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# A comprehensive study on amine performance in CO<sub>2</sub> capture: Insights from design of experiments and principal component analysis

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## Abstract

While amine absorption has been extensively researched, selecting the most suitable amine solvent for effective CO<sub>2</sub> capture remains a significant challenge due to the complex criteria involved. This study proposes a comprehensive framework to address these challenges by integrating process simulation, design of experiments (DoE), and principal component analysis (PCA) for the selection of optimal amine solvents. The framework is validated through a case study of a CO<sub>2</sub> capture process from a natural gas-fired power plant, comparing four types of amine solvents: MEA (30 wt%) as the benchmark, DEA (10, 20, 30, and 40 wt%), MDEA (10, 20, 30, and 40 wt%), and MDEA+PZ (30+5 and 30+10 wt%). PCA results indicate that MDEA+PZ 30+5 wt% and MDEA+PZ 30+10 wt% exhibit performance comparable to the benchmark solvent. Based on these findings, multi-objective optimization (MOO) is conducted to evaluate the economic viability of the selected amine candidates. Subsequently, all process information, including the economic assessment from the MOO, is consolidated into a comparison matrix that evaluates safety, environmental impacts, amine set-up cost, and CO<sub>2</sub> capture cost. The results reveal that while MEA (30 wt%) offers the lowest amine set-up cost, MDEA+PZ outperforms MEA in terms of safety, environmental impact, and CO<sub>2</sub> capture cost. Specifically, MDEA+PZ 30+5 wt% demonstrates the lowest overall impact, while MDEA+PZ 30+10 wt% achieves the lowest CO<sub>2</sub> capture cost.

*Keywords:* Amine absorption; amine solvents; CO<sub>2</sub> capture; process simulation; design of experiments; principal component analysis; multi-objective optimization

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## 1. Introduction

Carbon capture, utilization, and storage (CCUS) have become increasingly a crucial strategy for addressing climate change and achieving net zero emission targets [1]. Among the various CO<sub>2</sub> capture technologies, amine absorption stands out as one of the most extensively researched and well-developed technologies in the process industry. As reported in many studies, monoethanolamine (MEA) has become the most commonly used solvent [2], as it offers advantages such as high absorption rate, high reactivity with CO<sub>2</sub>, wide availability, and low cost [3]. However, its high solvent regeneration energy, toxicity, and corrosivity [3] have driven research to explore alternative solvents with

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better properties, including blended amines [3,4], such as methyl diethanolamine (MDEA) + piperazine (PZ). With the increasing number of available and newly developed amine solvents, an infinite number of amine combinations and compositions have emerged, leading to challenges in selecting the most suitable amine solvent for achieving the most effective CO<sub>2</sub> capture process.

Some of the criteria to be considered in the amine solvent selection process include technical aspects (chemical reactivity with CO<sub>2</sub>, separation equilibrium, solvent degradation, regeneration effectiveness, etc.), economic factors (set-up and operating costs), and environmental impacts (toxicity, corrosivity, etc.) [4]. At present, there is a lack of extensive studies comparing the performance of different amine solvents in a systematic manner. Most studies have relied on lab-based experiments to compare the performance of different amine solvents, which can be time-consuming and expensive. Moreover, the nonlinearity of relationships between variables in the CO<sub>2</sub> capture process, including amine types, amine concentration, and plant operating conditions, makes the problem even more challenging when setting the optimal operating conditions in the CO<sub>2</sub> capture process.

This study aims to address key questions by proposing a framework to select the most suitable amine solvent for the CO<sub>2</sub> capture process. The framework employs a process simulation approach combined with the design of experiments (DoE) and principal component analysis (PCA). The remainder of this paper is organized as follows: Section 2 provides a more detailed discussion of the amine solvent selection framework, including process simulation, DoE, PCA, multi-objective optimization (MOO), and a comparison matrix. Section 3 presents a case study on an amine-based CO<sub>2</sub> capture process from a natural gas-fired power plant in which the framework is implemented. Section 4 discusses the results and provides insights into the criteria trade-offs of each amine solvent candidate. Lastly, Section 5 concludes the study and suggests potential future research directions.

