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RESEARCH PAPER

Advanced Amine Solvent Strategies for Efficient CO_2 Capture in Post-Combustion Systems

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Abstract

Process simulations serve as an efficient and cost-effective method for evaluating the performance of various amine solvents and their blends in CO_2 capture technologies. This study utilized a performance indicator model to assess the effectiveness of n-methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) blends, supplemented with the activator piperazine (PZ). Key parameters such as solvent flow rates, equipment heat duties, and associated costs including energy consumption and carbon taxes were incorporated into the analysis. Among the tested formulations, a binary blend consisting of 25 wt% AMP and 5 wt% PZ demonstrated superior performance, achieving a 35% improvement over the baseline 30 wt% AMP solvent. Further enhancement was realized through the implementation of absorber intercooling (ICA) within the simulation design, which elevated the performance rating by an additional 9%. These results highlight the significant potential of optimizing solvent compositions and incorporating innovative process configurations to improve the efficiency of post-combustion CO_2 capture systems. The findings provide valuable insights for developing more effective and sustainable approaches to reducing carbon emissions in large-scale industrial applications.

Highlights

Performance indicator model is used for CO_2 capture solvent screening.
Assessment of the amine-based solutions for CO2 capture is performed.
MDEA and AMP in different blends along with the activator PZ are used.
25 wt.% AMP + 5 wt.% PZ + 70 wt.% H_2O is the best performing solvent.
ICA process configuration improves the rating of conventional configuration.

Keywords CO_2 capture · Performance · Post-combustion · Amines · Absorption · Process simulation

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Introduction

Carbon capture, storage, utilization, and sequestration (CCUS) are being pursued globally with urgency to achieve the COP26 targets of carbon neutrality by 2050. As a short-term solution, CCUS is essential for limiting global warming to below 1.5 °C (Hansen et al. 2008; Zhang et al. 2017). Power stations and refineries, the largest sources of CO_2 emissions, are of particular concern, as power generation traditionally depends on the combustion of carbon-based fuels. With the transition to a green economy and the increasing focus on renewable energy, capturing CO_2 remains a critical step. Additionally, in sectors that are difficult to decarbonize, carbon capture technologies will be indispensable. Immediate replacement of power generation with renewable energy sources is not feasible (Vortmeyer

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et al. 2013), making a diversified energy ecosystem necessary, with CCUS playing a crucial role during the transition away from fossil fuels. There is growing interest in utilizing carbon dioxide as a resource within this energy mix. The literature extensively covers the modification and optimization of existing materials for CO_2 capture from flue gas and stack gas. These materials include absorbents and adsorbents such as alkanolamines, zeolites, ionic liquids, amine-grafted silicas, carbon-based adsorbents, and metal-organic frameworks. Additionally, CO_2 capture applications involving gas hydrates, membranes, and biofixation methods are widely discussed in the literature. Although emerging solvents such as ionic liquids show potential, they are often hindered by high costs, viscosity challenges, and limited operational data, making amines a more practical choice for near-term deployment. Furthermore, industries still seek solution strategies and techniques for the upgrading of current methods (D'Alessandro et al. 2010; Yang et al. 2017). Absorption using alkanolamines and its blends are the focus of this study via process simulations.

Pre-combustion CO_2 capture involves converting fuel into a mixture of hydrogen and carbon monoxide (syngas), followed by a water-gas shift reaction to produce CO_2 and H_2, allowing for CO_2 separation prior to combustion. This method is commonly used in integrated gasification combined cycle (IGCC) power plants and chemical production facilities. Oxy-fuel combustion, on the other hand, burns fuel in pure oxygen instead of air, resulting in a flue gas that is primarily water vapor and CO_2, which simplifies downstream CO_2 separation. While both approaches offer high CO_2 capture efficiency, they often require significant modifications to existing plant infrastructure and have unique technical and economic considerations (Nwaoha et al. 2017). In contrast, post-combustion capture, applied in this study, is particularly attractive for retrofitting existing power stations due to its flexibility and lower integration cost (Kanniche et al. 2017). Furthermore, due to the comparatively low CO_2 content in the gas stream, this can be removed more efficiency via chemical than physical methods, as reported by various authors when comparing carbon capture technologies (Kanniche et al. 2010, 2017; Mondal et al. 2012).

This investigation considered a fossil fueled power plant, where the PCC plant is positioned after the main boiler. Therefore, the power production is not affected in the event of changes or malfunctioning in the carbon capture section of the plant. The inclusion of a PCC plant necessitates considerable capital investment with its operation consuming approximately 20% of the power plant's energy output (Gammer 2016). This high energy demand is due to inevitable energy losses during process operations, especially at larger scale. These findings support the need to improve PCC technology (Gammer 2016).

A range of processing methods are adopted in carbon capture operations. These include absorption (generally applied in post- and pre-combustion), adsorption, cryogenic distillation, membranes, gas hydrates and chemical looping, with the latter applicable to pre- and oxyfuel-combustion) (D'Alessandro et al. 2010; Yang et al. 2017). Although alternative CO_2 capture technologies such as adsorption, cryogenic distillation, membranes, gas hydrates, and chemical looping are being actively researched, each faces specific technical and economic limitations for post-combustion applications at commercial scale. Chemical absorption using amine-based solvents remains the most industrially viable method for large-scale retrofitting, which is why this study focuses exclusively on this approach.

Chemical absorption studies covering a vast range of amine solvents have been reported for the capture of CO_2. Popular amines include 2-amino-2-methyl-1-propanol (AMP), diethanolamine (DEA), N-methyldiethanolamine (MDEA), monoethanolamine (MEA) and piperazine (PZ), whose structures are also shown in Fig. 1. There are a number of studies in the literature which have considered blends of either MDEA or AMP with PZ in different concentrations (Ali and Aroua 2004; Brúder et al. 2011; Dash and Bandyopadhyay 2016; Dash et al. 2011, 2012; Derks 2006; Li et al. 2013; Liu et al. 1999; Tong et al. 2013; Wong et al. 2014; Yang et al. 2010). These amine-based solvents, and blends thereof, were selected for the simulation studies.

In addition, many CO_2 capture simulation studies report the use of MEA as a solvent, with the sole objective being process optimization and process modifications (Freguia and Rochelle 2003; Fisher et al. (2005; Abu-Zahra et al. (2007; Han et al. (2011; Arachchige and Melaaen (2012). In other studies, by Fisher et al. (2007), Kothandaraman et al. (2009), Lee et al. (2009), Chavarro Montenegro (2011), Molina and Bouallou (2013), Naskar et al. (2013), Yakub et

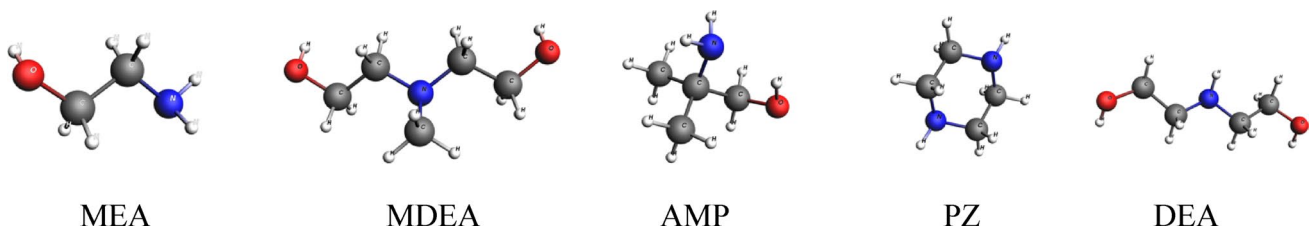


Fig. 1 Structures of the most common amines investigated in the literature

al. (2014) and Erfani et al. (2015) the performance of MEA was compared to solvents such as diethanolamine (DEA), methyldiethanolamine (MDEA), AMP, piperazine (PZ) and various combinations of blends using these amines. In using pilot plant data with MEA as the solvent, the results by (Øi L.E., 2007) demonstrated the efficiency in the addition of a capture plant to a parent power plant. Others have compared the simulation software data results to the pilot plant results (Aliabad and Mirzaei 2009; Luo et al. 2009; Mirzaei et al. 2009), including model development for improved CO_2 capture representation (Abu-Zahra et al. 2012; Ahmadi 2012; Lim et al. 2013; Lin et al. 2016; Øi L.E., 2012; Zhang et al. 2009) and a techno economic analysis of a CO_2 capture plant (Li and Liang 2012; Razi et al. 2013).

Process simulation studies by Adeosun and Abu-Zahra (2013), Daya (2017), Erfani et al. (2015), Fisher et al. (2007), Molina and Bouallou (2013), and Padurean et al. (2011), compared the performance of solvent blends to pure aqueous solvents or solvent blends. Jones et al. (2013) evaluated an aqueous tri-amine blend of MEA, MDEA and AMP, which to the best of our knowledge appears to be a novel study via process simulations involving an aqueous tri-amine blend. A summary of the key literature sources, capture methods, and their main findings discussed in the introduction is presented in Table 1.

Table 1 Summary of key literature on CO_2 capture technologies and solvents

Reference	Capture Method	Key Findings/Contributions
D'Alessandro et al. (2010)	Multiple (Adsorbents, MOFs)	Reviewed novel materials for CO_2 capture, highlighting performance, challenges, and industrial relevance.
Yang et al. (2017)	Modeling & Simulation	Provided comprehensive computational modeling of amine-based and non-amine CO_2 capture processes.
Mondal et al. (2012)	Adsorption, Membranes, Cryogenics	Summarized advances and limitations in alternative capture methods, focusing on post-combustion applicability.
Abu-Zahra et al. (2007)	Amine Absorption (MEA)	Presented parametric studies on MEA for post-combustion capture; established performance benchmarks.
Kothandaraman (2010)	Amine Absorption (MEA, AMP, MDEA)	Compared solvents; identified AMP as a favorable alternative for lower energy use and degradation.
Le Moullec et al. (2014)	Process Modification	Demonstrated operational benefits of absorber intercooling for energy savings in amine-based systems.
Li and Liang (2012)	Techno-Economic Analysis	Modeled capture plant economics; emphasized cost drivers for different solvent/process scenarios.
Veawab et al. (2001)	Corrosion Inhibition	Reported on effective use of corrosion inhibitors in amine systems for long-term operational stability.
Dash and Bandyopadhyay (2016)	Solvent Blends (MDEA, PZ)	Showed enhanced CO_2 solubility and absorption rates with piperazine-activated MDEA blends.
Brúder et al. (2011)	Solvent Blends (AMP, PZ)	Investigated synergy in AMP-PZ blends for improved post-combustion capture efficiency.

