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Article

# Energy Minimization in Piperazine Promoted MDEA-Based CO<sub>2</sub> Capture Process

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**Abstract:** A piperazine (PZ)-promoted methyldiethanolamine (MDEA) solution for a carbon dioxide (CO<sub>2</sub>) removal process from the flue gas of a large-scale coal power plant has been simulated. An Aspen Plus<sup>®</sup> was used to perform the simulation process. Initially, the effects of MDEA/PZ concentration ratio and stripper pressure on the regeneration energy of CO<sub>2</sub> capture process were investigated. The MDEA/PZ concentration ratio of 35/15 wt.% (35 wt. MDEA and 15 wt.% PZ) was selected as an appropriate concentration. The reboiler duty of 3.235 MJ/kg CO<sub>2</sub> was obtained at 35/15 wt.% concentration ratio of MDEA/PZ. It was considered a reference or base case, and process modifications including rich vapor compression (RVC) process, cold solvent split (CSS), and the combination of both processes were investigated to check its effect on the energy requirement. A total equivalent work of 0.7 MJ<sub>e</sub>/kg CO<sub>2</sub> in the RVC and a reboiler duty of 2.78 MJ/kg CO<sub>2</sub> was achieved in the CSS process. Similarly, the total equivalent work, reboiler duty, and condenser duty of 0.627 MJ<sub>e</sub>/kg CO<sub>2</sub>, 2.44 MJ/kg CO<sub>2</sub>, and 0.33 MJ/kg CO<sub>2</sub>, respectively, were obtained in the combined process. The reboiler duty and the total equivalent work were reduced by about 24.6 and 16.2%, respectively, as compared to the reference case. The total energy cost saving was 1.79 M\$/yr. Considering the additional equipment cost in the combined process, the total cost saving was 0.67 M\$ per year.

**Keywords:** CO<sub>2</sub> capture process; energy reduction; rich vapor compression process; solvent split

## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) capture through post-combustion with chemical solvent absorption approach is a promising and leading technology. It is a flexible and viable technique to abate CO<sub>2</sub> emissions from the flue gas of power plants [1,2]. The Boundary Dam Project in Saskatchewan, Canada, is the world's first commercial-scale CO<sub>2</sub> capture project using post-combustion carbon capture (PCC) process through aqueous amines. Aqueous amine solvents are mostly used for CO<sub>2</sub> capture processes from coal power plants and are considered at a mature stage of technical development [3]. These amines are classified into primary amines (monoethanolamine (MEA) and diglycolamine (DGA)), Secondary amines (diisopropylamine (DIPA) and diethanolamine (DEA)), and tertiary amines (N-methyldiethanolamine (MDEA) and triethanolamine (TEA)). The reactivity of

primary and secondary amines with CO<sub>2</sub> is very high, but these amines require high heat of regeneration. However, in the case of tertiary amines, unlike primary and secondary amines, the reactivity is low but they require less heat of regeneration [4].

Among these amines, MEA has the highest absorption power (MEA > AMP > DEA >> MDEA) [5]. Economically, MEA is the cheapest and MDEA is the second cheapest solvent to reduce the CO<sub>2</sub> emission. In CO<sub>2</sub> capture through MEA-based processes, the minimum reboiler duty is 3.1 GJ/tCO<sub>2</sub>, which reduces the net power efficiency from 38.9 to 29.8% [6,7]. This high energy requirement for absorbent regeneration is due to higher reaction enthalpy of MEA solvent and CO<sub>2</sub>. According to Li, Cousins [6], the heat of decomposition of carbamate is around 2.12 GJ/t CO<sub>2</sub>, which contributes about 68% of reboiler duty. The MEA's absorption reaction heat is about 95 kJ/mol CO<sub>2</sub> [8] and cannot be affected by the process improvements. Thus, further reduction in reboiler duty will be very difficult in MEA-based processes. Several solvents and process modifications have been adopted to reduce the energy requirements [9–12].

A suitable solvent must be selected in the capturing process that has low energy consumption, and MDEA is such a solvent. The decomposition heat of MDEA and CO<sub>2</sub> bicarbonate is 61 kJ/mol CO<sub>2</sub>, which is very much lower than the carbamate of MEA and CO<sub>2</sub> [13]. Moreover, MDEA has a low degradation and corrosion rate, which makes it more attractive for the CO<sub>2</sub> capture process [14]. However, MDEA also has the drawback of low absorption rate, which makes its application limited in CO<sub>2</sub> removal processes [14]. An absorption rate promoter is required to enhance the absorption rate of MDEA. Piperazine (PZ) has been investigated to be one of the effective promoters in potassium carbonate, MDEA, and MEA as it quickly makes the carbamates with CO<sub>2</sub> [15].

The reaction rate of PZ towards CO<sub>2</sub> compared to other amines is very high [14]. PZ-activated MDEA solution has been introduced by many leading companies, including Huntsman Corporation and Shell, Dow Chemical Company, etc. [13]. Bishnoi and Rochelle [16] have shown that MDEA/PZ blends can absorb CO<sub>2</sub> rapidly as compared to MEA or DEA blends with MDEA. Mudhasakul, Ku [4] have developed a model in Aspen Plus to capture CO<sub>2</sub> from the actual natural gas unit by using a mixed solvent of MDEA and PZ. They showed that the CO<sub>2</sub> absorption rate is greatly enhanced by increasing the PZ concentration and proposed that 5% of PZ is the most suitable concentration to be mixed with 45% of MDEA.

