	-

than a single process modification.

The main objective of this work is to reduce the regeneration energy by improvement in process configuration. In this work we have designed an advanced process configuration by intensive heat integration within the system for a 300 MW coal fired power plant. Many different process modifications like rich stream split, vapor heat recovery, heated reflux recycle, and stripper inter-heater using reboiler condensate were used to utilize the heat within the system. All the configurations were simulated using rigorous rate base modeling on Aspen Plus® V10.1. Different parameters were studied to optimize the system for heat integration and reduce the reboiler duty requirement. The configurations were compared using optimized parameters.

2. Modelling and Process Description

2.1 Modelling framework

The CO_2 capture process was simulated for 300 MW coal fired power plant, using 30 wt.% MEA as absorbent. The liquid phase was modelled using ENRTL property package while vapour phase was modelled using RK equation of state. Rigorous rate-based models were used for both absorber and stripper filled with FLEXIPAC 250Y structured packing.

2.2 Thermodynamic Framework

H_2O-MEA-CO_2 mixture was thermodynamically represented by ENRTL property package in Aspen Plus®. The reactions taking place in the system are given table 1 [8]. The rate-controlled reactions were modelled using power law given in eq 1. The values of reaction constant "k" and activation energy "E" are given in table 1.

$$r = k(T)^n \, exp\left[\left(\frac{-E}{R}\right)\right] \prod_{i=1}^{N} C_i^{a_i} \quad \textbf{Equation 1}$$

$K_{tot,i}$ represents the overall mass transfer coefficient and is calculated by equation 2 [9]. The individual coefficient of mass transfer in gas and liquid phase are represented by and respectively. Mass transfer coefficient were obtained from the work of Bravo et al [10]. Binary data for vapor liquid equilibrium was regressed to obtain parameters of henry's constant for carbon dioxide in water and parameter of henry's constant for carbon dioxide in MEA solvent were obtained from the work Wang et al. [11]. The interaction parameters between amine and water for ENRTL property package were obtained from the work of Austgen et al. [12]. For water and carbon dioxide these parameters were set as zero. This model has been validated in literature [13].

$$\frac{1}{K_{tot,i}} = \frac{RT}{k_i^g} + \frac{H_{E,i}}{k_i^l} \quad \textbf{Equation 2}$$

2.3. Process Description

2.3.1. Conventional process

Figure 1 shows the flowsheet of a conventional amine-base CO_2 capture process. Amine solvent and flue gas is fed from the top and bottom of absorber, respectively. Flue gas contains 13% CO_2, 10% H_2O, 72% N_2 & 5% O_2. CO_2 is absorbed in

amine solvent while clean gas moves out from the top of absorber and CO_2-rich solution moves to Economizer before entering the stripper. CO_2-rich solvent is then heated in the stripper column by a reboiler, removing CO_2 from solvent which leaves from the top of stripper along with water vapours produced. CO_2 and vapours leaving from top are cooled down to remove condensable species from CO_2 which are returned to stripper as reflux. Separated CO_2 is then compressed to 150 bar. The CO_2-Lean solvent from the stripper bottom, at high temperature, exchanges heat in economizer with CO_2-rich solvent coming from absorber. It is further cooled before pumping back to absorber.
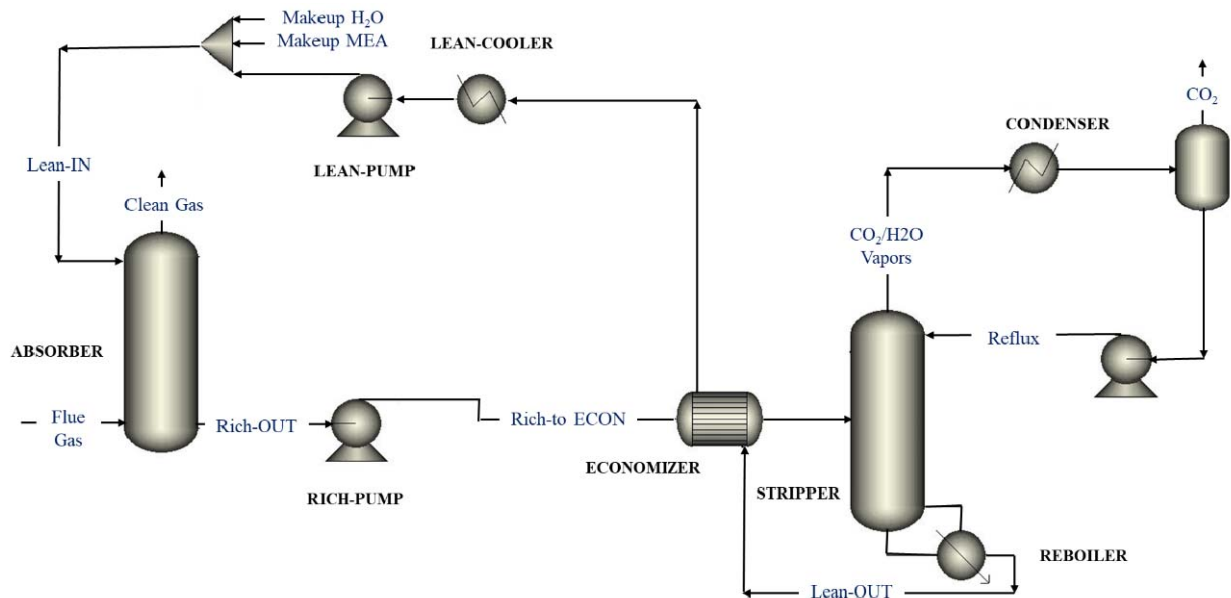