Using the basis of a PCC plant, process simulations were performed using Aspen Plus® V8.8 software, to evaluate and benchmark aqueous amine solvents and their blends against a 30 wt% AMP solution to achieve a rate of 90% carbon capture. This is a continuation of the work in applying a Performance Indicator Model (PIM), which was developed by Daya (2017), who had selected MEA as the solvent basis. For reasons explained earlier in the article, AMP was selected as the basis based on literature findings. The PIM is used to evaluate the performance of aqueous amine blends consisting of binary combinations of MDEA or AMP with PZ as an activator, in different concentrations. The amine concentrations selected in this studyare based on prior experimental and simulation studies that highlight their synergistic performance in post-combustion CO_2 capture. AMP offers high CO_2 loading capacity and stability, while PZ significantly enhances reaction kinetics when used in small quantities. Studies such as Dash and Bandyopadhyay (2016) confirm that increasing PZ concentration improves CO_2 solubility and enhances the reaction rate. Moreover, the concentration levels used here are within practical industrial ranges, as higher concentrations of AMP (>30 wt%) can increase viscosity and pose operational challenges.To enable a comprehensive evaluation tool, the inputs to this performance indicator model included the key parameters such as primarily solvent flow rates and equipment heat duties, calculated using the ASPEN Plus® process simulation designs. Other significant inputs to the model involved costs based on energy requirements, make-up flows, and carbon taxes. The usefulness of such a model provides insight into the viability of a large-scale process and enables the selection of promising solvent or blends without expensive experimental efforts.

Post-combustion CO_2 Capture Simulations and Data

In the Aspen Plus simulations, the Electrolyte Non-Random Two-Liquid (eNRTL) model was employed to represent the aqueous mixed electrolyte system, whilst the Peng-Robinson equation of state (PREoS) and Boston-Mathias alpha function was used to represent the gas phase.

System Chemistry and Kinetics

The reactions between amines with CO_2 takes place in the absorber resulting in the formation of the intermediate compounds. The absorption reaction is then reversed in the stripper to release the absorbed CO_2. The reactions mentioned below were considered for the absorption process using amines (AspenTech 2015b):

$$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+ \quad (1)$$

$$2H_2O \leftrightarrow H_3O^+ + OH^- \quad (2)$$

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H3O^+ \quad (3)$$

$$MEA^+ + H_2O \leftrightarrow MEA + H_3O^+ \quad (4)$$

$$MEACOO^- + H_2O \leftrightarrow MEA + HCO_3^- \quad (5)$$

$$MDEA^+ + H_2O \leftrightarrow MDEA + H_3O^+ \quad (6)$$

Table 2 Equilibrium constants used in the simulation

Reaction	A	B	C	D	Ref
1	231.465	− 12092.1	− 36.7816	0	Aspen-Tech. (2015a)
2	132.899	− 13445.9	− 22.4773	0	Austgen et al. (1991)
3	216.049	− 12431.7	− 35.4819	0	Austgen et al. (1991)
4	− 3.038	− 7008.36	0	− 0.003135	Austgen et al. (1991)
5	− 0.521	− 2545.53	0	0	Austgen et al. (1991)
6	− 9.417	− 4234.98	0	0	Aspen-Tech. (2015a);
7	− 3.686	− 6754.69	0	0	Dash et al. (2011)
8	− 62.28	− 2564	6.787	0	Aspen-Tech. (2015a);
9	466.497	1614.5	− 97.54	0.2471	Dash et al. (2012)
10	6.822	− 6066.9	− 2.29	0.0036	Dash et al. (2011)
11	− 11.563	1769.4	− 1.467	0.0024	Dash et al. (2011)

$$AMP^+ + H_2O \leftrightarrow AMP + H_3O^+ \quad (7)$$

$$PZH^+ + H_2O \leftrightarrow PZ + H_3O^+ \quad (8)$$

$$PZ + CO_2 + H_2O \leftrightarrow PZCOOO^- + H_3O^+ \quad (9)$$

$$HPZCOO + H_2O \leftrightarrow PZCOO^- + H_3O^+ \quad (10)$$

$$PZCOO^- + HCO_3^- \leftrightarrow \mathrm{PZ}(COO^-)_2 + H_2O \quad (11)$$

In order to define the equations describing the equilibrium constants of the aforementioned reactions in Aspen Plus the following equation was used (temperature is in Kelvin):

$$\ln(K_{eq}) = A + \frac{B}{T} + Cln(T) + DT \quad (12)$$

in which the equilibrium constants A, B, C and D are represented in Table 2.

Flowsheet Setup

The CO_2 capture system has inherent convergence issues due to its ionic nature and the presence of chemical reactions within the absorber and stripper. It was thus decided to model the closed-loop system with an open loop (where the recycle stream is not connected to the absorber), to simplify the simulation calculations. Open-loop simulations were used to facilitate stable convergence in the complex ionic systems modeled here. This approach is supported by several literature studies: for instance, Ahmadi (2012) reports that energy requirement discrepancies between open- and closed-loop simulations are typically less than 2% for post-combustion CO_2 capture processes. Kothandaraman (2010) and Daya (2017) also demonstrate that open-loop simulations provide quantitatively reliable performance data for steady-state studies. Thus, open-loop simulations are widely accepted for comparative and design analyses at steady state, though closed-loop models may be preferable for studies focused on process dynamics or control. To achieve the desired CO_2 capture rate of 90% whilst maintaining commercial sizes for the separation columns, four parallel trains were used in the capture section of the flowsheet. Maintaining commercial column sizes influences solvent circulation rates and energy requirements, with fixed dimensions ensuring consistency across simulations and alignment with industrial practice.

Convergence in the Aspen Plus® simulations was challenging due to the complex ionic interactions modeled by the Electrolyte Non-Random Two-Liquid (eNRTL) model and the rapid reaction kinetics of CO_2 with amines, particularly piperazine (PZ). The eNRTL model accounts for

ionic species (e.g., H_3O^+, HCO_3^-, PZH^+) and their non-linear interactions (Eqs. 1–11), which often destabilize solver iterations in the absorber and stripper. Additionally, PZ's high rate constant (~10^4 $M^{-1}s^{-1}$, Dash et al. 2011) creates steep concentration gradients in the packed columns, exacerbating numerical instability. The closed-loop recycle of lean amine further amplifies errors in initial flow rate and composition guesses. To mitigate these, an open-loop configuration was adopted, disconnecting the recycle stream to stabilize calculations, with results validated against closed-loop literature (e.g., <2% energy discrepancy, Abu-Zahra et al. 2007). Robust initial guesses were derived from literature (Table 3), damping factors (e.g., 0.5 for ionic species) were applied to eNRTL calculations, and absorber/stripper blocks were solved sequentially before connecting parallel trains. These strategies ensured stable convergence while maintaining simulation fidelity.

Figure 2. shows the process flow diagram for post-combustion CO_2 capture using absorption. This consists of three main units, including cooling and compression of the flue gas, CO_2 absorption and solvent regeneration, and CO_2 compression which are explained in detail in the next sections (Kothandaraman 2010). The interaction between flue gas cooling, absorption, and CO_2 compression significantly impacts process efficiency. Flue gas cooling to 40 °C enhances absorption kinetics and reduces solvent degradation, lowering reboiler duty. The absorber's CO_2 output determines compression work, which is minimized by higher CO_2 purity from efficient absorption, as seen in the intercooled absorber configuration. These interactions are reflected in the PIM's cost calculations.

Table 3 The various inputs required to use the performance indicator model (PIM)

Inputs into Aspen	Inputs into PIM from Aspen	External inputs into PIM
Flue gas flow rate	Cooler duties	Amine price(s)
Flue gas composition	Stripper condenser duty	Make-up water price
Solvent composition	Direct cooler water flow	Cooling water price
CO_2 capture rate	Stripper reboiler duty	Steam price
	Lean solvent flow from stripper	Corrosion inhibitor price
	Amine flow(s) into absorber	Amine reclaim cost
	Compressor power required	Amine disposal cost
	Pumping power required	Carbon tax rate
	Power required for blower	Amine degradation rate(s)
	Amine make-up flow(s)	Power plant efficiency
	Water make-up flow	
	CO_2 flow into process	

Flue Gas Compression and Cooling Section

Figure 2 shows a direct contact cooler (DCC) which operates at the temperature of the absorber (40 °C), a blower for the flue gas compression and cooling section to adjust the flue gas temperature to the operating conditions prior it enters the absorber. It is well established that DCC has great advantages over indirect coolers. The operational benefits of using a Direct Contact Cooler (DCC) instead of an indirect (surface) heat exchanger in post-combustion CO_2 capture are substantial. In a DCC, the flue gas is brought into direct contact with a cooling liquid (typically water), which enables highly efficient heat transfer and effective removal of water-soluble contaminants such as SO_2, HCl, and particulates. This direct approach provides several operational benefits:

- Lower cooling water requirements: DCCs achieve higher heat transfer coefficients compared to indirect coolers, reducing the volume of cooling water needed for the same temperature drop.
- Reduced capital and operating costs: The simpler design (no large surface area for heat exchange, less scaling/fouling) means DCCs are less expensive to build and maintain.
- Lower pressure drop: The absence of tube bundles or complex flow paths results in a lower pressure drop across the DCC, minimizing fan/blower energy use and operational cost.
- Simultaneous gas scrubbing: DCCs can efficiently remove trace acid gases and particulates from the flue stream, improving downstream equipment life and process reliability.
- Temperature control and solvent protection: The direct quench provides tighter temperature control, which helps minimize solvent degradation in the absorber and reduces reboiler duty.
- In contrast, indirect coolers (shell-and-tube or plate heat exchangers) have lower heat transfer rates for gas-to-liquid systems, higher capital and cleaning costs, and are more susceptible to fouling when exposed to contaminated flue gas.