Generally, a blended solution of MDEA/PZ with 5 wt.% PZ and 45 wt.% MDEA has been used to capture CO<sub>2</sub> from the flue gas of natural gas and ammonia plants [14]. Frailie [13] investigated different concentrations of MDEA and PZ solutions to remove CO<sub>2</sub> from coal-fired power plants, including 8 wt.% of PZ and 42 wt.% MDEA, and 21 wt.% of PZ and 29 wt.% MDEA. Zhao, Liu [17] showed that 5 wt.% PZ is not enough to properly remove CO<sub>2</sub> from a coal power plant's flue gas. They have obtained reboiler duty 2.74 GJ/t CO<sub>2</sub> at MDEA/PZ concentration ratio of 30/20 wt.%. They proposed different process modifications including simple rich-split, absorber intercooling, stripper inter-heating, advanced rich-split, and their combinations to further reduce the energy demand up to 2.24 GJ/t CO<sub>2</sub>.

Similarly, to reduce the energy requirement in NH<sub>3</sub> and MEA based processes, researchers have widely studied various modifications, including rich split [18], lean vapor compression (LVC) [19], and rich vapor compression (RVC) [20] processes. In addition to parameters optimization, process modification or optimization can also play an important role to reduce the energy demand in CO<sub>2</sub> capture processes.

In this paper, the operating parameters were optimized to reduce energy consumption. Process modifications, including rich vapor compression (RVC), cold solvent split (CSS), and the combination of both processes, have been proposed to further reduce the energy consumption. The total equivalent work of the process modifications was compared with the reference case and the total equivalent work of MEA-based RVC and lean vapor compression (LVC) processes. Aspen capital cost estimator (ACCE) was used to calculate the direct cost of the main equipment. Moreover, to ensure the process is economically feasible, a tradeoff between extra equipment cost and energy savings was performed.

## 2. Methodology

### 2.1. Process Description

A base process has been considered in which 90% CO<sub>2</sub> can be captured by using MDEA/PZ solution from the flue gas of 650 MW power plant. The process consists of two main columns, stripper and absorber, a heat exchanger, and other unit operation accessories. Flue gases, after desulphurization, denitrification, and cooling, are fed into the bottom of the absorber where they come across the downward MDEA/PZ solvent stream, known as lean solvent. This lean solvent, after contacting the flue gas, absorbs CO<sub>2</sub> from it and exits from the bottom of the absorber. The exiting stream, also known as richout, is passed through the heat exchanger to exchange heat and fed into the stripper. In the stripper, with the help of reboiler, CO<sub>2</sub> gas is released by regenerating the solvent and leaves the stripper top as CO<sub>2</sub> out. A hot stream, commonly known as leanout, exits the bottom of the stripper and is pumped back into the absorber to repeat the cycle.

The flue gas properties, including flow rate, pressure, temperature, etc., were taken from the work of Zhao, Liu [17] and are shown in Table 1. The flue gas flow rate was assumed from the 650 MW power plant, which is 3100 t/h. It is a very high flow rate; therefore, four parallel process trains have been proposed, where each process train has the capacity of removing 1 Mt CO<sub>2</sub>/yr.

**Table 1.** Properties of the flue gas.

| Flow Rate (t/h) | Pressure (MPa) | Temperature (°C) | Mole Fraction (%) |                |                  |
|-----------------|----------------|------------------|-------------------|----------------|------------------|
|                 |                |                  | CO <sub>2</sub>   | N <sub>2</sub> | H <sub>2</sub> O |
| 775             | 0.11           | 40               | 12                | 78             | 10               |

In the base process, PZ concentration was varied from 5 to 20 wt.%, to analyze its effects on the absorption rate of CO<sub>2</sub> and reboiler duty while keeping the total amine concentration of both MDEA and PZ 50 wt.%. The stripper pressure for different PZ concentration was varied to find an optimal value where the reboiler duty is lower.