## 2. Methodology

The five key elements of the amine solvent selection framework proposed in this study are process simulation, design of experiments (DoE), principal component analysis (PCA), multi-objective optimization (MOO), and a comparison matrix. Aspen HYSYS is used for process simulation of the amine-based CO<sub>2</sub> capture process. One of the key strengths of using this software is that it is equipped with an amine modeling package, in which the amine types, thermodynamics, and kinetics have been validated against experimental data with reasonable accuracy [5]. DoE is employed to systematically vary multiple variables and obtain output data, which are then recorded and compiled into a dataset highlighting the process operational variables for each amine solvent candidate. PCA is used to visualize and compare the amine performance dataset in 3D space, revealing similarities and differences between the amine solvent candidates in the form of data clusters. MOO is applied to assess the economic aspects of the amine solvent candidates that exhibit similar behavior (i.e., form overlapping clusters in the PCA plot) to the benchmark solvent. Finally, a comparison matrix is used to evaluate the overall performance of the amine solvent candidates against the benchmark solvent, considering process performance, safety, environmental impact, and economic criteria.

Fig. 1 illustrates the proposed amine solvent selection framework in this study. The first step involves data collection, which includes amine solvent candidates, the benchmark solvent, a basic CO<sub>2</sub> capture process flowsheet, and the CO<sub>2</sub> emissions profile. The second step is designing the experiments, which entails specifying the process input variables, their respective operating ranges, and output variables in the form of a DoE table. For this, the Box-Behnken design (BBD) is chosen, as it captures process nonlinearity using three input variable levels (minimum, center value, and maximum), thus requiring fewer experimental runs than other DoE methods [6]. In the third step, a simulation-based experiment is performed by modifying the input variables according to the DoE table. The output of this simulation step is a dataset for each amine solvent candidate, containing the process output variables. In the fourth step, the dataset of output variables is condensed into three principal components (PCs), which are then visualized in 3D space to observe any cluster formations between the amine solvent candidates and the benchmark solvent. The next step involves identifying overlapping clusters corresponding to different amine types and concentrations, as they indicate similar performance. These amines are then further evaluated using MOO, with the objective functions of maximizing CO<sub>2</sub> capture percentage (%) and minimizing CO<sub>2</sub> capture cost (operational cost, in USD/tonne CO<sub>2</sub>). Finally, all available information is compiled into a comparison matrix, which includes safety and environmental impact, amine set-up cost, and CO<sub>2</sub> capture cost for each amine solvent candidate. The output of the comparison matrix is the final decision regarding the selection of the most suitable amine solvent candidate.