These combined operational benefits support the choice of DCC as the cooling method in our system design, as also noted by (Kothandaraman 2010). Table 4 presents the specifications of the flue gas fed to the blower. The same composition of the flue gas as used by Khalil and Gerbino (2007) was applied in this study. Insignificant impurities such as sulphur trioxide (SO_3), hydrochloric acid (HCl) and nitrogen dioxide (NO_2) with neglectable concentrations were

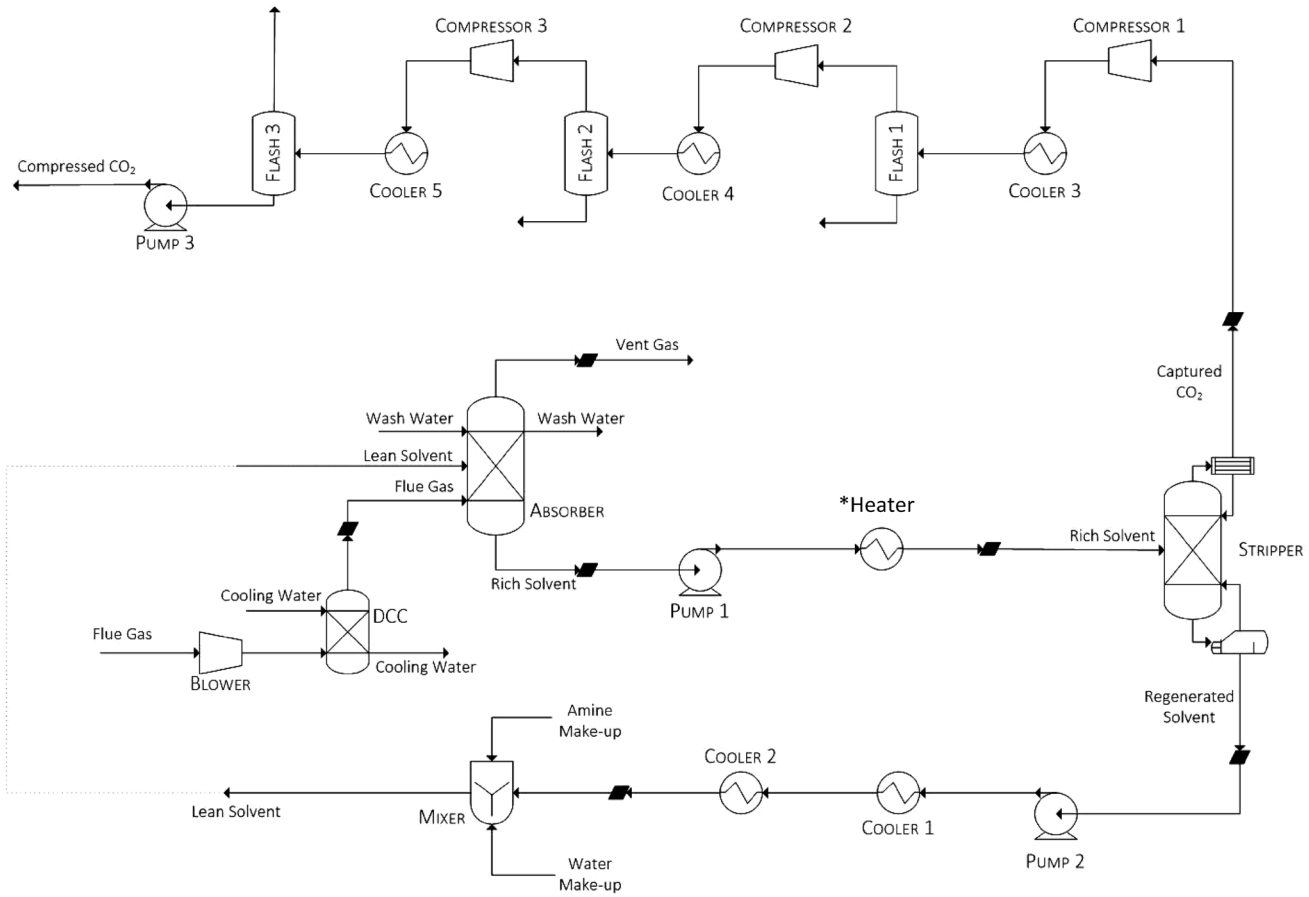


Fig. 2 Flowsheet of the Aspen simulation for CO_2 capture by amine absorption. *In an open loop system, the rich/lean heat exchanger present in conventional configurations of a post-combustion CO_2 capture plant must be represented by a separate heater (HEATER) and cooler (COOLER 1). The heat duties of this heater and cooler are equal in magnitude since in reality this is one heat exchanger. A second cooler (COOLER 2) is needed to further cool the recycled lean solvent to the desired temperature of the absorber

Table 4 Properties of flue gas from a coal-fired power plant, used in this study

Flow Rate (ton/hr)	2516
Temperature (°C)	125
Pressure (kPa)	101.33
Composition (mole fraction)	
Nitrogen (N_2)	0.73470
Oxygen (O_2)	0.05512
Water vapour (H_2O)	0.07975
Carbon Dioxide (CO_2)	0.12010
Argon (Ar)	0.00877
Nitrous Oxide (NO)	0.00030
Sulphur Dioxide (SO_2)	0.00126

ignored and the compositions of the remaining compounds were normalized.

A RadFrac column was utilized within the simulation of the DCC in Aspen Plus® for which the column specifications are presented in Table 5. In the simulation, the blower provided a pressure equal to 111.25 kPa ensuring that the gas enters the absorber under optimal conditions for CO_2 capture. The blower contributes to maintaining favorable flue gas pressure and temperature conditions for effective CO_2 absorption. Although its energy use is not quantified separately, it is incorporated into the overall electrical consumption considered in the performance indicator model (PIM), which evaluates the cost-effectiveness of the capture system.

Table 5 Specifications of the direct contact cooler

Calculation type	Equilibrium
No. of stages	10
Process stream inlet temperature (°C)	134
Process stream outlet temperature (°C)	42
Height (m)	5
Condenser	None
Reboiler	None

CO_2 Capture Section

This vital part of the CO_2 capture plant is comprised mainly of two pieces of equipment for CO_2 capture i.e., the absorber and stripper columns.

Typically, a packed column is selected for the absorber in which the flue gas and the lean amine solvent enter from the bottom and the top, respectively. The addition of a water wash section at the top of the column is recommended by Li et al. (2016) in order to cool and clean the vent gas (Li et al. 2016a). The simulation of the absorber was performed using a RadFrac column. The specifications of the four identical absorbers, connected in parallel are given in Table 6.

Similar to the absorber, a packed column is also used for the stripper which is mainly responsible for the separation of the captured CO_2 from the rich amine solvent. The operational pressure of the stripper was set at 1.8 atm. Basically, the stripper utilizes the heat provided by the steam in the kettle reboiler to reverse whatever reaction occurs in the absorber resulting in the production of the lean solvent at the bottom of the column and a stream mainly containing CO_2 and H_2O at the top. The regenerated solvent exits from the bottom and is recycled to the absorber (Fisher et al. 2007; Kothandaraman 2010).

A RadFrac column was also employed to simulate four identical strippers, connected in parallel for which the column specifications are given in Table 7.

In order to provide a higher operational pressure in the stripper, a pump is included after the absorber. Furthermore, the rich amine solvent with elevated pressure prevents corrosive acid gas release which can cause fatal damage to the vital equipment and piping (Fisher et al. 2005). Similarly, for the aforementioned reasons a pump is also placed after the stripper to recycle the lean amine solvent to the absorber.

In an energy-conservation approach, prior to the regeneration of the amine solvent in the stripper the rich amine from the absorber is pre-heated using the hot lean amine from the stripper reboiler. The temperature of the rich amine is increased to approximately 110 ˚C, concerning a 10˚C temperature approach on the hot side of the heat exchanger (Fisher et al. 2005).

Further cooling of the lean amine is achieved by placing a cooler in the recycle loop in order to bring the lean amine temperature to the absorber operating temperature (±40 °C) (Fisher et al. 2005).

CO_2 Compression Train

In order to compress the CO_2 product stream prior to it being sent for storage, a 4-stage reciprocating compressor, with inter-stage cooling and maximum compression of about 9 MPa, is usually utilized. The resulting supercritical liquid CO_2 is subsequently pumped to the necessary discharge pressure of about 13 MPa (Kothandaraman 2010).

The compression of the captured CO_2 in the simulation in this study is performed using a sequence of three compressors with inter-stage cooling and CO_2 separation from the condensed H_2O. The resultant pressures achieved from each compressor are 430 kPa, 1.9 MPa and 8 MPa, respectively. The supercritical liquid CO_2 is then pumped to the pressure of 11 MPa.

Table 6 Specifications of the absorber

	Section 1	Section 2
	Wash water section	Capture Section
Calculation type	Equilibrium	Equilibrium
No. of stages	2	20
Top pressure (kPa)	105	–
Height (m)	2	20
Diameter (m)	12	12
Condenser	None	–
Reboiler	–	None

Table 7 Specifications of the stripper

Calculation type	Equilibrium
No. of stages	21
Top Pressure (kPa)	200
Height (m)	17
Diameter (m)	14
Condenser	Partial
Reboiler	Kettle

Performance Indicator Model

The evaluation of the performance of the amine solvents considered in this study for CO_2 capture is carried out by entering the simulation results into a performance indicator model (PIM). In this model, the parameters including solvent make-up, cooling water and make-up water, steam, corrosion inhibitor, amine reclaim and disposal, and carbon taxes, were selected as inputs to the model on a cost basis. As indicated in a previous study by Daya (2017) it is more suitable to base the PIM model on the cost of CO_2 avoided, instead of the cost of CO_2 captured since in some cases capturing CO_2 increases the CO_2 emissions. For example, in power plants since the power required for the capture process usually comes from the plant itself the efficiency of the plant decreases resulting in more fuel combusted by the plant to meet the electrical load. A conceptual illustration of CO_2 captured vs. CO_2 avoided is represented in Fig. 3.