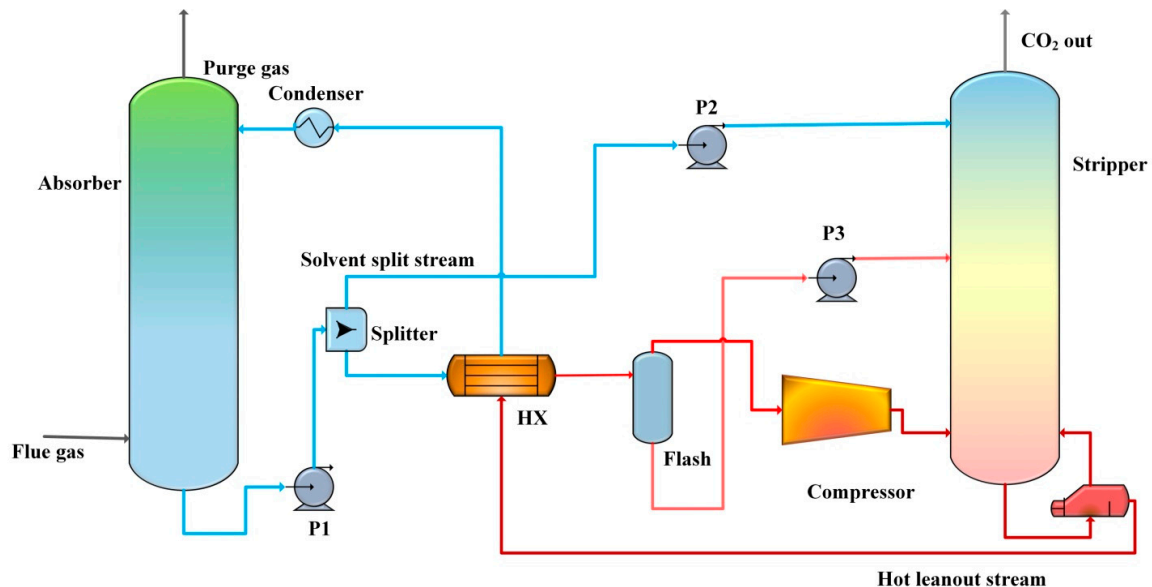
### 2.2. Model Development

In this paper, a rate-based model for both stripper and absorber was developed in Aspen Plus® V10 to simulate a MDEA/PZ-based CO<sub>2</sub> capture process. The rate-based model requires some rigorous initialization such as packing specifications, liquid holdup, column dimensions, absorbent specifications, etc. In this study, the flue gas properties are taken from the work of Zhao, Liu [17]. Therefore, the absorber column has the same diameter (18 m) and height (6 m) as used by Zhao, Liu [17] with Flexipac 250Y packing material. The stripper column has a 10 m height and 6.8 m diameter with the same packing material as the absorber. The column diameter of the stripper was adjusted to set the flooding approach below 80%. Both absorber and stripper consist of 20 theoretical stages. A mixed flow model was used, and the interfacial area factor was set at 1. The mass transfer, heat transfer coefficients, liquid holdup, etc. were used from the built-in simulation model in Aspen Plus, called the “rate-based model of the CO<sub>2</sub> capture process by mixed PZ and MDEA using Aspen Plus”.

The electrolyte non-random two liquid (NRTL) for the calculation of liquid-phase properties and Redlich-Kwong (RK) equation of state was used for the vapor phase properties. N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CO, and H<sub>2</sub> were chosen as Henry-components, and aqueous was taken as an activity coefficient for these components. All the chemical equilibrium and kinetic reactions were the same as in the built-in model of MDEA/PZ in Aspen [21,22]. In the built-in model, the equilibrium constants were computed from the standard Gibbs-free energy change.

### 2.3. Rich Vapor Compression Process (RVC) with Cold Solvent Split (CSS)

RVC is an advanced process modification technique consisting of additional equipment including compressor, pumps, and a flash vessel. Figure 1 depicts the RVC combined with the CSS process where the richout stream after exiting from the bottom of the absorber is split into two streams: one stream bypassing the heat exchanger and the other stream flowing directly into it. The bypassed stream is directed to the stripper top, where the vapors potential heat is recovered in the upward gaseous stream, which reduces both the condenser and reboiler duty, and this configuration is known as the CSS process. To generate extra vapors, the pressure of P1 is lower than stripper pressure.



**Figure 1.** Flowsheet diagram of rich vapor compression (RVC) with cold solvent split (CSS) process.

The other stream, after passing through the heat exchanger, is fed into the flash vessel as shown in Figure 1. In the flash vessel, the stream is flashed to produce vapor and liquid streams. The liquid stream is passed through the P2 to increase its pressure and flows into the mid-section of the stripper. The vapor stream is passed through the compressor, where the stream is compressed, and its temperature and pressure rise and are fed into the bottom of the stripper. The RVC process is basically used to increase the thermal capacity of the stream passing through the heat exchanger by utilizing the latent heat of that stream, and as a result, the reboiler duty reduces.

### 2.4. Total Equivalent Work and Cost of the Main Equipment

As for the operation of compressors and pumps, electric energy is required, and for the reboiler, thermal energy is needed. Both energy types are very different from each other with respect to their qualities. Therefore, the thermal energy of the reboiler needs to be converted into equivalent thermodynamic work. For this purpose, Equation (1) has been used to obtain the total equivalent work.

$$W_{eq} = \alpha \cdot Q_r + W_c + W_p \quad (1)$$

where  $Q_r$ ,  $W_c$ , and  $W_p$ , are the reboiler's, compressor's, and pump's work, and term  $\alpha$  is used for the turbine power loss. The term  $\alpha$  depends on the quality of the steam, and its value of 0.23 was obtained from the study of Bolland [23]. This value is for the case where the temperature of the steam must be in the range of 120–150 °C to heat the stripper. In this study, the stripper temperature lies in the above temperature range; therefore, a value of 0.23 has been used for  $\alpha$ . The efficiency of the compressor and pumps were assumed to be 75%.

The capital costs of the main equipment were calculated with the help of Aspen Capital Cost Estimator (ACCE). ACCE (V10) using 1st Quarter 2016 pricing basis for the equipment cost calculation, and instead of a factor-based model it uses a very sophisticated model [24]. Carbon steel was considered for the equipment material.

### 3. Results and Discussion

The operating parameters used in the base case are listed in Table 2. In the base case, the reboiler duty of 3.6 MJ/kg CO<sub>2</sub> was obtained at CO<sub>2</sub> lean loading of 0.036 and solvent flow rate of 3500 t/h. In all cases, including the base one, CO<sub>2</sub> removal efficiency was kept at 90%.