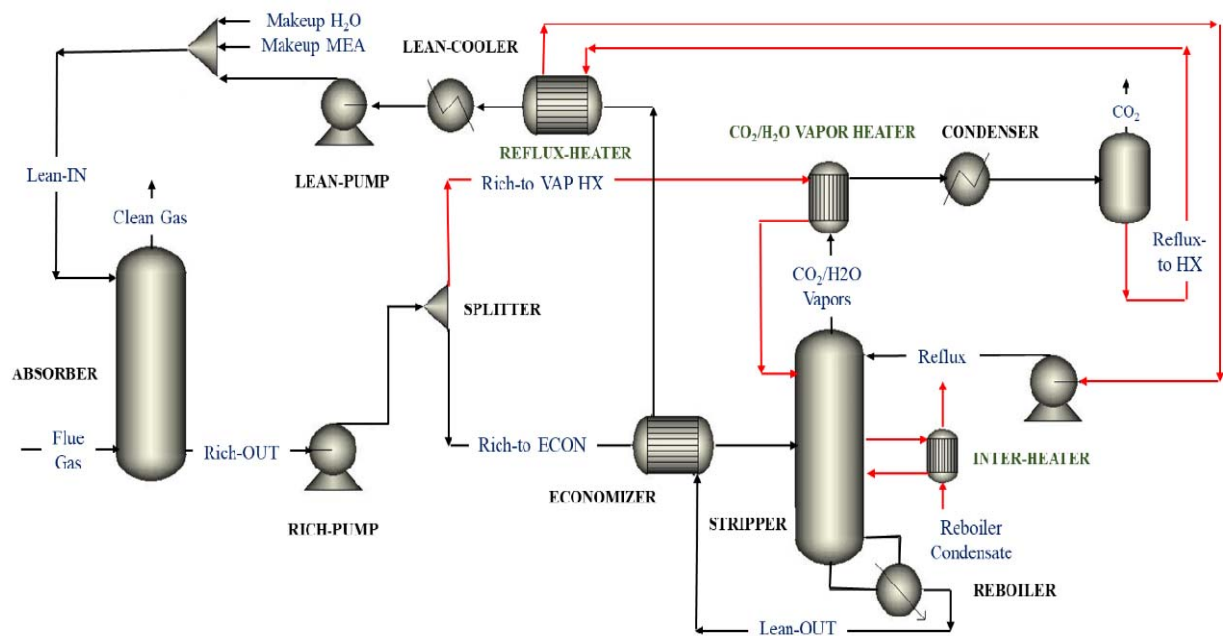**Figure 1:** Flowsheet of Conventional Process

Figure 2: Flowsheet of Advance Process

2.3.2. Advanced Process

The advanced process is a combination of different process modifications including rich split flow, stripper reflux heating and stripper inter-heater in a single flowsheet. In contrast to conventional process, CO_2-rich stream from the absorber bottom, is split into two streams. One stream exchanges heat in economizer with CO_2-lean sovent from stripper bottom while the other stream exchanges heat in vapor heater with CO_2 & water vapor from the top of stripper column. The CO_2-rich solvent from stripper vapor heat exchanger is fed to stripper. The stripper is integrated with a pump-around heater(stripper inter-heater). The steam condensate from the stripper reboiler is used as heating utility to operate the stripper interheater. CO_2-lean solvent after lean-rich exchanger further exchanges heat in reflux heater to heat the stripper reflux. Figure 2 shows the advanced process configurations with modifications shown in red color.

