Improved process modifications of aqueous ammonia-based CO₂ capture system

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Abstract. Extensive research works on CO_2 capture process using MEA have been carried out and showed promising results. Nevertheless, it has been acknowledged that the use of MEA is associated with high cost, solvent degradation issues and corrosion. The issues above have motivated researchers to explore and test other potential solvents such as aqueous ammonia (NH_3). As result, NH_3 based CO_2 capture systems have recently attracted much attention as an alternative to MEA based counterparts. Despite their encouraging applications, high volatility of NH_3 raise concerns on the energy requirement related to the solvent recovery. Consequently, energy efficient NH_3 based CO_2 capture systems by modifying the process is desirable. This study, therefore, aims to propose and evaluate three different stand-alone process configurations of absorption-desorption processes in a NH_3-based system and compare them with the traditional absorption-desorption system in respect to total energy consumption. These modifications include Rich Solvent Split (RSS), Lean Vapor Compression (LVC), and Rich Vapor Compression (RVC). Results indicate that among these three proposed process modifications, LVC led to the highest reboiler energy savings of 38.3% and total energy savings of 34.5% compared to NH_3 based conventional configuration. These findings can serve as essential recommendations for further studies on and large-scale implementations of aqueous NH_3 as a better solvent.

1 Introduction

Non-renewable fossil-fuels still become major fuel for power generation. In 2016, the World Energy Council listed several key findings which include statistical reports showing that coal fuels 40% of the global electricity. Despite the industry reliant on coal, it causes great concern in terms of CO_2 emissions, the primary component of greenhouse gases and a culprit of global warming. Statistically, CO_2 emissions from power plants contribute 35% to the total global CO_2 emissions, with a majority of it released from coal-fired power plants [1]. Even though several coal-fired plants have successfully complied with the air pollution standards, the aim to further reduce CO_2 emissions remains a global struggle. As such, CO_2 capture and storage (CCS) is potentially the best option available [2].

Chemical-based absorption, a practical approach for post CO_2 capture (PCC) process is the most technically mature and widely used process to separate CO_2 gas from flue gas streams. The fact that it is also capable of handling larger gas volumes renders it a preferred option for industrial CO_2 capture processes. However, the choice of chemical absorbent used plays a significant role in determining energy consumption and CO_2 removal efficiency. Thus far, monoethanolamine (MEA) has been highly regarded as the benchmark solvent due to its fast absorption rates, good CO_2 absorption capacity, low volatility, and ease of purchase [3]. Nevertheless, the operational drawbacks of MEA such as severe solvent degradation, formation of heat stable salts that leads to corrosion, high cost, and especially intensive reboiler energy consumption have triggered the initiative of researchers to shift their attention towards better solvents such as aqueous NH_3 [2, 4]. Aqueous NH_3, which has been proven to potentially reduce specific reboiler energy consumption by over 60% [5], achieve better CO_2 removals greater than 90%, less corrosive behavior, negligible solvent degradation, chemically stable, and lower cost [6] becomes a motivation to commercialize the solvent for industrial PCC processes [4]. Nevertheless, a major burden which holds back the commercialization of aqueous NH_3 is its highly volatile nature that leads to solvent losses, a less probable situation when using MEA. However, this problem can be avoided by controlling the absorption process temperature [6]. Additionally, although worldwide research and development work concerning the use of NH_3 as PCC solvent is still ongoing, several demonstration and pilot plants have been built for techno-economic feasibility study of the process.

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Alstom's CAP (Chilled Ammonia Process), Powerspan, and CSIRO (Commonwealth Scientific and Industrial Research Organization) and KIER (Korea Institute of Energy Research) are few of the organizations that embarked on the research and have affirmed the benefits that NH_3 has to offer. Besides the search for different solvents, proposing various process flowsheet modifications has gained increasing interest in the attempt to further reduce energy consumption of the conventional PCC process. Nevertheless, the existing studies on energy efficient process modifications are mostly related to MEA based systems and in the literature improved process modifications for NH_3 based systems are very scarce. Therefore, this study aims to propose process modifications for NH_3 based systems to attain lower energy consumptions.

2 Simulation set up

2.1 Conventional post carbon capture process

The simulated conventional flowsheet of the NH_3-based PCC process of this simulation study is illustrated in Fig. 1. The absorption process commences when pre-cooled flue gas from a coal-fired power plant enters through the bottom of a packed absorber column. The flue gas properties are as shown in Table 1.