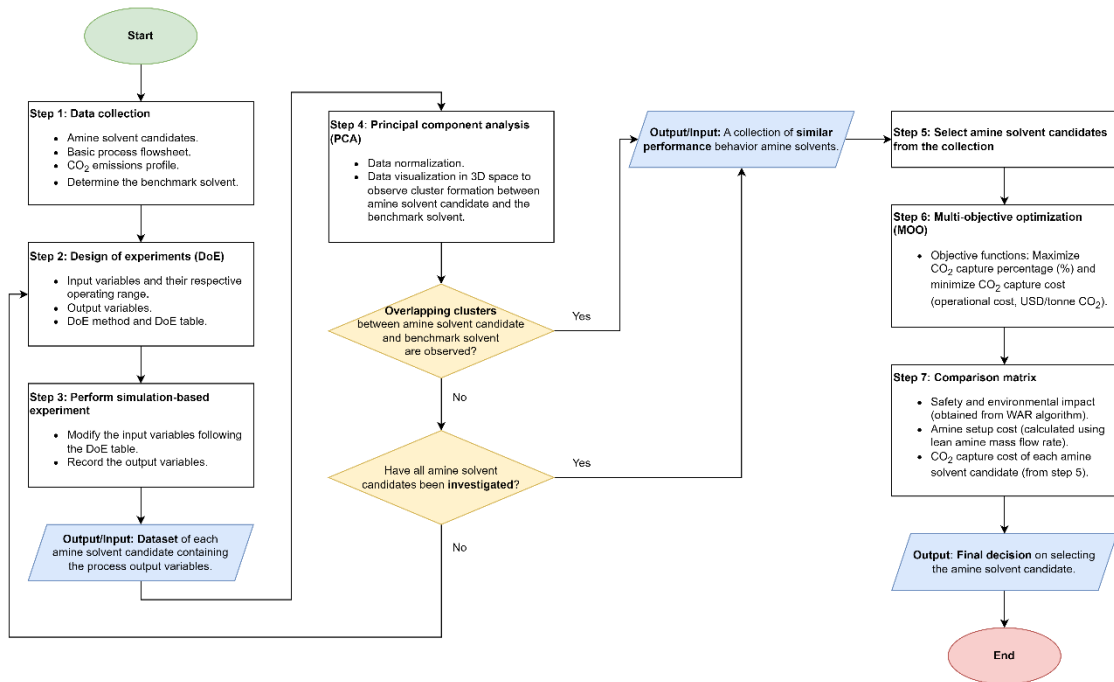


Fig. 1. Proposed amine solvent selection framework.

### 3. Case study: CO<sub>2</sub> capture process from power plant

Fig. 2 illustrates a typical amine-based CO<sub>2</sub> capture process flowsheet, where an absorption column contacts flue gas with lean amine, and a distillation column separates the CO<sub>2</sub> from the amine. The flue gas is assumed to originate from Singapore's natural gas-fired power plants, which typically contain 4-5 mol% CO<sub>2</sub> [7,8]. In Singapore, the power industry accounts for 36.5% of the total CO<sub>2</sub> emissions [9], with 91.6% of this coming from natural gas used in electricity generation [10]. The simulation experiments for this process assume the same flue gas source, process configuration, and equipment design, regardless of the amine types and concentrations used. Table 1 presents the fixed process parameters and their respective values for our simulation.

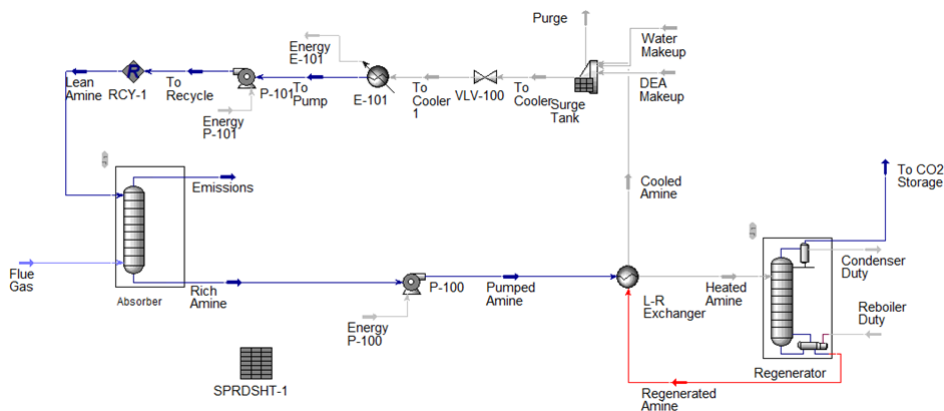
Fig. 2. Amine-based CO<sub>2</sub> capture process flowsheet in Aspen HYSYS.

Table 1. Fixed process parameters and values used in the simulation.