Since solvent regeneration is an energy-intensive approach that contributes nearly two-thirds of the operating cost of the CO_2 capture plant, for evaluation of the solvent performance many researchers merely focus on the energy consideration (Khalil and Gerbino 2007). However, in the

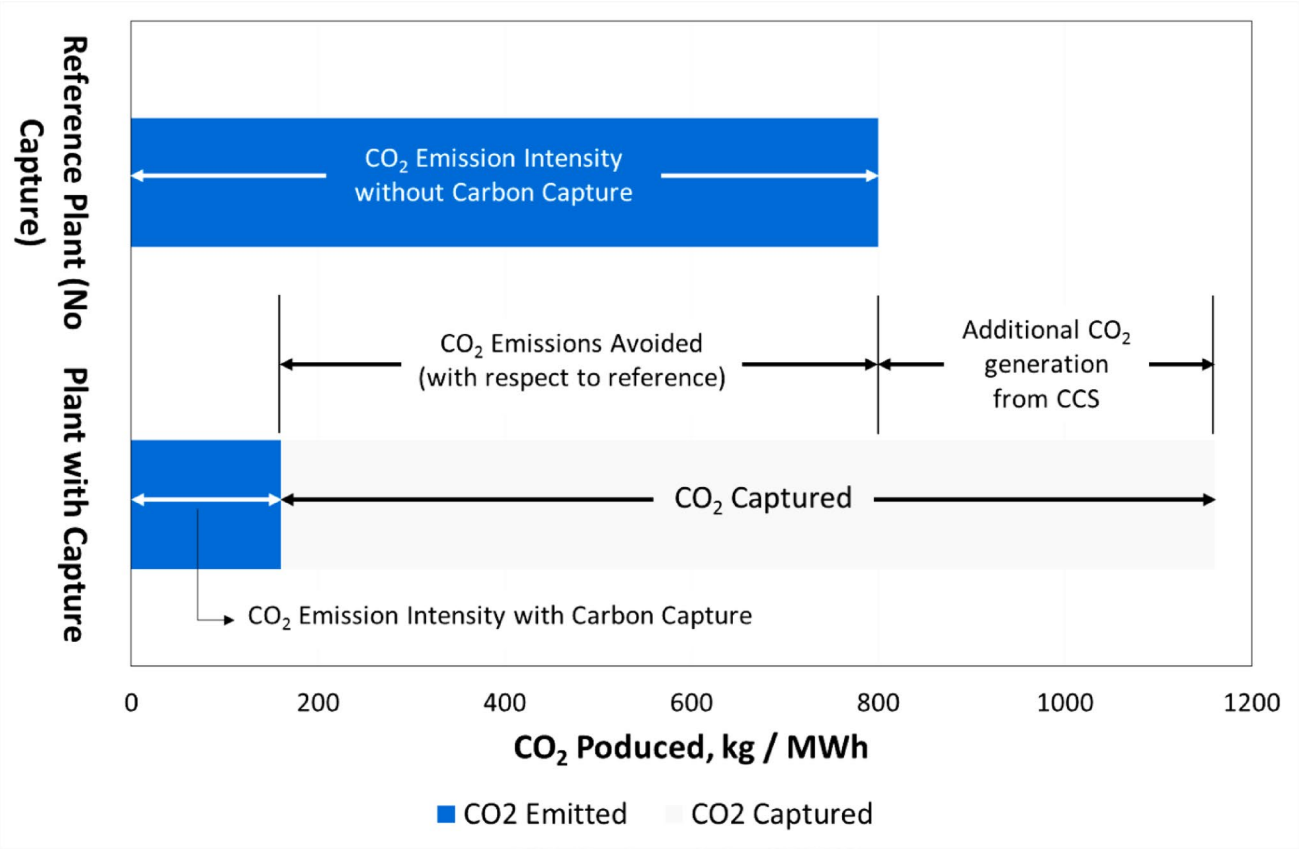


Fig. 3 Illustrative diagram of the CO_2 captured vs. CO_2 avoided concept (Canadian Clean Power Coalition 2013)

model used in this study, many other factors that influence the operating costs were considered and are discussed in the following sections. Further details of how the costs for all of these factors were calculated can be found in Fourie (2018).

Amine reclaiming and disposal costs, which account for solvent degradation and waste management, are calculated externally based on solvent flow rates and degradation rates. These costs were calculated externally using a spreadsheet model that factors in the recirculating solvent rate and associated losses, with unit costs obtained from updated chemical price data (Fourie 2018). Although these costs were not directly simulated in Aspen Plus, they were integrated into the performance indicator model. Their impact on the overall solvent rating was notable, especially in cases with high solvent circulation rates, such as MDEA+PZ blends, which incurred elevated reclaim and disposal costs compared to AMP+PZ systems.

Amine Type

The influence of amine type on the model (besides variation in costs between different amines) is due to the variation of the solvent flow rate necessary to absorb the required amount of CO_2 when amine type is varied. The prices for the amines investigated in this study are given in Table 8. The prices from different sources were averaged to obtain a single representative cost. In the case of outdated values, in order to get more updated prices, a ratio of the chemical consumer index of the source year and the current year was utilized.

Table 8 Prices of the amines studied

Amine	Price (*R*/ton)*	Reference(s)
AMP	88,374	Eachus and Bollmeier (2000); Zauba Technologies & Data (2016); Daya (2017)
MDEA	58,556	Kohl and Nielsen (1997); Zauba Technologies & Data (2016)
MEA	39,271	Kohl and Nielsen (1997); Sinnott (2005)
PZ	75,880	Sridhar and Carter (2000); Sigma-Aldrich (2016); Zauba Technologies & Data (2016)

*The prices cited are for 2016

Amine Degradation Rates

In this study, both oxidative and thermal degradation rates were included to account for the full range of amine loss mechanisms occurring under typical process conditions.

Oxidative degradation, driven by the presence of oxygen in the flue gas at moderate absorber temperatures, and thermal degradation, which occurs at higher temperatures in the stripper, together represent the main routes for solvent breakdown. Including both rates provides a comprehensive assessment of solvent consumption and degradation product formation, which is critical for reliable estimation of make-up, reclamation, and disposal costs within the PIM. Amine losses due to amine degradation have a direct effect on the operating cost of the capture plant. However, the diversity of the factors and parameters involved in the degradation reactions makes it too complicated to be used in the simulations (Fytianos et al. 2016). Hence, to take the amine degradation into consideration a general degradation model was used in this study, which was incorporated outside the simulation work. Further details on the inclusion of the reclamation into the model are explained in Fourie (2018).

As illustrated in the literature the contributors to degradation which directly influence the process streams are oxidative and thermal degradation rates. Hence, in this study these rates were utilized to represent the amines degradation (Shao and Stangeland 2009). For MEA, MDEA and AMP the degradation rates were selected from the data published by Lepaumier et al. (2009a, b, c) which are reported in Table 9. The values reported are based on the fraction of amine degraded per hour and are the summation of oxidative and thermal degradation contributions in the presence of both O_2 and CO_2. In the case of PZ, as illustrated by Freeman et al. (2010), this does not degrade at temperatures below 140 °C, and since the equipment in which PZ exists, operate at lower temperatures, the degradation of PZ was ignored in the model. The negligible degradation of PZ reduces disposal costs, contributing to the superior performance of AMP + PZ blends.

Another important cause of degradation is the presence of a trace amount of impurities in the flue gas stream such as NO_x, SO_2, fly ash and NH_3. In order to purify the system from these degradation products as well as any other undesirable impurities such as sludge, a reclaimer unit is placed after the reboiler of the stripper (Rochelle et al. 2011). The reclaimer unit was not included in the simulations due to the complexity of the degradation reactions mechanism and diversity of the degradation products. Instead, the contributions of these reclamation costs, estimated as a fractional loss of the recirculating solvent rate, as well as the disposal costs due to amine degradation were calculated manually using an excel spreadsheet along with the other PIM calculations (Fourie 2018).

Table 9 Degradation rates of the amines studied*

Amine	Combined degradation rate (%/hr)
MEA	0.3137
AMP	0.0739
MDEA	0.0970
PZ	Assumed negligible

*(Lepaumier et al. 2009a) (Lepaumier et al. 2009b) (Lepaumier et al. 2009c)

Corrosion

Usually, the absorption reaction of CO_2 with amines leads to the production of several highly corrosive chemicals which can cause fatal damage to the process equipment. One solution to this problem is the application of corrosion inhibitors such as sodium metavanadate and copper carbonate (Veawab et al. 2001). In this study, the same corrosion inhibitors were employed, and the cost was calculated from a fraction of the recirculating solvent rate (Fourie 2018).

Energy Consumption

The energy consumption in a CO_2 capture plant can be divided into three major uses: electrical power consumption, steam usage and water usage. The electrical consumption is mainly due to the flue gas blower, CO_2 compressors and all pumps in the process. In this study the energy required in the capture plant is provided by the power plant, consequently, the developed performance model is based on the "cost of CO_2 avoided".

In the capture plant, the only equipment that consumes steam is the stripper reboiler and the compressors which were modeled to be electrically driven. The amount of steam consumed by the stripper is directly proportional to the value of the heat duty calculated using the simulations and it was estimated by dividing the heat duty by the steam heat of vaporization.

Direct contact cooler (DCC), stripper condenser, CO_2 compression intercoolers and the lean amine cooler are the major equipment that consume cooling water. For stripper condenser and CO_2 compression intercoolers the amount of cooling water required was obtained using the duties in the simulations while, the flow of cooling water through the DCC was directly obtained from the simulation. In order to preserve the composition of aqueous solvent the addition of make-up water to the system is also necessary.

Carbon Tax

The levy imposed on the release of CO_2 by the industrial facilities is referred to as carbon tax which is a form of pollution tax. This levy serves to encourage companies to reduce their CO_2 emissions. The price of carbon tax has been set to $10/ton with a possible 10% yearly increase between 2016 and 2019 (The World Bank 2014). In this study the rate of

carbon capture was fixed, therefore the value of carbon tax allocated for each solvent blend stays constant.

Model Inputs and Outputs

The PIM developed in this study requires two types of inputs, viz. user-defined inputs and result inputs. User-defined inputs can be changed by user. In Table 3 the user-defined inputs are divided into two groups "inputs into Aspen" and "external inputs". The result inputs, which are basically the outputs from the Aspen simulation, are identified as "inputs into PIM from Aspen". The ultimate output achieved from the performance model is the rating of a specific amine solvent or blend relative to an identified baseline solvent.

Model Implementation

In this section the determination of the rating with the PIM is explained in detail.

For the evaluation of the overall cost for CO_2 captured ($C_{T,\,j,captured}$) the summation of each factor i for each case j is used. Generally, the cost factors are equivalent to the product of price of the process chemicals or utilities and their corresponding flow rates.

$$C_{T,j,captured} = \sum_{k=0}^{n} C_{ij} \tag{13}$$

The total cost of CO_2 avoided is obtained using the following equation:

$$C_{T,j,avoided} = C_{T,j,captured} \times \frac{\epsilon_{OP}}{\epsilon_{j}} \tag{14}$$

in which ε_{OP} represents the original operating efficiency of the power plant without the capture plant and (ε_j) is the reduced efficiency of the power plant in the presence of the capture plant which is dependent on the solvent used in case j.

The following equation is then used to obtain the rating for each case j, R, in which $C_{i,\,b,avoided}$ and $C_{i,\,j,avoided}$ represent the avoided costs of the base case and case j, for each factor i respectively.

$$R = \sum_{i}^{n} x_{i,j} \times \frac{C_{i,b,avoided}}{C_{i,j,avoided}} \tag{15}$$

In Eq. (15), x_{ij}, is the factor fraction which is obtained by dividing the cost of the factor i for case j by the total cost of CO_2 avoided for case j.

$$x_{ij} = \frac{C_{i,j,avoided}}{C_{T,i,j,avoided}} \tag{16}$$

In Eq. (16), x_{ij} can be used as an indicator to compare each case to the benchmark case. If a lower cost avoided calculated for case j than that of the benchmark case, it suggests a superior performance of the solvent in case j in the simulation of post-combustion CO_2 capture. For the solvents that are more cost-effective as determined by Eqs. 15 and 16, a greater rating value (than the benchmark with R is equal to 1) would be obtained if multiplying the ratio of cost avoided calculated for case j and the benchmark by x_{ij}. Consequently, for the less cost-effective solvents than the benchmark, a rating value of less than one would be obtained.