**Table 2.** Base case operating parameters.

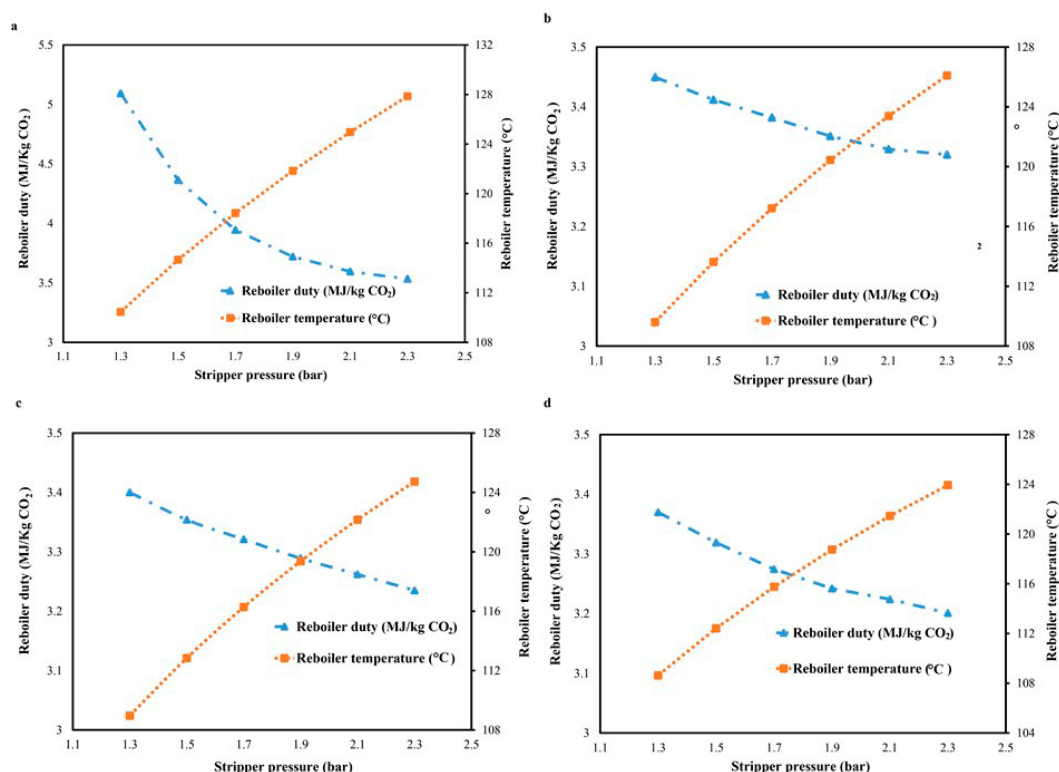
| Simulation Parameters        | Values |
|------------------------------|--------|
| Absorber pressure (bar)      | 1.1    |
| Absorbent flow rate (t/h)    | 3500   |
| Absorbent temperature (°C)   | 40     |
| MDEA/PZ concentration (wt.%) | 45/5   |
| Heat exchanger LMTD (°C)     | 10     |
| Stripper pressure (bar)      | 2.1    |
| Reboiler temperature (°C)    | 124.97 |

#### 3.1. Parameter Sensitivity Study

##### 3.1.1. Stripper Pressure Effect

Figure 2 shows stripper pressure effects on the regeneration energy of different MDEA/PZ concentration. The pressure of the stripper has been varied in the range of 1.3 bar to 2.3 bar for each 45/5, 40/10, 35/15, and 30/20 wt.% MDEA/PZ ratio. At high pressure, the heat energy primarily decreases due to the suppressing of water vapors from the stripper. In the CO<sub>2</sub> capture process of 5 wt.% PZ, the reboiler duty decreases from 5.1 to 3.6 MJ/kg CO<sub>2</sub> as the stripper pressure increases from 1.5 to 2.1 bar. In 10% PZ content, the reboiler duty decreases from 3.45 to 3.33 MJ/kg CO<sub>2</sub> in the pressure range of 1.3–2.1 bar. In both processes of 5 and 10% PZ content, the energy penalty cannot be reduced significantly, and the reboiler temperature also exceeds 125 °C, at above 2.1 bar stripper pressure. Biliyok, Lawal [25] suggested that reboiler temperature should be lower than 125 °C in order to keep the amine thermally stable. Therefore, the stripper pressure of 2.1 bar is suitable for both 5 and 10% PZ content CO<sub>2</sub> capture processes.

Figure 2c,d shows that the reboiler duty reduces from 3.4 to 3.235 MJ/kg CO<sub>2</sub> in 15% PZ and 3.37 to 3.20 MJ/kg CO<sub>2</sub> in 20% PZ content with the increase of stripper pressure from 1.3 bar to 2.3 bar. At 2.3 bar stripper pressure, the reboiler temperatures are 124.73 °C and 123.94 °C for 15 and 20% PZ content, respectively. Further increasing the stripper pressure cannot significantly reduce the energy requirement but increases the reboiler temperature. Moreover, at high stripper pressure, the solvent pump's energy consumption and steam extraction also increase. Therefore, 2.3 bar stripper pressure for 15 and 20% PZ content process is suitable.



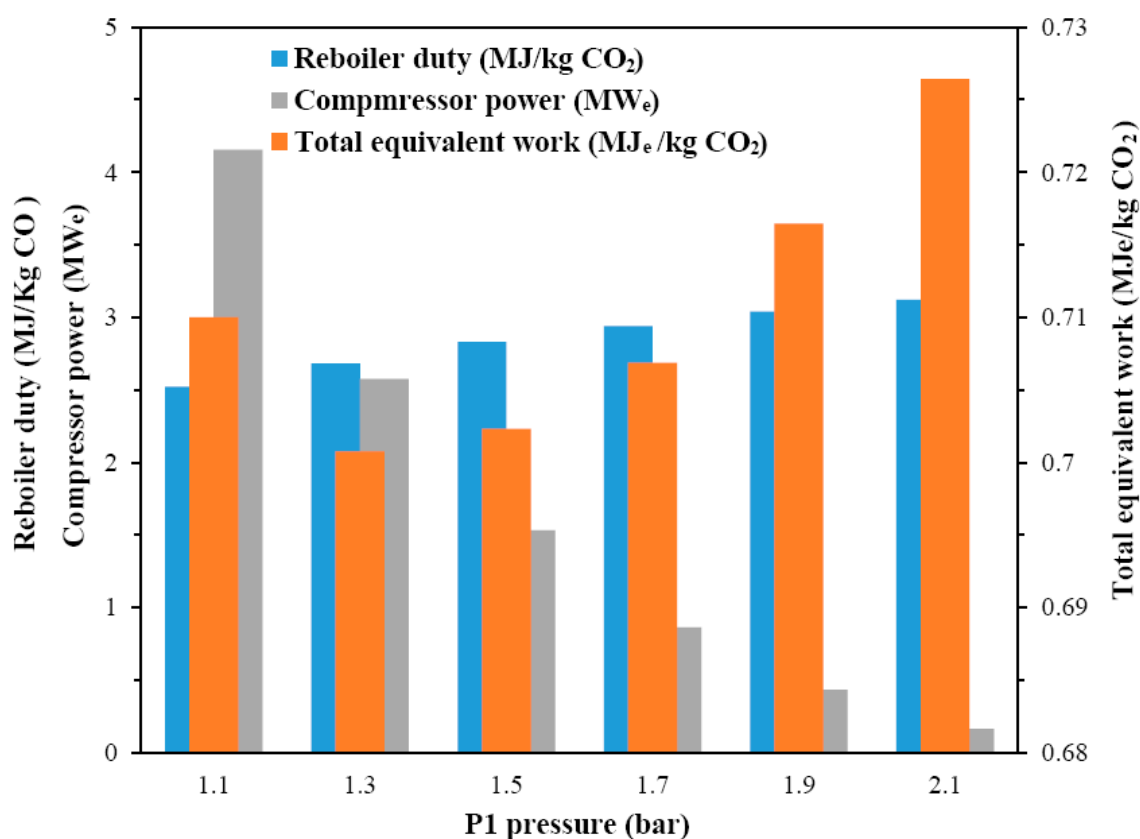
**Figure 2.** Effect of stripper pressure on reboiler duty and regeneration temperature of: (a) 5% PZ and 45% MDEA solution, (b) 10% PZ and 40% MDEA solution, (c) 15% PZ and 35% MDEA solution, and (d) 20% PZ and 30% MDEA solution.