Lean NH_3 solvent enters from the opposite direction and flows counter-currently to the flue gas. Scrubbed gas is vented to the atmosphere via the top of the absorber. Solvent properties, absorber, and stripper column simulation settings are summarized in Tables 2 and 3.

Table 1. Flue gas properties and composition [7].

Temperature and Pressure	: 15 ºC, 101.3 kPa
Mass Flowrate	: 676 kg/hr.
Gas composition (mol%)	: **N₂:** 75.50; **H₂O:** 6.0; **CO₂:** 10.70; **O₂:** 7.8

Table 2. Aqueous ammonia solvent properties

Std. Ideal Liq. Vol Flow	: 134 L/min
Temperature and Pressure	: 25 ºC; 101.3 kPa
Compositions of components in solvent (wt.%) **NH₃:** 4.08; **CO₂:** 5.21; **H₂O:** 90.71	

Table 3. Packed absorber and stripper column simulation setup

Specifications	Absorber	Stripper
No of Stages	10	10
Diameter (m)	0.5	0.6
Packed Space (m)	0.6096	0.6096
Pressure (kPa)	101.3	150

Following the absorption process, the lean solvent was regenerated and recycled back to the absorber. The gaseous stream rich in CO_2 was discharged from the top of the stripper. The most significant process parameter being noted in the simulated process was the energy consumed by the reboiler unit, presented in terms of specific duty (kJ/kg CO2) [8].
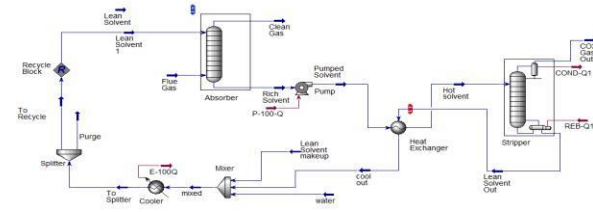

Figure 1. NH_3 based PCC simulation flowsheet.

2.2 Proposed process modifications

As researchers begin to realize the need to improve energy efficiency of the conventional amine-based CO_2 capture, more process improvement patents were being introduced since year 2004 [9]. However, to date, most of the patented process modification studies limited to MEA-based systems. Limited studies were carried out for modifications involving NH_3-based systems. As a consequence, the following sections describe three individual process modifications previously applied to amine-based PCC systems and they were then adopted for an NH_3 based system. These modifications include Rich Solvent Split (RSS), Lean Vapor Compression (LVC), and Rich Vapor Compression (RVC). All simulations were carried out using Aspen Hysys V10.

2.2.1 Rich solvent split (RSS)

The simplicity of the RSS enables it to be easily retrofitted into a traditional PCC configuration. The traditional flowsheet was modified by splitting the rich solvent into two separate streams, where one is to be heated and the other left unheated. The unheated stream was fed at a stage nearer to the stripper top with the purpose of recovering the heat possessed by the uprising NH_3-H_2O vapour. On the other hand, the heating of the rich solvent produces vapour that is capable of pre-stripping some CO_2 gas, thus resulting in lower regeneration duty [10]. In an effort to achieve maximum energy savings, split ratio and injection stage of heated stream were optimized. Fig. 2 shows the RSS flowsheet simulation with the modified section enclosed in a red-lined box.
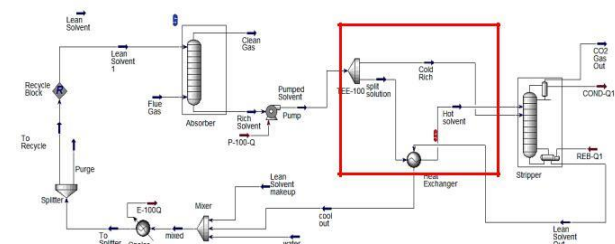