All the factors included in the PIM are associated to the operating cost of a CO_2 capture plant. Since the capital costs are not included in the model, in the solvent assessment it is required that equipment sizes remain unchanged during all the simulation cases being evaluated. In a practical condition, this would be equivalent to varying the solvent of an existing capture installation to establish whether it enhances the performance of the plant.

Results and Discussion

Test Systems

In this study, an aqueous amine solvent of MEA with a concentration of 30 wt% was used in a simulation as the benchmark case for which the main inputs to the PIM are given in Table 10.

When using the PIM to analyze the results, the optimum operating point (the point at which the different costs combine to form the lowest total CO_2 capture cost and thus the highest rating) must be found. To determine the optimum operating cost, the simulation was performed for a range of lean solvent loadings and the loading which resulted in the highest overall rating as determined by the PIM is then the optimum point for that solvent. This method was used for all solvent blends considered.

The validation of the performance indicator model is achieved by comparing the main results of the benchmark using the 30% MEA process simulation to those in the literature. Table 11 shows this comparison. For this purpose, the energy requirements were noted and the results obtained in this study as well as those from the literature indicate that the energy required is affected directly by the number of employed trains (hence number of absorbers and strippers). For example the energy required for CO_2 capture process using MEA is between 3 and 4.5 GJ/(ton CO_2) (Zahra 2009). While, as shown in Table 11 the energy requirement

Table 10 Main inputs to the performance model for the base case, 30% MEA

Parameter	Unit	Value
Amine Price	R/ton	39,271[a]
Make-up Water Price	R/ton	11.52[b]
Cooling Tower Water Price	R/ton	0.54[b]
Steam Price	R/ton	150[b]
Corrosion Inhibitor Price	R/ton	3784[b]
Amine Reclaim Cost	R/ton	10,078[b]
Amine Disposal Cost	R/ton	3008[b]
Carbon Tax Rate	R/ton	120[c]
Amine Degradation Rates	%/hr	0.3137[d]
Power Plant Efficiency	%	42.4[e]

[a]Kohl and Nielsen (1997); Sinnott (2005)

[b]Daya (2017)

[c]The World Bank (2014)

[d] Lepaumier et al. (2009a, b, c)

[e]Gammer (2016)

reported by researchers who used multiple equipment trains is similar to the amount in this range multiplied, though by the number of trains.

As shown in Table 11, for the benchmark system (30% MEA, 80% CO_2 capture), the energy required per reboiler unit is equal to 3.09 GJ/ton CO_2. This is 5% less than the value obtained by Daya (2017), using very similar conditions. This was deemed as an acceptable difference. By adjusting the capture rate (30% MEA, 90% capture) and comparing the result to the AMP system to the literature the energy required per reboiler unit is 4.9 GJ/ton CO_2. This is 16% higher than the value obtained by Fisher et al. (2007), with conditions and inputs being very quite similar, but still deemed as an acceptable difference. Not all simulation conditions can be identical, especially when there exists a great difference in the column diameters used in different simulations. It is worth mentioning that in this study open-loop simulations were used while Fisher et al. (2007) used closed-loop simulations. However, the discrepancy in the results of open-loop and closed-loop processes are not always high. For example, as indicated in Table 11, the percentage difference between the energy requirements obtained in the work of Fisher et al. (2007), with closed-loop, and Kothandaraman (2010), with open-loop, is less than 2%. This and a study by Ahmadi (2012) confirm that the results obtained in this study which are based on open-loop process simulations are equivalent to the results achieved using simulation of closed-loop processes.

The output of the simulation using 30% AMP as the solvent, with the benchmark as 30% MEA alongside the results obtained by Daya (2017) and Padurean et al. (2011) are depicted in Fig. 4. The preliminary rating obtained in this study was not exactly the same as the ratings calculated by the other two references. After performing a sensitivity analysis, the range of (0.932–1.151) was obtained as a probable range of ratings for which the upper limit is placed within the range of the literature values (refer to error bars in Fig. 4). Hence, it is confirmed that the rating results for the 30% AMP simulation were satisfactory, and this case was utilized as the benchmark for the investigations of the study. Table 12 shows a comparison between 30% AMP benchmark of this study to simulations for 30% AMP obtained in the literature.

It can be interpreted from the solvent and flue gas flow rates in Table 12 that the work carried out by Lee et al. (2009) and Chavarro Montenegro (2011) was performed on a smaller scale than this work. The comparatively large energy requirements obtained in both studies confirm that the results are highly dependent on the scale at which the simulations performed. Excluding these two sources, a maximum deviation of about 26% between this work and literature is obtained. (considering 2.9 GJ/ton CO_2 for the energy requirement per reboiler in this study) with an average percentage deviation of 14.5%. The deviations obtained are satisfactory since not all the conditions are the same as used in literature.

Table 11 Comparative analysis between the 30% MEA benchmarks established in this study and those reported in the literature

	This study (80% capture)	This study (90% capture)	Fisher et al. (2007)	Kothandaraman (2010)	Padurean et al. (2011)	Daya (2017)
Open/closed Process	Open	Open	Closed	Open	Closed	Open
[a]Solvent Lean Loading (mol CO_2/mol amine)	0.21	0.14	[b]n/s	0.22	[b]n/s	0.18
[a]Solvent Flowrate (ton/hr)	1484	1786	24,237	[b]n/s	3500	2073
Flue Gas CO_2 Content (mol %)	12	12	12.38	[b]n/s	8.4	12
Flue Gas Flow Rate (ton/hr)	2283	2283	2448	[b]n/s	2928	2516
CO_2 capture rate (%)	80	90	90	85	90.3	80
Total Energy Requirement (GJ/t CO_2)	12.4	19.6	16.82	16.61	3.29	13.00
Stripper diameter (m)	14	14	7.9	7	[b]n/s	14
No. of trains	4	4	4	4	1	4
Energy Required per Stripper (GJ/t CO_2)	3.09	4.9	4.21	4.15	3.29	3.25

[a]all sources referenced in this table use 30 wt% MEA as a solvent

[b]not specified by source

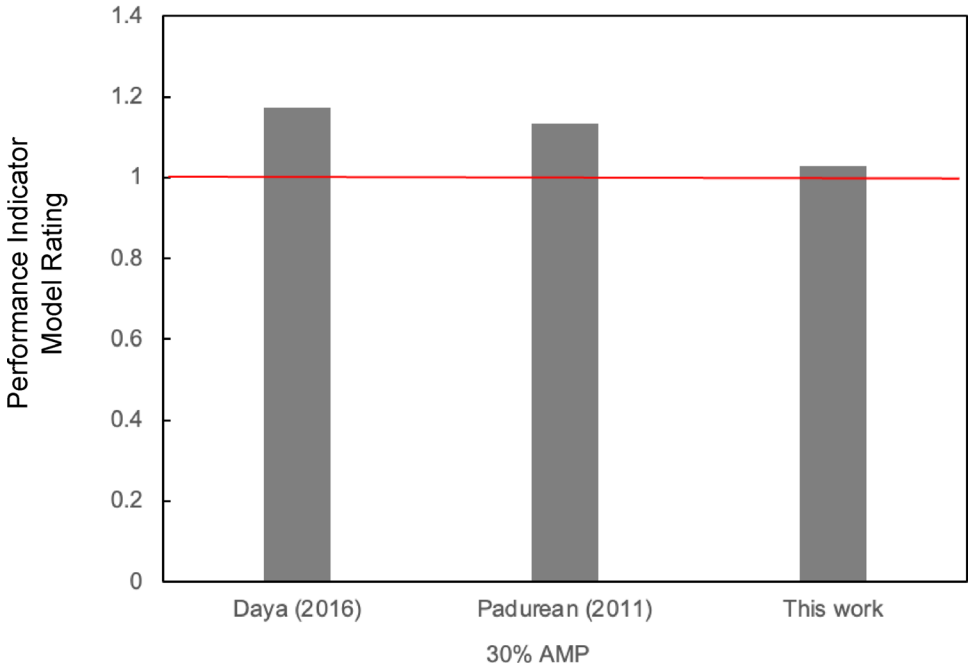


Fig. 4 Comparison of the 30% AMP simulation results with the literature

Table 12 Comparative analysis between the AMP benchmark adopted in this investigation and similar AMP simulation studies documented in existing literature

	This work	Padurean et al. (2011)	Lee et al. (2009)	Chavarro Montenegro (2011)	Li et al. (2016b)
Solvent Lean Loading (mol CO_2/mol amine)	0.135	n/s[a]	n/s	n/s	0.33
Solvent Flowrate (ton/hr)	2383	n/s	0.974	n/s	n/s
Flue Gas CO_2 Content (mol %)	12	8.4	8.34	12.57	13.3
Flue Gas Flow Rate (ton/hr)	2283	2928	0.563	324	3122
CO_2 capture rate (%)	90	93.8	95	90	90
Total Energy Requirement (GJ/t CO_2)	11.6	2.82	8.76	8	2.295
Stripper diameter (m)	14	n/s	n/s	7	n/s
No. of trains[b]	4	1	1	1	1

[a]not specified by source

[b]if number of trains were not specified, it was assumed to be 1

New Systems

In this study several blends of the amines, i.e., AMP, MDEA and PZ were selected as the new systems in the CO_2 capture simulations. In order to examine the effect of increasing the amine concentration on the rating, binary solvent blends with total amine concentrations of 30% and 40% were simulated. Within each scenario, the lean loading of the solvent (mol CO_2/mol amine) was varied to find the optimum operating point (where the rating was highest). Subsequently, the resultant conditions became the demonstrative case for that particular amine blend, as shown in Fig. 5. The rating for the benchmark case is set to 1, based on the output from the PIM. As indicated previously, in the PIM calculations the ratings above one are considered as a superior performance to the benchmark whilst the ratings below one are considered inferior to the benchmark. The 30% AMP aqueous solution was applied as the benchmark for all cases.