### 3.1.2. MDEA/PZ Ratio Effect

PZ content in MDEA/PZ solution plays an important role in the CO<sub>2</sub> capture process. It can effectively promote the absorption rate of MDEA solution and can quickly absorb CO<sub>2</sub> from the flue gas. Figure 3 shows that PZ content in MDEA/PZ solution has significant effects on the reboiler duty and CO<sub>2</sub> lean loading. Regeneration energy on MDEA/PZ ratio of 45/5, 40/10, 35/15, and 30/20 wt.% has been investigated. The reboiler duty reduces from 3.6 to 3.22 MJ/kg CO<sub>2</sub> as PZ content increases from 5 to 20% at 2.1 bar stripper pressure.

Lean CO<sub>2</sub> loading should be increased with the increasing of PZ content in the solution, while keeping the MDEA/PZ ratio fixed at 50 wt.%. This is due to the carbamate's higher stability, as CO<sub>2</sub> reacts preferentially with PZ to produce carbamate instead of bicarbonate of MDEA in MDEA/PZ solutions. Therefore, lean CO<sub>2</sub> loading has been increased from 0.036 to 0.24 mol/mol with the increasing of PZ content from 5 to 20 wt.%.

As shown in Figure 2c,d, the regeneration energy of both 15 and 20 wt.% PZ at 2.3 bar stripper pressure is 3.235 and 3.20 MJ/kg CO<sub>2</sub>, respectively. The losses of PZ increase from 172 to 257 ppm from the absorber as PZ content increases from 15 to 20 wt.% in MDEA/PZ solution. The energy requirement at 15 wt.% is slightly higher than 20 wt.%. Therefore, 15% PZ content is suitable for CO<sub>2</sub> capturing process. CO<sub>2</sub> lean loading was 0.18 mol/mol for 15 wt.% PZ content.



**Figure 3.** Effect of P1 pressure on reboiler duty, compressor, and total equivalent work.

### 3.2. Process Modification

In the above section of optimizing the operating parameters, the reboiler duty was reduced from 3.6 to 3.235 MJ/kg CO<sub>2</sub>. However, according to Zhao, Liu [17], 1.6 GJ/t CO<sub>2</sub> is the reaction heat, which means that the reboiler duty can be further reduced. Therefore, RVC and CSS processes have been proposed to further minimize the energy requirement.

#### 3.2.1. Effect of Rich Vapor Compression Process (RVC)

In the analysis of the RVC process, it was shown that P1 pressure plays a significant role in the reduction of regeneration energy. The pressure in P1 was reduced up to 1.1 bar to generate extra vapors in the stream passing through the heat exchanger. After flashing, these extra vapors were compressed in the compressor and fed into the stripper bottom, which results in the reduction of the reboiler duty. The liquid stream was passed through the solvent pump P2 to increase its pressure and fed into the middle of the stripper.

Extra vapors of high temperature can minimize the reboiler duty, but they can also increase the compressor work because of more vapors flow and compression pressure ratio in the compressor. A suitable value of pressure for the P1 must be selected where both the compressor and reboiler duty are lower. Therefore, P1 pressure was varied from 1.1 to 2.1 bar to analyze the reboiler duty, compressor work, and the total equivalent work as shown in Figure 3.

Figure 3 shows that reducing pressure at P1 from 2.1 to 1.1 bar reduces the reboiler duty from 3.12 to 2.52 MJ/kg CO<sub>2</sub>. The condenser duty is also reduced with the lowering of pressure at P1. However, the compressor power was increased from 0.164 to 4.16 MW<sub>e</sub>, and consequently, the total equivalent work increases. The optimum value of P1 was 1.3 bar where the total equivalent work is minimum. Further reducing the pressure can decrease the reboiler duty, but the total equivalent work increases due to compressor power increasing. Therefore, 1.3 bar is the suitable value for P1 at



which the total equivalent work is 0.7 MJ<sub>e</sub>/kg CO<sub>2</sub> and the reboiler duty is 2.68 MJ/kg CO<sub>2</sub>. The reboiler duty and the corresponding total equivalent work are about 17% and 6.3% lower than the previous optimized process.

### 3.2.2. Effect of Cold Solvent Split Process (CSS)

CSS is a well-known method used to reduce both the reboiler and condenser duties with no usage of any additional energy-consuming equipment. To figure out energy minimization in both reboiler and condenser duties, the split fraction was increased from 5 to 20%.