3. Result and Discussion

3.1 Parametric Optimization

3.1.1 Effect of Split Ratio

In order to recover maximum heat from the top (CO_2 & water vapors) and bottom products of the stripper column, the CO_2-rich stream is splitted in two streams. The efficiency of heat recovery in the advanced process, mainly depends on the split ratio of CO_2 rich stream. In order to find the optimum value, split ratio was varied from 0.55 to 0.71 and its effect on reboiler duty was studied (as
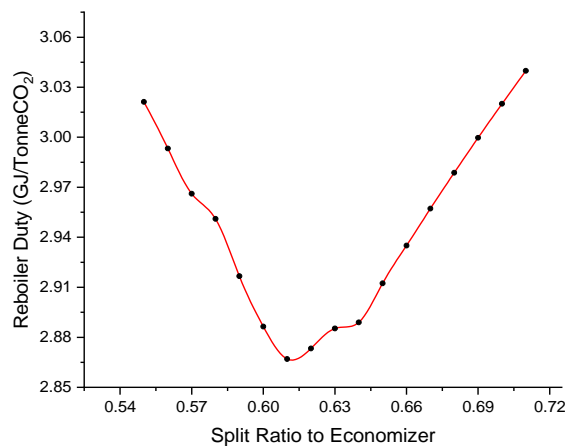
shown in figure 3). The split ratio of 0.61 to economizer corresponds to minimum reboiler duty. The target of this modification is to extract maximum heat from lean solvent and stripper top vapors. The quantity of heat a stream can recover from other stream is proportional to its flowrate. Split ratio less than 0.61 reduces the heat recovery in economizer and vice versa in vapor heater. Split ratio above 0.61 reduces the heat recovery in vapor heater and vice versa in economizer. The sum of total heat extracted in economizer and vapor heater is maximum at 0.61 so it is the optimum split ratio.

3.1.2 Effect of stripper inter-heater location

In order to recover the heat from reboiler condensate, a small portion of the amine solvent from the stripper was withdrawn from a higher stage, heated using reboiler condensate in stripper inter-heater and then fed back to stripper at a lower stage, reducing the stripper reboiler duty. Withdrawl stage and feed back stage to stripper were varied to find the optimum location. Figure 4 shows the impact of stripper withdrawl and feed stage on stripper reboiler duty. The amount of heat recovery from reboiler condensate depends on withdrawl stage temperature. The temperature of the stripper decreases from bottom to top. Withdrawl from a stage near the top has higher temperature difference with reboiler condensate temperature thus it can bring more impact on reboiler duty reduction. Figure 6 also shows the
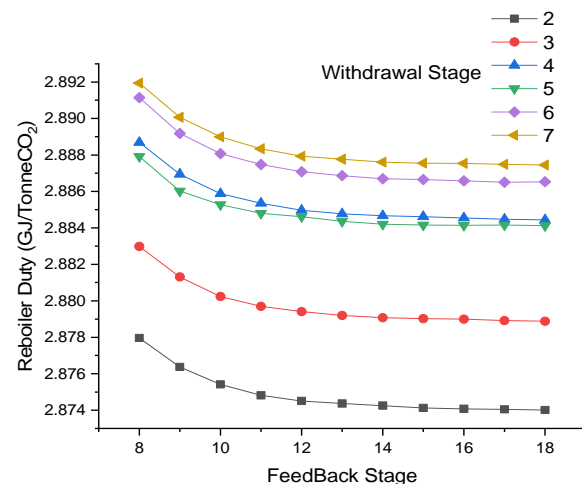

Figure 3: Optimum Split Ratio to Economizer

Figure 4: Optimum Location of Stripper Inter-Heater

Table 2: Optimum Parameters of Different Configurations

Parameters	Conventional Process	Advance Process
Absorber Height & Diameter (m)	24/13	24/13
Absorber Height & Diameter (m)	11/8	11/8
CO_2 Capture Efficiency (Molar %)	90	90
Stripper Pressure (Bar)	1.9	1.9
Cold Side $\triangle T$ (Rich-Lean HX) (℃)	5	15.7
Hot Side $\triangle T$ (Rich-Lean HX) (℃)	16.3	9.5
Split Ratio (to Economizer)	-	0.61
Rich Solvent Feed Stage	3	6
Inter-Heater Flowrate (kmol/hr.)	-	1500
Inter-Heater Withdrawal Stage	-	2
Inter-Heater Feed Withdrawal Stage	-	18
CO_2 Condenser Duty (GJ/tCO_2)	1.095	0.209
Reboiler Duty (GJ/tCO_2)	3.32	2.85
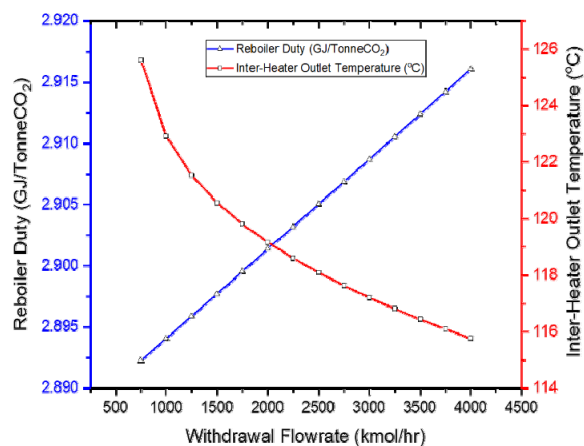
Figure 5: Effect of Inter-Heater Withdrawal Flowrate on Reboiler Duty

same trend. CO_2 and water vapors were produced in stripper inter-heater. When they are fed back to a lower stage, they not only add energy to the stripper but also act as mass stripping agent. So it is more beneficial to feed back in the lower stages as shown in figure 4.