Table 13 shows results for all the systems considered in this study. One can observe from the results shown in Table 13 that even though the reboiler duty and solvent flow rate encompass a great portion of the ratings obtained by the PIM, the best rating is not always obtained when the reboiler duty and solvent flow rate are minimum. Experimental investigations show that the solubility of CO_2 in the solvents considered in this study increases in the order MDEA < AMP < PZ. A similar trend was also observed in the flowrates reported for the different amine blends in which the flowrate decreased with decreasing solvents capacity for CO_2 capture. For example, the blends of MDEA + PZ show flow rates considerably higher than that of the AMP + PZ blends. In the case of the tri-amine blends since all three components exist, flow rates lie in between. Solvent flow

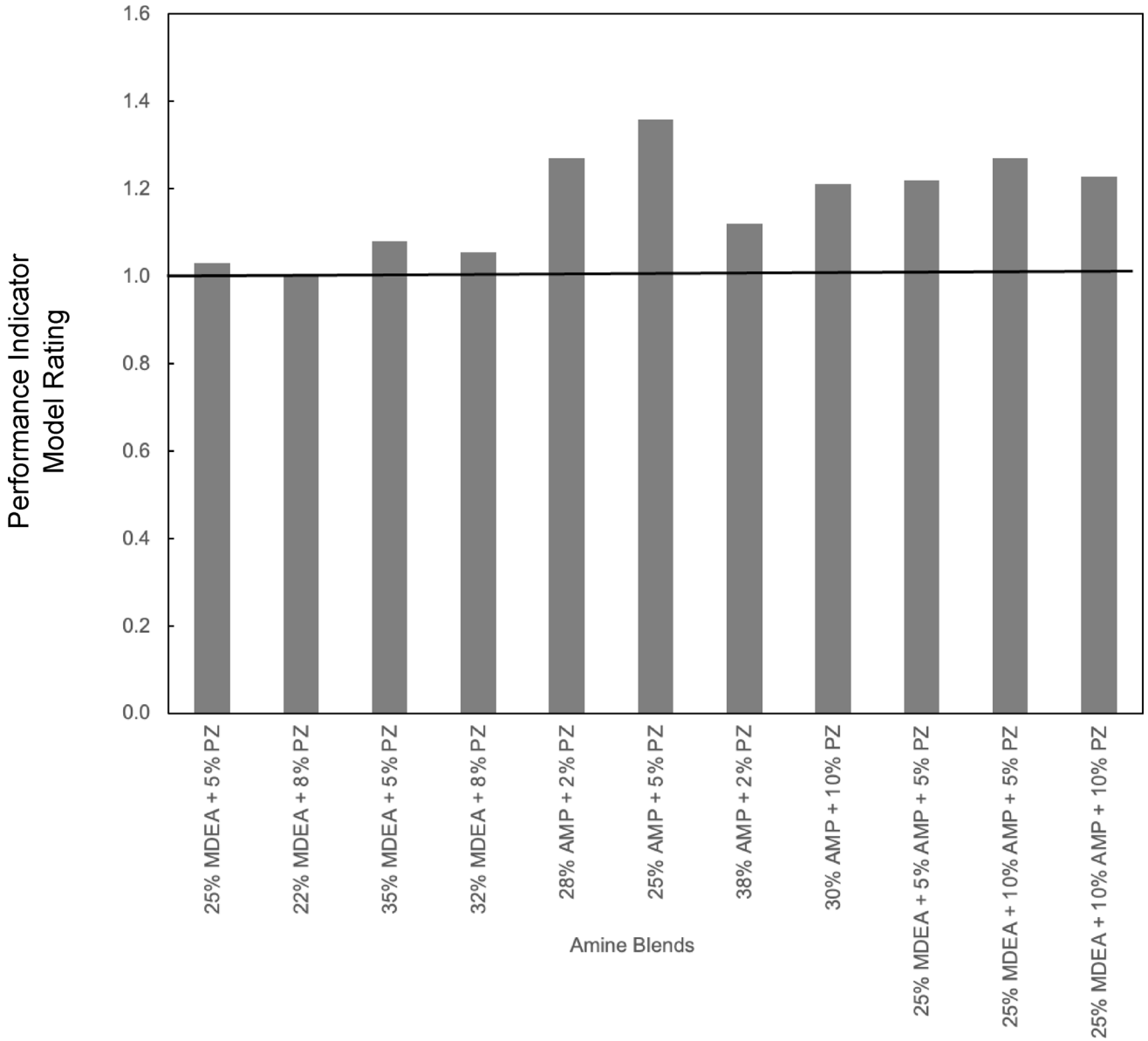


Fig. 5 Ratings for the new systems simulated in this work

rate and the reaction rate of amine blend with CO_2 (which also follows the trend PZ>AMP>MDEA) are also directly related. Consequently, it is expected that for a fixed capture rate the solvents with a higher rate of reaction with CO_2 show a lower required flow rate as presented in Table 13.

Amongst the amine blends considered, MDEA+PZ did not exhibit the best performance, primarily due to the chemical nature of MDEA as a tertiary amine. Unlike primary and secondary amines, which react rapidly with CO_2 to form carbamate intermediates, MDEA's tertiary structure precludes direct carbamate formation, resulting in a much slower base-catalyzed reaction mechanism that produces bicarbonate (HCO_3^-) as the principal product (Dash and Bandyopadhyay 2016; Rochelle et al. 2011). Although piperazine (PZ) serves as an effective activator and can significantly accelerate the overall absorption kinetics, the combined system typically still requires higher solvent circulation rates to achieve the same CO_2 capture efficiency as blends based on primary or secondary amines. This accounts for the increased operational costs and the lower performance indicator ratings observed for MDEA+PZ systems in our study. CO_2 solubility data confirms that the solubility of CO_2 increases with increasing the PZ concentration in the blend (Dash and Bandyopadhyay 2016) which is also observed in the solvent flow rate trends (see Table 13). The reclaim and disposal costs of the amines are estimated in separate calculations based on the flowrates of the solvent. Consequently, a higher flowrate also results in a surge in

Table 13 An overview of the outcomes achieved for the analyzed configurations in this study

System	Lean loading (mol CO_2/mol Amine)	Rating	Reboiler duty (MW)	Solvent flow rate (ton/hr)
30% AMP	0.135	1.000	296	2323
25% MDEA+5% PZ	0.150	1.030	122	3778
22% MDEA+8% PZ	0.215	1.004	148	3893
35% MDEA+5% PZ	0.110	1.080	205	3345
32% MDEA+8% PZ	0.160	1.052	147	3446
28% AMP+2% PZ	0.170	1.270	164	1874
25% AMP+5% PZ	0.210	1.359	136	1859
38% AMP+2% PZ	0.170	1.120	130	1863
30% AMP+10% PZ	0.250	1.212	91	1936
25% MDEA+5% AMP+5% PZ	0.125	1.220	116	2858
25% MDEA+10% AMP+5% PZ	0.110	1.269	107	2473
25% MDEA+10% AMP+10% PZ	0.177	1.228	95	2641

these costs. Hence, although the energy consumption for the MDEA+PZ blend is lower than the benchmark, by considering the additional factors mentioned in the calculations, a lower rating for AMP+PZ blends is observed.

The combination of the low reboiler duty and low solvent flow rate resulted in the highest ratings overall achieved for the AMP+PZ blends. A relatively low reboiler duty was achieved for the tri-amine blends, which is possibly due to the combination of AMP and MDEA knowing that both have lower heats of reaction with CO_2 (resulting in a reduction in the regeneration duty). Nevertheless, since a large portion of the solvent's amine concentration is MDEA, a high solvent flowrate leads to the higher costs of solvent make-up and reclaim, resulting in a lower PIM rating.

Hence, even though the tri-amine blends showed an outstanding performance with respect to the energy consumption, when including other parameters, these blends were inferior in performance compared to AMP+PZ binary blends (see Table 13).

Modified Configuration

The ratings reported in Table 13 are obtained based on the conventional process configuration. In order to investigate the effect of the process configuration on the simulation results, a modified process configuration, namely, intercooled absorber (ICA) was simulated in which the best-performing solvent blend (i.e., 25% AMP+5% PZ+70% H_2O wt% obtained in conventional configuration studies), was used.

In the ICA process configuration, a fraction of the solvent in the absorber is withdrawn, cooled, and then fed to the absorber (Le Moullec et al. 2014). Figure 6 depicts an ICA process configuration used in the simulation in which one cooling stage was used. A 22-stage colums (where stages are numbered from top to bottom) was utilized in the simulation amongst which stage 17 was primarily attempted as the cooling stage. After changing the stage number of the cooling stage it was found that stage 15 resulted in an optimal performance of the process. Table 14 shows the results obtained using stage number 15 as well as those obtained using stage number 17 as the cooling stage. Similar results can be observed in both scenarios however, more stable simulations were achieved using stage 15 as the cooling stage. It can be inferred that using the stages below 15 may result in unstable simulation runs which can cause convergence errors. As indicated in Table 14, different exiting and entering stages were chosen to assess the column performance (cases 1–8). Only one cooling stage was utilized to

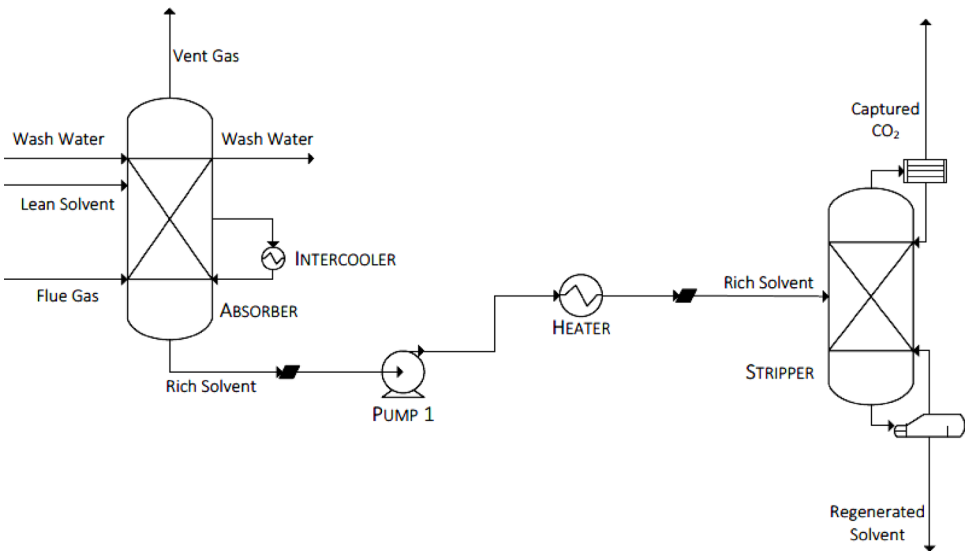


Fig. 6 The intercooled absorber configuration as applied to the capture section of the flowsheet