Figure 4 shows that the reboiler duty is reduced significantly from 2.99 to 2.78 MJ/kg CO<sub>2</sub> as the split fraction increases from 5 to 15%. The condenser duty is reduced from 0.62 to 0.26 MJ/kg CO<sub>2</sub> up to 15% split fraction. This is due to the significant reduction in the heat of vaporization, which subsequently reduces the regeneration energy. Above a 15% split fraction, the reboiler duty again increases and reaches 2.81 MJ/kg CO<sub>2</sub> at a 20% split fraction. This is because more sensible heat is required to heat the cold split solvent to the required temperature. Therefore, a split fraction of 15% is used for all the subsequent simulation processes. The reboiler duty of about 14% and the condenser duty is reduced from 0.92 to 0.26 MJ/kg CO<sub>2</sub> as compared to the base process.

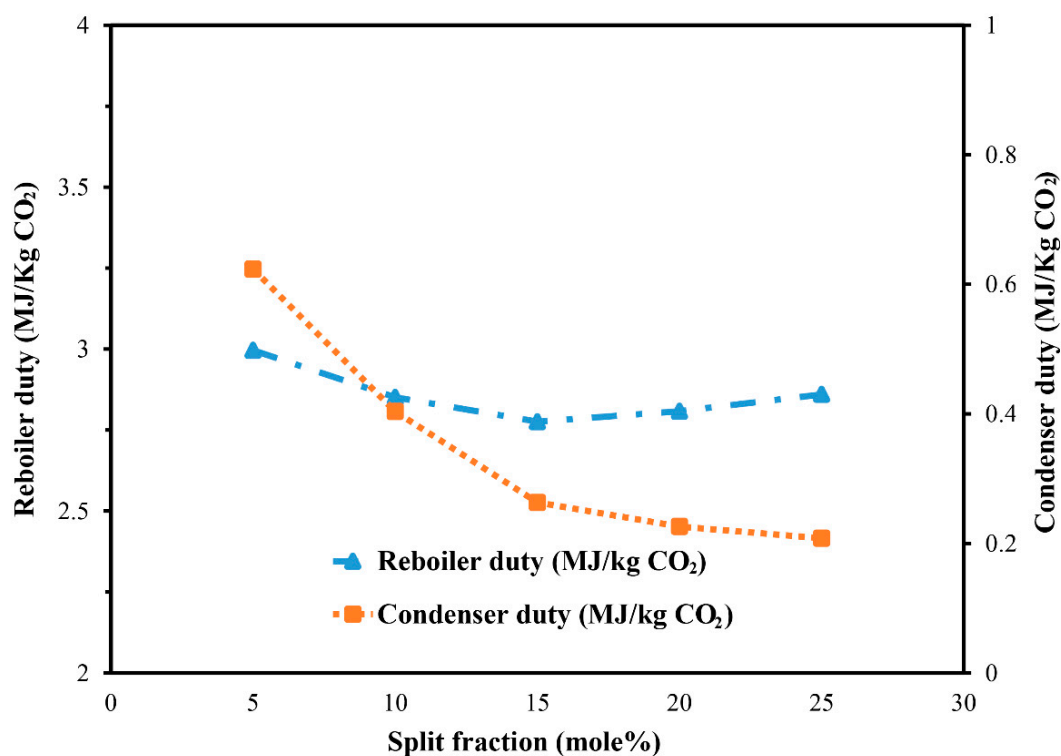


Figure 4. Effect of solvent split on reboiler and condenser duty.

### 3.2.3. Effects of Combined RVC and CSS Processes

The energy consumption can be further reduced by combining RVC and CSS processes to get advantages from the properties of both. In the combined process, the pressure of pump P1 was varied from 1.1 to 2.1 bar and the reboiler duty, compressor work, pumps work, heat exchanger duty, and the total equivalent work were analyzed, as shown in Table 3. Furthermore, the stripper pressure and heat exchanger logarithmic mean temperature difference (LMTD) were fixed at 2.3 bar and 10 K, respectively, for all the simulation processes. In the CSS process, 15 mol.% of the stream exiting the absorber was split and put into the stripper top, while the remaining 85% was passed through the heat exchanger. In 20 stages of the stripper, cold solvent (15% split) was provided to the stripper at stage 2, the liquid stream from the flash vessel at the middle (stage 10), and the vapor stream to the bottom.

**Table 3.** Effects of the pressure drops on the equipment duties and total equivalent work.

| Pressure in P1 (bar) | Heat Exchanger $MW_{Th}$ | Vapors Fraction (mol.%) | Compressor Work ( $MW_e$ ) | Pumps ( $MW_e$ ) | Condenser Duty ( $MW_{Th}$ ) | Reboiler Duty ( $MW_{Th}$ ) | Total Equivalent Work (MJ/kg $CO_2$ ) |
|----------------------|--------------------------|-------------------------|----------------------------|------------------|------------------------------|-----------------------------|---------------------------------------|
| 1.1                  | 165.4                    | 6.56                    | 5.056                      | 0.121            | 0.299                        | 68.73                       | 0.653                                 |
| 1.3                  | 163.0                    | 5.50                    | 3.242                      | 0.121            | 0.316                        | 73.54                       | 0.631                                 |
| 1.5                  | 159.9                    | 4.56                    | 1.993                      | 0.121            | 0.331                        | 78.34                       | 0.626                                 |
| 1.7                  | 157.3                    | 3.80                    | 1.160                      | 0.121            | 0.343                        | 82.23                       | 0.628                                 |
| 1.9                  | 154.4                    | 3.13                    | 0.599                      | 0.121            | 0.352                        | 85.92                       | 0.637                                 |
| 2.1                  | 151.7                    | 2.58                    | 0.232                      | 0.121            | 0.358                        | 89.22                       | 0.645                                 |