3.1.3 Effect of stripper withdrawl flowrate

The temperature of stream fed back to stripper from inter-stripper heater depends on withdrawl flowrate. Figure 5 shows the effect of withdrawl

flowrate on reboiler duty. At higher flowarte rate, temperature change is not prominent and less CO_2 and water vapors were produced in stripper inter-heater which reduces the effect of CO_2 & water vapors as mass stripping agent in stripper. A higher stripper inter-heater outlet temperature can be achieved at lower flowrate thus producing more CO_2 and water vapors, increasing the effect of CO_2/H_2O as mass stripping agent and reducing the stripper reboiler duty. Figure 5 shows the same trend in reboiler duty due to variation in withdrawl flowrate. However, the solvent temperature is limited to 120°C due to thermal degradation of amine. 1500 kmol/hr is selected as the optimum flowrate which corresponds to strippper inter-heater outlet temperature of 120°C.

3.2 Reboiler Duty Comparison

The advanced process was optimized using sensitivity analysis of various parameters i.e. split ratio, inter-heater location and withdrawal flowrate. The advanced process was simulated using optimum parameters and results were compared with conventional process. Table 2 shows the comparison of optimum value for different parameters and reboiler duty. The comparison of reboiler duty shows a reduction of 14% in advanced process. Reboiler duty cost is almost 50% of the total cap-

ture cost. Although the addition of exchanger will slightly increase the capital cost of process but the reduction in reboiler duty can reduce the overall capture cost.

Conclusion

In this work we have simulated the conventional process and an advanced configuration for post-combustion CO_2 capture process. The advance process was designed to integrate various heat sources within the sytem & reduce the reboiler duty. Aspen Plus® rigorous rate-based model was used for simulation and optimization. The configurations were optimized by studying various parameters including stripper pressure, economizer pinch temperature, split fraction, inter-heater location and withdrawal flowrate. The conventional and advanced process have 3.35 & 2.85 GJ/tCO$_2$ reboiler duty respectively. The advanced process not only reduces the regeneration energy by 14% but also reduces the condenser duty by 80%.

Acknowledgement

Reference

[1] Olajire AA. 2010, CO_2 capture and separation technologies for end-of-pipe applications - A review. Energy Volume 35, Issue 6, Pages 2610-2628.

[2] Kohl AL, 1997, Gas purification. Gulf Publishers.

[3] Damartzis T, 2016, Process flowsheet design optimization for various amine-based solvents in post-combustion CO_2 capture plants. Journal of Cleaner Production Volume 111, Part A, Pages 204-216.

[4] Øi LE, 2014, Comparison of Energy Consumption for Different CO_2 Absorption Configurations Using Different Simulation Tools. Energy Procedia Volume 63, Pages 1186-1195.

[5] Amrollahi Z, 2012, Optimized process configurations of post-combustion CO_2 capture for natural-gas-fired power plant − Power plant efficiency analysis. International Journal of Greenhouse Gas Control, Volume 8, Pages 1-11

[6] Ashleigh Cousins, 2012, Model verifi cation and evaluation of the rich-split process modifi cation at an Australian-based post combustion CO_2 capture pilot plant, Greenhouse Gases: Science and Technology, Volume 2, Issue 5

[7] Knudsen JN, 2011, Evaluation of process upgrades and novel solvents for the post combustion CO_2 capture process in pilot-scale, Energy Procedia, Volume 4, Pages 1558-1565.

[8] ASPEN PLUS. Rate-Based Model of the CO_2 Capture Process by MEA using Aspen Plus. 2013

[9] Binay K. Dutta , 2007, Principles of Mass Transfer and Separation Processes. PHI Learning Pvt LTD.

[10] G. Q. Wang, 2005, Review of Mass-Transfer Correlations for Packed Columns, Ind. Eng. Chem. Page 8715-8729.

[11] 1992, Solubility of N_2O in alkanolamines and in mixed solvents, The Chemical Engineering Journal, Volume 48, Issue 1, Pages 31-40

[12] Austgen DM, 1989, Model of vapor-liquid equilibria for aqueous acid gas-alkanolamine systems using the electrolyte-NRTL equation. Ind. Eng. Chem Res. Page 1060-1073

[13] Moioli S, 2012, Simulation of CO_2 capture by MEA scrubbing with a rate-based model. Procedia Engineering, Volume 42, Pages 1651-1661