Table 14 A summary of the simulations conducted for the intercooled absorber under various operating conditions

	Split fraction	Entering stage	Exiting stage	Stripper reboiler duty (MW)	Intercooler duty (MW)	Solvent flow rate (ton/hr)	Temperature difference in intercooler (°C)	Estimated rating
Case 1	0.20	20	12	142.6	−6.255	1716	19.09	1.431
Case 2	0.40	20	12	139.9	−10.48	1684	16.31	1.487
Case 3	0.55	20	12	139.3	−12.60	1679	13.66	1.509
Case 4	0.60	20	12	139.4	−13.12	1680	13.66	1.509
Case 5	0.20	17	9	142.1	−6.977	1709	21.36	1.463
Case 6	0.40	17	9	138.8	−11.51	1668	18.07	1.546
Case 7	0.55	17	9	137.8	−13.72	1656	15.79	1.577
Case 8	0.60	17	9	137.7	−14.26	1655	15.06	1.578
Case 9	0.20	17	17	141.3	−3.783	1694	11.76	1.413
Case 10	0.20	15	15	142.9	−4.581	1720	14.00	1.429
Case 11	0.30	15	15	141.2	−5.953	1700	12.28	1.453
Case 12	0.40	15	15	139.9	−6.977	1684	10.90	1.471

Table 15 Additional exploration of employing stage 15 as a cooling stage through an expanded range of split fractions

Split fraction	Cooling stage	Stripper reboiler duty (MW)	Intercooler duty (MW)	Solvent flow rate (ton/hr)	Temperature difference in intercooler (°C)	Estimated rating
0.2	15	142.9	−4.581	1720	14.00	1.429
0.3	15	141.2	−5.953	1700	12.28	1.453
0.4	15	139.9	−6.977	1684	10.90	1.471
0.5	15	138.8	−7.774	1671	9.80	1.483
0.6	15	138.0	−8.412	1660	8.90	1.483

perform cases 9–12. Even though there are few cases from 1 to 8 with higher ratings than one cooling stage cases, it can be concluded that implementing one cooling stage would be more practical, therefore the results of cases 1–8 were ignored and presented here merely for illustration purposes. The results from the PIM showed that amongst the cases utilizing stage 17 and 15 as the cooling stage, case 12 (which uses stage 15 as cooling stage) yielded the best rating.

In an attempt to obtain higher ratings, the split fraction, as well as the solvent lean loading were increased. For this purpose, as shown in Table 15 firstly the split fraction range was extended to see whether a maximum could be achieved at some point. The results in Table 15 show that the split fractions 0.5 and 0.6 produce a rating of 1.483 which is the highest obtained. Since the split fraction 0.6 did not improve the results significantly, it is decided to select the split fraction 0.5 for further investigations. Ultimately, the results obtained confirm that when using stage 15 as cooling stage, with a split fraction of 0.5 and a solvent lean loading equal to 0.2 mol CO_2/mol amine, the ICA configuration produces a maximum rating of 1.483 which is an improvement of 9% comparing to that of the conventional configuration (1.359). The simultaneous effect of mitigated energy requirements as well as reduced solvent supplies improved the rating in the ICA configuration which also can affect the cost of other parameters, like waste disposal.

This study focused on selected amines and its blends. It is possible to extend the work to other promising amines and blends, and apply the same simulations to assess the performance against those investigated in this work. In addition, alternate process configurations and modifications to the capture unit design are possible. Using a rate-based model instead of an equilibrium model for the simulations could also be considered for future work, especially where equipment design is concerned. These are recommendations for continuation of this work in assessing solvent blends and process modifications for improved carbon capture techniques with energy reductions.

Conclusions

The performance of the mixture of various aqueous amine solvents for post-combustion CO_2 capture from a coal-fired power plant was examined by means of a performance indicator model. A solvent of 30 wt% AMP was used as the baseline instead of the preliminary 30 wt% MEA, since previous investigations carried out have already proven that AMP is a more promising agent for CO_2 capture than MEA. Different blends of aqueous solvent of AMP or MDEA with piperazine (PZ) were assessed, as well as tertiary amine aqueous blends with AMP, MDEA, and PZ. In the case of binary amine mixtures, the overall amine concentrations of 30

wt% and 40 wt% were assessed, whereas the overall amine concentration of the tertiary amine blends were 45 wt%. It was found that 25% AMP+5% PZ (wt%), is the best-performing blend with the highest rating of 1.359. The worst-performing blend was found to be 22% MDEA+8% PZ, with a rating of 1.004, which was very close to the benchmark solvent of AMP. Up to 5% improvement in ratings was obtained for the MDEA+PZ blends, when increasing the total amine concentration, while for the AMP+PZ blends, it showed a reverse effect on the rating (up to 21% decrease). The ratings for all the binary amines increased with increasing PZ concentration. For the binary blends of AMP+PZ, an increase of 7% and 8% in ratings were obtained for the overall amine concentrations of 30 wt% and 40 wt%, respectively. For MDEA+PZ blends, ratings increased by 2.5% and 2.7% for total amine concentrations of 30 wt% and 40 wt%, respectively. Higher ratings were obtained for the tri-amine blends (1.220–1.269) comparing to the ratings obtained for MDEA+PZ blends (1.004–1.080) but it is lower than that of AMP+PZ blends with a total amine concentration of 30 wt% (1.270–1.359). Finally, a modification in the process configuration was made (modified intercooled absorber configuration) in order to improve further the rating obtained for the best-performing blend (i.e. 25% AMP+5% PZ). In this case, the rating was increased to 1.483 (9% improvement of conventional configuration), when using stage 15 (of a 22 stage RADFRAC column) as cooling stage, with a split fraction of 0.5 and a solvent lean loading equal to 0.2 mol CO_2/mol amine. Further work is recommended to investigate other and new solvents, which were not part of this study, and examine alternatives to the process configurations, in achieving lower operating costs and energy reductions. While the simulation results demonstrate promising energy savings and improved performance using AMP–PZ blends and intercooling strategies, practical implementation of these configurations poses several real-world challenges. These include increased corrosion risk at high amine concentrations, the need for effective solvent reclaiming systems to handle oxidative and thermal degradation, and potential pressure drops across intercooler-integrated columns. Additionally, integrating such systems into existing power plants requires careful retrofitting, which may affect capital expenditure and operational flexibility. Addressing these factors through pilot-scale validation and techno-economic assessments is essential for translating the simulation benefits into industrial viability.

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References

Abu-Zahra MR, Schneiders LH, Niederer JP, Feron PH, Versteeg GF (2007) CO_2 capture from power plants: part I. a parametric study of the technical performance based on monoethanolamine. Int J Greenhouse Gas Control 1:37–46

Abu-Zahra MR, Jansens PJ, Knudsen JN, Goetheer EL (2012) Experimental verification of equilibrium-stage and rate-based simulations. Int J Enhanced Res Sci Technol Eng 1:37–46

Adeosun A, Abu-Zahra MRM (2013) Evaluation of amine-blend solvent systems for CO_2 post-combustion capture applications. Energy Procedia 37:211–218

Ahmadi F (2012) Assessing the performance of Aspen plus and Promax for the simulation of CO_2 capture plants. Faculty of Graduate Studies and Research. University of Regina

Ali BS, Aroua M (2004) Effect of piperazine on CO_2 loading in aqueous solutions of MDEA at low pressure. Int J Thermophys 25:1863–1870

Aliabad ZH, Mirzaei S (2009) Removal of CO_2 and H_2S using aqueous alkanolamine solusions. Int J Chem Mol Nuclear Mater Metall Eng 3:49–59

Arachchige USP, Melaaen MC (2012) Aspen plus simulation of CO_2 removal from coal and gas fired power plants. Energy Procedia 23:391–399

AspenTech (2015a) Aspen physical property system, V8.8. Aspen Technology Inc., Cambridge

AspenTech (2015b) Electrolyte NRTL activity coefficient model (GMENRTL), Aspen plus help. Aspen Technology Inc., Bedford, Massachusetts

Austgen DM, Rochelle GT, Chen CC (1991) Model of vapor-liquid equilibria for aqueous acid gas-alkanolamine systems. 2. Representation of hydrogen sulfide and carbon dioxide solubility in aqueous MDEA and carbon dioxide solubility in aqueous mixtures of MDEA with MEA or DEA. Ind Eng Chem Res 30:543–555

Brúder P, Grimstvedt A, Mejdell T, Svendsen HF (2011) CO_2 capture into aqueous solutions of piperazine activated 2-amino-2-methyl-1-propanol. Chem Eng Sci 66:6193–6198

Canadian Clean Power Coalition (2013) Capture Cost Definitions Facts Sheet

Chavarro Montenegro HJ (2011) Novel solvents for CO_2 capture. Flowsheet analysis, school of chemical engineering and analytical science, faculty of engineering and physical sciences. University of Manchester

D'Alessandro DM, Smit B, Long JR (2010) Carbon dioxide capture: prospects for new materials. Angew Chem Int Ed 49:6058–6082

Dash SK, Bandyopadhyay SS (2016) Studies on the effect of addition of piperazine and sulfolane into aqueous solution of N-methyldiethanolamine for CO_2 capture and VLE modelling using eNRTL equation. Int J Greenhouse Gas Control 44:227–237

Dash SK, Samanta A, Samanta AN, Bandyopadhyay SS (2011) Vapour liquid equilibria of carbon dioxide in dilute and concentrated aqueous solutions of piperazine at low to high pressure. Fluid Phase Equilib 300:145–154

Dash SK, Samanta AN, Bandyopadhyay SS (2012) Experimental and theoretical investigation of solubility of carbon dioxide in concentrated aqueous solution of 2-amino-2-methyl-1-propanol and piperazine. J Chem Thermodyn 51:120–125

Daya A (2017) Development of a performance indicator for carbon capture applications. University of Kwa-Zulu Natal

Derks PWJ (2006) Carbon dioxide absorption in piperazine activated N-methyldiethanolamine. University of Twente, The Netherlands

Eachus AC, Bollmeier AF (2000) Alkanolamines from nitro alcohols, Kirk-Othmer encyclopedia of chemical technology. John Wiley & Sons, Inc.