Table 3 shows that reducing the pressure in P1 from 2.1 to 1.1 bar can increase the vapor fraction from 2.58 to 6.56 mole%, resulting in a reduction in reboiler duty from 2.78 to 2.14 MJ/kg  $CO_2$ . However, the compressor power was increased from 0.23 to 5.05  $MW_e$ , and consequently the total equivalent work increased. The heat exchanger heating duty also increases with the lowering of pressure in P1 as shown in Table 3. The optimum value of pressure for P1 was 1.5 bar, at which the total equivalent work was the lowest. Further reducing the pressure can decrease the reboiler duty, but the total equivalent work increases due to compressor power increasing. Therefore, 1.5 bar is the suitable value for P1 at which the total equivalent work is 0.627  $MJ_e/kg CO_2$ , reboiler duty is 2.44 MJ/kg  $CO_2$ , and the condenser duty is 0.33 MJ/kg  $CO_2$ . Table 4 shows that the reboiler duty is reduced by about 24.6% and the total equivalent work is reduced by about 16.2% as compared to the reference case.

**Table 4.** Comparison of all the processes.

| Simulation Conditions                    | Reference Case (Optimal Conditions) | Cold Solvent Split | Rich Vapor Compression | Combined Process |
|--|-------------------------------------|--------------------|------------------------|------------------|
| Absorbent flow rate (t/h)                | 3500                                | 3500               | 3500                   | 3500             |
| Flue gas flow rate (t/h)                 | 775                                 | 775                | 775                    | 775              |
| L/G (mass)                               | 4.52                                | 4.52               | 4.52                   | 4.52             |
| Lean $CO_2$ loading (mol/mol)            | 0.18                                | 0.18               | 0.18                   | 0.18             |
| Split fraction (%)                       | –                                   | 15                 | –                      | 15               |
| <b>Results</b>                           |                                     |                    |                        |                  |
| $CO_2$ mole purity (%)                   | 99                                  | 99                 | 99                     | 99               |
| Compressor power (MW)                    | –                                   | –                  | 2.57                   | 1.99             |
| Reflux ratio (mass)                      | 0.325                               | 0.082              | 0.256                  | 0.106            |
| Condenser temperature ( $^{\circ}C$ )    | 20                                  | 20                 | 20                     | 20               |
| Condenser duty (MJ/kg $CO_2$ )           | 0.92                                | 0.26               | 0.73                   | 0.33             |
| Reboiler duty (MJ/kg $CO_2$ )            | 3.235                               | 2.78               | 2.68                   | 2.44             |
| Total Equivalent work ( $MJ_e/kg CO_2$ ) | 0.7478                              | 0.643              | 0.7                    | 0.627            |
| Total equivalent energy saving (%)       | –                                   | 14                 | 6.4                    | 16.2             |

### 3.3. Comparison with MEA-Based RVC and Lean Vapor Compression (LVC) Processes

Table 5 shows a comparison of the reboiler duty, compressor work, and total equivalent energy of this study with the RVC and LVC for MEA-based processes proposed by Jung, Jeong [20]. It is shown that the reboiler duty of MDEA/PZ-based  $CO_2$  capture process is lower than the MEA-based process. The RVC with CSS process can also save 16.2% of total equivalent energy, which is greater than 8.4% of RVC+CSS and 3.3% of LVC+CSS in MEA-based processes.

**Table 5.** Comparison with MEA-based LVC and RVC processes.

| Processes              | Reboiler Duty <sup>b</sup><br>(MJ <sub>e</sub> /kg CO <sub>2</sub> ) | Compressor Work <sup>c</sup><br>(MJ <sub>e</sub> /kg CO <sub>2</sub> ) | Pumps Work <sup>c</sup><br>(MJ <sub>e</sub> /kg CO <sub>2</sub> ) | Total Work<br>(MJ <sub>e</sub> /kg CO <sub>2</sub> ) | Total Energy Saving (%) |
|------------------------|--|--|---|--|-------------------------|
| Reference (this study) | 0.744  | -  | 0.0038  | 0.7478   | -                       |
| RVC (this study)       | 0.616  | 0.08   | 0.0038  | 0.7  | 6.4                     |
| RVC + CSS (this study) | 0.561  | 0.0626   | 0.0038  | 0.627  | 16.2                    |
| Base <sup>a</sup> [20] | 0.813  |  | 0.068   | 0.881  | -                       |
| RVC + CSS [20]         | 0.652  | 0.087  | 0.068   | 0.807  | 8.4                     |
| LVC + CSS [20]         | 0.692  | 0.092  | 0.068   | 0.852  | 3.3                     |

<sup>a</sup> Absorber intercooling. <sup>b</sup> Conversion factor: 0.23. <sup>c</sup> Efficiency of compressor and pump: 75.

### 3.4. Direct Cost of Main Equipment and Annual Cost Saving

In the RVC process, the capital cost increases due to the additional equipment such as compressor, flash vessel, and pumps. The main equipment that increases the capital cost significantly is the compressor. In the previous section, it was shown that lowering the pressure in P1 from 2.1 to 1.1 bar reduces the reboiler and condenser duties. This results in the reduction of the heat transfer areas of both reboiler and condenser and consequently their capital costs. The reboiler cost decreased from 0.616 to 0.52 M\$ and the condenser cost from 0.167 to 0.161 M\$ with the pressure drop from 2.1 to 1.1 bar. The cost of the heat exchanger was almost the same as the base case heat exchanger's cost, and the flash vessel required 0.541 M\$. However, the vapor stream flow rate to the compressor increased from 16.6 kg/s at 2.1 bar to 36.2 kg/s at 1.1 bar, and as a result, the compressor consumption power increased from 0.232 to 5.06 MW. Therefore, the cost of the compressor increases significantly from 1.95 to 22.16 M\$ with the reduction of P1 pressure. In the previous section on the RVC with CSS process, 1.5 bar was considered to be an appropriate pressure for P1 in terms of total equivalent energy saving. However, at 1.5 bar, the compressor cost was 6.25 M\$, which cannot ensure the economic feasibility of the RVC process. From an economic point of view, 1.9 bar was an appropriate pressure, where the compressor, heat exchanger, reboiler, condenser, and flash vessel costs were 2.67, 3.38, 0.594, 0.166, and 0.541 M\$, respectively.