Process variable	Value	Reference
Flue gas – Temperature (°C)	55	[11]
Flue gas – Pressure (kPa)	110	[11]
Flue gas – Molar flow rate (kmol/h)	80,730	[8]
Flue gas – O <sub>2</sub> mole fraction	0.10	-
Flue gas – N <sub>2</sub> mole fraction	0.74	-
Absorber – Number of stages	10	[11]
Regenerator – Number of stages	14	[11]

The benchmark solvent chosen is MEA 30 wt%. The three amine solvent candidates to be compared are DEA (at 10, 20, 30, and 40 wt%), MDEA (at 10, 20, 30, and 40 wt%), and MDEA+PZ (at 30+5 and 30+10 wt%). Six input variables were selected for this experiment: lean amine temperature, lean amine mass flow rate, mole fraction of CO<sub>2</sub> in the flue gas, heated amine temperature, condenser temperature, and reboiler temperature. Table 2 shows the value ranges for the input variables used in the DoE. The range for lean amine mass flow rate was selected to ensure the process simulation achieves CO<sub>2</sub> capture percentage between 80% and 95%.

Table 2. Value ranges for the input variables used in the DoE.

Solvent	Solvent concentration (wt%)	Lean amine temperature (°C)		Lean amine mass flow rate (kg/s)		Mole fraction of CO <sub>2</sub> in the flue gas (mol%)	
		Min	Max	Min	Max	Min	Max
MEA	30	30	50	2,250	5,139	4	5
DEA	10	30	50	21,389	59,722	4	5
	20	30	50	21,944	61,667	4	5
	30	30	50	21,667	61,667	4	5
	40	30	50	20,556	58,333	4	5
MDEA	10	30	50	22,444	61,667	4	5
	20	30	50	24,278	67,778	4	5
	30	30	50	26,389	72,778	4	5
	40	30	50	28,000	77,222	4	5
MDEA+PZ	30+5	30	50	2,556	7,778	4	5
	30+10	30	50	2,294	4,444	4	5

Table 2. Value ranges for the input variables used in the DoE (continued).

Solvent	Solvent concentration (wt%)	Heated amine temperature (°C)		Condenser temperature (°C)		Reboiler temperature (°C)	
		Min	Max	Min	Max	Min	Max
MEA	30	70	100	30	45	125.8	126.7
DEA	10	70	100	30	45	122.6	123.5
	20	70	100	30	45	123.9	124.3
	30	70	100	30	45	125.1	125.3
	40	70	100	30	45	126.4	126.6
MDEA	10	70	100	30	45	121.3	123.4
	20	70	100	30	45	122.7	123.9
	30	70	100	30	45	123.4	124.5
	40	70	100	30	45	123.9	125.1
MDEA+PZ	30+5	70	100	30	45	122.0	124.2
	30+10	70	100	30	45	121.4	124.2

Based on the process flowsheet in Fig. 2, the nine output variables or process performance metrics chosen for this experiment are the cooling water mass flow rate of cooler E-101 (kg/h), steam mass flow rate of reboiler (kg/h), cooling water mass flow rate of condenser (kg/h), CO<sub>2</sub> capture percentage (%), CO<sub>2</sub> emission mass flow rate (kg/h), CO<sub>2</sub> purity, CO<sub>2</sub> final product mass flow rate (kg/h), pump duty of P-100 (kW), and pump duty of P-101 (kW).

## 4. Results and discussions

### 4.1. PCA plots and cluster formation

Fig. 3, 4, and 5 present the PCA plots comparing MEA 30 wt% with the respective amine solvent candidates. The 3D visualization offers valuable insights into the process performance by highlighting the cluster formation of each candidate relative to the benchmark solvent, MEA 30 wt%. The plots reveal that DEA (10, 20, 30, and 40 wt%) and MDEA (10, 20, 30, and 40 wt%) form distinct clusters, indicating significant differences in performance compared to MEA 30 wt%. In contrast, MDEA+PZ (30+5 and 30+10 wt%) exhibit overlapping clusters with MEA 30 wt%, suggesting similar performance. Given that similarity to the benchmark is the desired characteristic, MDEA+PZ 30+5 wt% and MDEA+PZ 30+10 wt% are selected as the amine solvent candidates for the next evaluation stage.