Figure 2. RSS process simulated flowsheet

2.2.2 Lean vapor compression (LVC)

The LVC process works based on partial recovery of sensible heat from the regenerated lean solvent by flashing it into a vapour and liquid stream. Subsequently,

the flashed vapour stream was compressed and reinjected into the stripper as illustrated in **Fig. 3**. Apparently, the capture several process equipment leads to an increased investment cost that runs parallel to a substantial reduction in total energy consumed. Hence, there exists a trade-off between performance and investment cost. Xue [11] reported a reboiler duty reduction of about 12.8% in an MEA-based LVC process. Moreover, in achieving maximum energy efficiency, optimization of flash tank pressure drop and pressure of recompressed vapor is necessary.
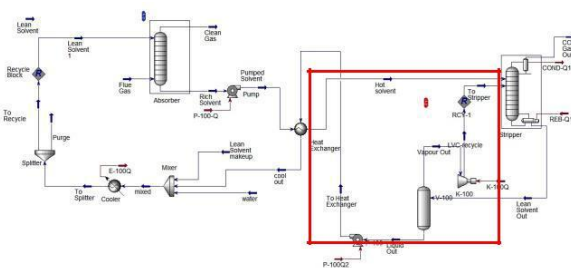

Figure 3. LVC process simulation flowsheet

2.2.3 Rich vapor compression (RVC)

The RVC process shown in **Fig. 4** is similar to the LVC. However, instead of flashing the lean solvent, the rich hot solvent is flashed into a rich vapor and liquid stream. The flashed rich vapour undergoes compression and is thereafter sent to the stripper bottom, whereas the flashed liquid was injected to the top of the stripper. Additional auxiliary equipment installed for conditioning purposes may potentially lead to an increased capital and operating cost due to a hike in electricity usage.
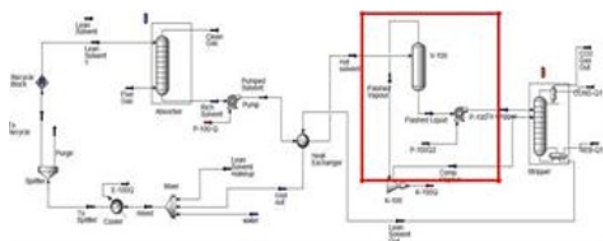

Figure 3. RVC process simulation flowsheet.

3 Results and discussion

It should be noted that the changes in carbon capture efficiencies are relatively constant when traditional NH_3 process were compared to the modified ones as shown in Table 4. A tabulated summary of all simulation results from this study are presented in Table 5.

Table 4. Carbon Capture Efficiency (%)

Cases	MEA	NH3	RSS	LVC	RVC
Carbon Capture (%)	92.66	97.80	97.61	97.24	98.06

Table 5. Summary of Simulation Key Parameters

Cases	Specific Reboiler Duty (MJ/kg CO2)	Specific Condenser Duty (kJ/kg CO2)	Total Energy (GJ/hr)
MEA Base	82.16	1.101 x 10⁴	17.4
NH3 Base	3.395	138.50	3.73
RSS	3.854	92.67	3.49
LVC	2.096	135.1	2.44
RVC	3.234	151.2	3.75

3.1 Base case simulation results

The simulation results of this study showed that the NH_3 and MEA base case achieved 97.80% and a lower 92.66% CO_2 removal efficiency, respectively. The overwhelming 97% achieved in this study can be validated by experimental works undertaken by Yeh and Bai [12] which reported that NH_3 has the capacity to achieve CO_2 removal efficiency of 99%, while MEA could only accomplish up to 94%. To further justify NH_3's potential in capturing more CO_2 gas, Jilvero [8] reported a 98.9% capture CO_2 capture level when using a similar flue gas composition and lean solvent NH_3 concentration. From the perspective of absorption capacity, NH_3, too, has a superior performance over MEA. Yeh and Bai et al [12] in their experimental investigations to evaluate the performance of NH_3 and MEA reported that the absorption capacity of these solvents were 1.2 kg CO_2/kg NH_3 and 0.38 kg CO_2/kg MEA. As such, it is distinct that NH_3 is a preferable solvent as its advantages are distinct even at very low concentrations of 4 wt.%, as simulated in this study. Furthermore, this study justifies that using NH_3 led to 80% reboiler energy savings as oppose to using MEA as solvent. The large amount of energy saved when using NH_3 is also comparable with a study undertaken by McLarnon and Duncan et al. [13], where the specific reboiler energy dropped drastically from 1430 kJ/kg CO_2 to 205 kJ/kg CO_2, saving 86% of energy.