To ensure that the RVC process is economically reasonable, a tradeoff was performed between the additional equipment cost and energy savings. The RVC process requires an additional 3.05 M\$ to purchase the equipment. The annual depreciation change was obtained using Equation (2).

$$\text{Annual depreciation change} = \text{installation factor} \times \sum \frac{\Delta \text{Purchase cost change}}{\text{Equipment lifetime}} \quad (2)$$

Table 6 shows the list of parameters used to calculate the annual depreciation change and energy cost saving. The values of equipment lifetime were taken from the study of Fernandez, Bergsma [19] and average electricity cost for industries from EIA [26]. The lifetimes of both reboiler and condenser were assumed to be 20 years.

**Table 6.** List of parameters used to calculate the energy cost and annual depreciation change.

| Parameter                       | Value     |
|---------------------------------|-----------|
| Installation factor             | 4         |
| Compressor lifetime             | 10        |
| Flash vessel lifetime           | 25        |
| Heat exchangers lifetime        | 20        |
| Electricity (\$/MWh)            | 67.5 [22] |
| Annual plant operation time (h) | 7450      |

The annual depreciation change was calculated as 1.22 M\$/yr for the RVC with the CSS process of 1.7 bar of P1 pressure as shown in Table 7. This respective case can save 0.11 MJ/kg CO<sub>2</sub> total equivalent energy, which is equal to 1.79 M\$/yr energy cost. By considering the equipment cost, the total cost saving in one year is 0.67 M\$.

**Table 7.** Total annual cost savings.

| Equipment Cost (M\$)                       | Base  | RVC+CSS |
|--|-------|---------|
| Heat exchanger                             | 3.398 | 3.385   |
| Compressor                                 | -     | 2.67    |
| Reboiler                                   | 0.68  | 0.594   |
| Flash vessel                               | -     | 0.541   |
| Condenser                                  | 0.232 | 0.166   |
| Purchase cost changes                      |       | 3.05    |
| <b>Annual depreciation change (M\$/yr)</b> |       | 1.122   |
| Energy cost saving                         |       | 1.791   |
| Total cost saving                          |       | 0.67    |

Table 7 shows that RVC with CSS process for MDEA/PZ-based CO<sub>2</sub> capture process is economically feasible. However, most of the process modifications also have their own drawbacks, such as requiring additional equipment and complexifying the process. Therefore, an overall techno-economic and experimental investigation of this process is required to find out whether it would be feasible or not.

#### 4. Conclusions

In this paper, a PZ-promoted aqueous solution of MDEA was proposed for the CO<sub>2</sub> capture process from the flue gas of a 650 MW coal power plant. The process was simulated with the help of Aspen Plus V.10, and the operating parameters, including PZ and MDEA concentration, and stripper pressure, were optimized in the first stage to reduce the energy consumption. The optimal process was considered as the reference case, and process modifications were proposed to further reduce the energy consumption. The proposed process modifications include rich vapor compression (RVC), cold solvent split (CSS), and the combination of both processes. The RVC process was analyzed by varying P1 pressure to find an appropriate pressure of P1 to get low energy consumption. The process modifications were compared with the reference case from an energy point of view. Moreover, the total equivalent energy obtained in both RVC and RVC with CSS processes of this study were compared with the energy consumption of MEA-based RVC and lean vapor compression (LVC) processes. Aspen capital cost estimator (ACCE) was used to calculate the direct cost of the main equipment. To ensure the process is economically feasible, a tradeoff between extra equipment cost and energy savings was performed. The conclusions of the study are as follows.

- I. Among different MDEA/PZ concentration ratios (45/5, 40/10, 35/15, and 30/20 wt.%), from an energy minimization point of view, 35/15 wt.% was selected to be an appropriate ratio. Although the energy requirement at 15 wt.% PZ was slightly higher than at 20 wt.%, PZ losses from the absorber were also higher (257 ppm) at 20 wt.% than at 15 wt.% PZ (172 ppm). The reboiler duty of 3.235 MJ/kg CO<sub>2</sub> was obtained at a MDEA/PZ ratio of 35/15 wt.%. A stripper pressure of 2.3 bar was selected because above that pressure, the reboiler temperature was increased from 125 °C.
- II. In only the RVC process, the lowest total equivalent energy (among other P1 pressure) of 0.7 MJ/kg CO<sub>2</sub> was obtained at 1.3 bar P1 pressure, which was 6.4% lower than the reference case. Similarly, a split fraction of 15% was chosen for the CSS process. The lowest reboiler duty of 2.78 MJ/kg CO<sub>2</sub> was achieved at 15% split, and it was 14% lower than the reference case.

- III. In the combined RVC and CSS process, 1.5 bar P1 pressure and 15% split fraction were appropriate values. The total equivalent work was 0.627 MJ<sub>e</sub>/kg CO<sub>2</sub>, the reboiler duty was 2.44 MJ/kg CO<sub>2</sub>, and the condenser duty was 0.33 MJ/kg CO<sub>2</sub>. The reboiler duty was reduced about 24.6% and the total equivalent work about 16.2% as compared to the reference case. The reboiler duty was reduced further, but due to the increasing of compressor power, the total equivalent work was also raised. The annual depreciation change was calculated as 1.22 M\$/yr for the RVC with CSS process. The total energy cost saving was 1.79 M\$/yr, and when considering the equipment cost, the total cost saving in one year was 0.67 M\$.

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