Erfani A, Boroojerdi S, Dehghani A (2015) Simulation of an operational amine based CO_2 removal plant as an example of CO_2 capture at Coal-Fired power plants. Petroleum Coal 57:85–92

Fisher KS, Beitler C, Rueter C, Searcy K, Rochelle GT, Jessim M (2005) Integrating MEA regeneration with CO_2 compression and peaking to reduce capture costs. US Department of Energy

Fisher KS, Searcy K, Rochelle GT, Ziaii T, Schubert C (2007) Advanced amine solvent formulations and process integration for Near-Term CO_2 capture success. US Department of Energy

Fourie R (2018) Extension of a multi-criterion performance indicator model for post combustion CO_2 capture using amine solvents. University of Kwa-Zulu Natal

Freeman SA, Dugas R, Van Wagener DH, Nguyen T, Rochelle GT (2010) Carbon dioxide capture with concentrated, aqueous piperazine. Int J Greenhouse Gas Control 4:119–124

Freguia S, Rochelle GT (2003) Modeling of CO_2 capture by aqueous monoethanolamine. AIChE J 49:1676–1686

Fytianos G, Vevelstad SJ, Knuutila HK (2016) Degradation and corrosion inhibitors for MEA-based CO_2 capture plants. Int J Greenhouse Gas Control 50:240–247

Gammer D (2016) Reducing the cost of CCS - Developments in capture plant technology. Energy Technologies Institute, United Kingdom

Han C, Graves K, Neathery J, Liu K (2011) Simulation of the energy consumption of CO_2 capture by aqueous monoethanolamine in pilot plant. Energy and Environment Research

Hansen J, Sato M, Kharecha P, Beerling D, Berner R, Masson-Delmotte V, Pagani M, Raymo M, Royer DL, Zachos JC (2008) Target atmospheric CO_2: where should humanity aim? Open Atmos Sci J 2:217–231

Istown NJ, Kohl AL, Nielsen R (1997) Gas purification, Fifth Edition ed. Gulf Professional Publishing, Texas

Jones DA, McVey TF, Friedmann SJ (2013) Technoeconomic evaluation of MEA versus mixed amines for CO_2 removal at Near-Commercial scale at Duke energy Gibson 3 plant. Lawrence Livermore National Laboratory

Kanniche M, Gros-Bonnivard R, Jaud P, Valle-Marcos J, Amann J-M, Bouallou C (2010) Pre-combustion, post-combustion and oxy-combustion in thermal power plant for CO_2 capture. Appl Therm Eng 30:53–62

Kanniche M, Le Moullec Y, Authier O, Hagi H, Bontemps D, Neveux T, Louis-Louisy M (2017) Up-to-date CO_2 capture in thermal power plants. Energy Procedia 114:95–103

Khalil YF, Gerbino AJ (2007) Simultaneous Removal of SO_2 and CO_2 From Flue Gases at Large Coal-Fired Stationary Sources, OLI's 24th User Conference, Morr

Kothandaraman A (2010) Carbon dioxide capture by chemical absorption: a solvent comparison study. Massachusetts Institute of Technology

Kothandaraman A, Nord L, Bolland O, Herzog HJ, McRae GJ (2009) Comparison of solvents for post-combustion capture of CO_2 by chemical absorption. Energy Procedia 1:1373–1380

Le Moullec Y, Neveux T, Azki A, Chikukwa A, Hoff A, K.A (2014) Process modifications for solvent-based post-combustion CO_2 capture. Int J Greenhouse Gas Control 31:96–112

Lee BD, Kim DM, Cho J, Park SW (2009) A comparative study on the carbon dioxide capture power between 30 wt% 2-amino-2-methyl-1-propanol and 30 wt% methyldiethanol amine aqueous solutions. Korean J Chem Eng 26:818–823

Lepaumier H, Picq D, Carrette P-L (2009a) Degradation study of new solvents for CO_2 capture in post-combustion. Energy Procedia 1:893–900

Lepaumier H, Picq D, Carrette P-L (2009b) New amines for CO_2 capture. I. Mechanisms of amine degradation in the presence of CO_2. Ind Eng Chem Res 48:9061–9067

Lepaumier H, Picq D, Carrette P-L (2009c) New amines for CO_2 capture. Part II. Oxidative degradation mechanisms. Ind Eng Chem Res 48:9068–9075

Li J, Liang X (2012) CO_2 capture modelling for pulverised coal-fired power plants: a case study of an existing 1 GW ultra-supercritical power plant in Shandong, China. Sep Purif Technol 94:138–145

Li H, Li L, Nguyen T, Rochelle GT, Chen J (2013) Characterization of piperazine/2-aminomethylpropanol for carbon dioxide capture. Energy Procedia 37:340–352

Li B-H, Zhang N, Smith R (2016a) Simulation and analysis of CO_2 capture process with aqueous monoethanolamine solution. Appl Energy 161:707–717

Li Z, Chen S, Hopkinson D, Luebke D (2016b) Verification of a solvent optimization approach for postcombustion CO_2 capture using commercial alkanolamines. Int J Greenhouse Gas Control 44:59–65

Lim Y, Kim J, Jung J, Lee CS, Han C (2013) Modeling and simulation of CO_2 capture process for Coal- based power plant using amine solvent in South Korea. Energy Procedia 37:1855–1862

Lin Y-J, Chen E, Rochelle G (2016) Pilot plant test of the advanced flash stripper for CO_2 capture. Faraday Discuss. https://doi.org/10.1039/c6fd00029k

Liu H-B, Zhang C-F, Xu G-W (1999) A study on equilibrium solubility for carbon dioxide in Methyldiethanolamine – Piperazine – Water solution. Ind Eng Chem Res 38:4032–4036

Luo X, Knudsen J, De Montigny D, Sanpasertparnich T, Idem R, Gelowitz D, Notz R, Hoch S, Hasse H, Lemaire E (2009) Comparison and validation of simulation codes against sixteen sets of data from four different pilot plants. Energy Procedia 1:1249–1256

Mirzaei S, Abadi HZA, Gholami F, Gholami Z (2009) Removal of CO_2 and H_2S using aqueous alkanolamine solutions. Eng Technol 37:194–203

Molina CT, Bouallou C (2013) Kinetics study and simulation of CO_2 absorption into mixed aqueous solutions of methyldiethanolamine and diethanolamine. Chem Eng Trans 35:319–324

Mondal MK, Balsora HK, Varshney P (2012) Progress and trends in CO_2 capture/separation technologies: a review. Energy 46:431–441

Mudhasakul S, Ku H-m, Douglas PL (2013) A simulation model of a CO_2 absorption process with Methyldiethanolamine solvent and piperazine as an activator. Int J Greenhouse Gas Control 15:134–141

Naskar S, Jana K, De S (2013) Comparative performance study of CO_2 capture with monoethyl and diethyl amines using ASPEN PLUS®. Int J Emerg Technol Adv Eng 3:490–497

Nwaoha C, Supap T, Idem R, Saiwan C, Tontiwachwuthikul P, Al-Marri MJ, Benamor A (2017) Advancement and new perspectives of using formulated reactive amine blends for post-combustion carbon dioxide (CO_2) capture technologies. Petroleum 3:10–36

Øi LE (2007) Aspen HYSYS Simulation of CO_2 Removal by Amine Absorption from a Gas Based Power Plant, in: Bunus, P., Fritzson, D., Fuhrer, C. (Eds.), The 48th Scandinavian Conference on Simulation and Modeling Linkoping University Electronic Press, Goteborg (Saro)

Øi LE (2012) Comparison of Aspen HYSYS and Aspen plus simulation of CO_2 absorption into MEA from atmospheric gas. Energy Procedia 23:360–369

Padurean A, Cormos C-C, Cormos A-M, Agachi P-S (2011) Multicriterial analysis of post-combustion carbon dioxide capture using alkanolamines. Int J Greenhouse Gas Control 5:676–685

Razi N, Svendsen HF, Bolland O (2013) Cost and energy sensitivity analysis of absorber design in CO2 capture with MEA. Int J Greenhouse Gas Control 19:331–339

Rochelle G, Chen E, Freeman S, Van Wagener D, Xu Q, Voice A (2011) Aqueous piperazine as the new standard for CO_2 capture technology. Chem Eng J 171:725–733

Shao R, Stangeland A (2009) Amines used in CO_2 Capture - Health and environmental impacts. Bellona Foundation, Oslo, Norway

Sigma-Aldrich (2016) Sigma-Aldrich Products

Sinnott R (2005) Chemical engineering design. Richardson's Chemical Engineering Series, vol 6. Elsevier Butterworth Heinemann, Oxford

Sridhar S, Carter RG (2000) Diamines and higher amines, aliphatic, Kirk-Othmer encyclopedia of chemical technology. John Wiley & Sons, Inc.

The World Bank (2014) Putting a Price on Carbon with a Tax

Tong D, Maitland GC, Trusler MJP, Fennell PS (2013) Solubility of carbon dioxide in aqueous blends of 2-amino-2-methyl-1-propanol and piperazine. Chem Eng Sci 101:851–864

Veawab A, Aroonwilas A, Chakma A, Tontiwachwuthikul P (2001) Solvent formulation for CO_2 separation from flue gas streams, First National Conference on Carbon Sequestration, Washington, DC. Citeseer

Vortmeyer N, Schneider Rd, Hohe S (2013) Post-combustion carbon Capture - Leading mature technology for decarbonization of fossil power generation, world energy Congress. Siemens, South Korea

Wong MK, Murshid G, Bustam MA, Tyutyu S, Shariff AM (2014) Solubility of carbon dioxide in piperazine-activated methyldiethanolamine and 2-amino-2-methyl-1-propanol. J Appl Sci 14:3114–3117

Yakub MI, Samah M, Danladi SU (2014) Technical and economic considerations of post-combustion carbon capture in a coal fired power plant. Int J Adv Eng Technol 7:1549–1581

Yang Z-Y, Soriano AN, Caparanga AR, Li M-H (2010) Equilibrium solubility of carbon dioxide in (2-amino-2-methyl-1-propanol + piperazine + water). J Chem Thermodyn 42:659–665

Yang X, Rees RJ, Conway W, Puxty G, Yang Q, Winkler DA (2017) Computational modeling and simulation of CO_2 capture by aqueous amines. Chem Rev 117:9524–9593

Zahra MRA (2009) Carbon dioxide capture from flue gas: development and evaluation of existing and novel process concepts. Technische Universiteit Delft

Zauba T, Data (2016) Search Import Export Data of India

Zhang Y, Chen H, Chen C-C, Plaza JM, Dugas R, Rochelle GT (2009) Rate-based process modeling study of CO_2 capture with aqueous monoethanolamine solution. Ind Eng Chem Res 48:9233–9246

Zhang W, Chen J, Luo X, Wang M (2017) Modelling and process analysis of post-combustion carbon capture with the blend of 2-amino-2-methyl-1-propanol and piperazine. Int J Greenhouse Gas Control 63:37–46

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