3.2 RSS based process modification

The key parameter affected by the implementation of the RSS process was the specific condenser duty instead of specific reboiler duty. In fact, the RSS resulted in a tremendous specific condenser energy saving of 33.1%, as the unheated rich portion was fed closer to the stripper top. Nevertheless, the RSS was still able to save 6.4% in terms of total energy consumed. Theoretically, the reboiler heat functions to increase the stripper feed temperature to the reboiler temperature. However, at an optimum split ratio of 0.05, the maximum temperature of the heated rich portion is limited by the heat exchanger's capability. As such, there was only a minimal 8.6 % drop in reboiler duty. Per contra, when flowrate of CO_2 exiting the stripper was considered, there was an increase in specific reboiler duty by 11.9%. This goes to show that a trade-off exists between amount of CO_2 gas exiting the stripper column and the specific reboiler duty It should be noted that specific duties are preferable to gauge the energy efficiency of a process because specific duty takes

into account the amount of energy consumed in stripping each kilogram of CO_2 from the rich solvent.

3.3 LVC based process modification

The superiority of the LVC process was observed when a comparison was done against the NH_3 base case. The process resulted in a staggering specific reboiler and condenser duty saving of 35.8% and 0.5%, respectively. Unlike the RSS, the LVC clearly targeted greater reductions in the reboiler than the condenser. To date, the LVC is limited to amine-based CO_2 capture systems. Dubois [14] reported a specific reboiler saving of 13.4% when simulating an MEA-based LVC process. An optimum flash tank pressure drop of 100 kPa was used in this study. Although flashing the lean solvent to lower pressures greatly reduced reboiler duties by providing additional stripping steam to the reboiler, it has a drawback in compressor energy consumption. As compressors are dependent on electrical power, operating cost would increase. To justify the statement, Cousins [10, 15] reported a surge in electric power by about 53% from 1.55 kW to 3.30 kW in an MEA- based LVC process due to the installation of a pump and a compressor. Nevertheless, as economic analysis is beyond the scope of this study, the conversion of electrical power consumed into monetary value was not computed. In terms of total energy, though additional equipments may appear as an obstacle in saving energy, the results obtained in this study proved otherwise. Total energy savings of 34.5% was achieved. In fact, it exceeds the total energy savings obtained through the RSS and RVC processes simulated in this study.

Reddy [16] in his vapor compression process patent, too, claimed a decrease in the net energy requirements of the whole system.

3.3.4 RVC based process modification

When comparison against the NH_3 base case was made, very minimal specific reboiler savings of only 0.99% was attained through the RVC process. Meanwhile, a substantial increase in specific condenser duty by 10.19% was obtained. However, it is no surprise that the RVC is less efficient than the LVC in energy consumption. The huge discrepancy in specific reboiler duty savings of both processes is due to the heat flow content of the compressed vapour stream entering the stripper. From the simulation data obtained, the latent heat content in the recompressed vapour stream of the RVC was approximately 6 times smaller than that of the LVC process. Consequently, the compressed vapour of the RVC process was incapable of reducing reboiler steam requirements. Dr. Paul Feron, the lead of the CSIRO PCC research program, also claimed that the RVC is less favourable because of the high CO_2 concentration in the compressed vapour stream. The statement applies well to this study. A 0.580 CO_2 mole fraction was found in the RVC's recompressed vapour stream whereas only 0.069 was present in same stream for the LVC process [17]. In a fairly similar process modification developed by

Moullec and Kanniche et al [18] there was an increase in the reboiler heating requirement, deeming the process inefficient.

4 Conclusion

The high regeneration duty associated with MEA as PCC solvent becomes a motivation to search for new solvents and implement process modifications to improve process efficiency. The simulations carried out in this study verify that aqueous NH_3 was indeed capable of saving 80% regeneration energy. Moreover, CO_2 removal percentage was found to be 5% greater than when using MEA. In an effort to further maximize energy savings, 3 process modifications were simulated. Among the three standalone models simulated, the LVC achieved the highest specific reboiler duty savings of 38.3%, followed by RVC, accomplishing only a mere 4.8%.

RSS however, led to an increase in specific reboiler duty by 11.9%. Nonetheless, in terms of condenser duty reduction, RSS, exhibited a staggering energy saving of 33.1%. Therefore, for future research works, the RSS and LVC standalone models can be combined to exploit their respective strengths leading that may possible lead to an overwhelming specific reboiler and condenser duty savings. The simulated standalone process configurations were ranked according to their respective total energy savings as shown below:

1st : LVC : - 34.5 % (decrease)
2nd : RSS : - 6.4 % (decrease)
3rd : RVC : + 0.3 % (increase)

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