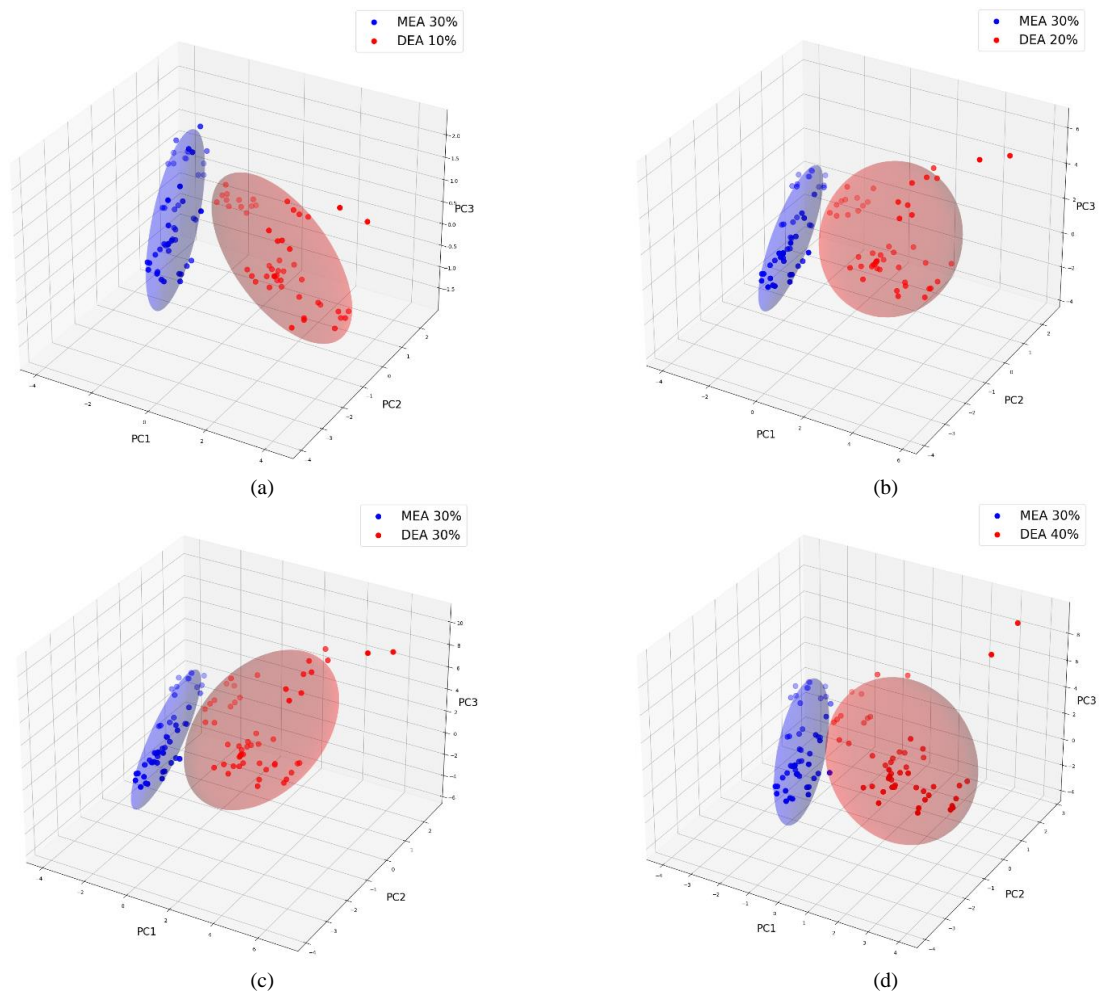


Fig. 3. PCA plot comparing MEA 30 wt% and (a) DEA 10 wt%, (b) DEA 20 wt%, (c) DEA 30 wt%, and (d) DEA 40 wt%.

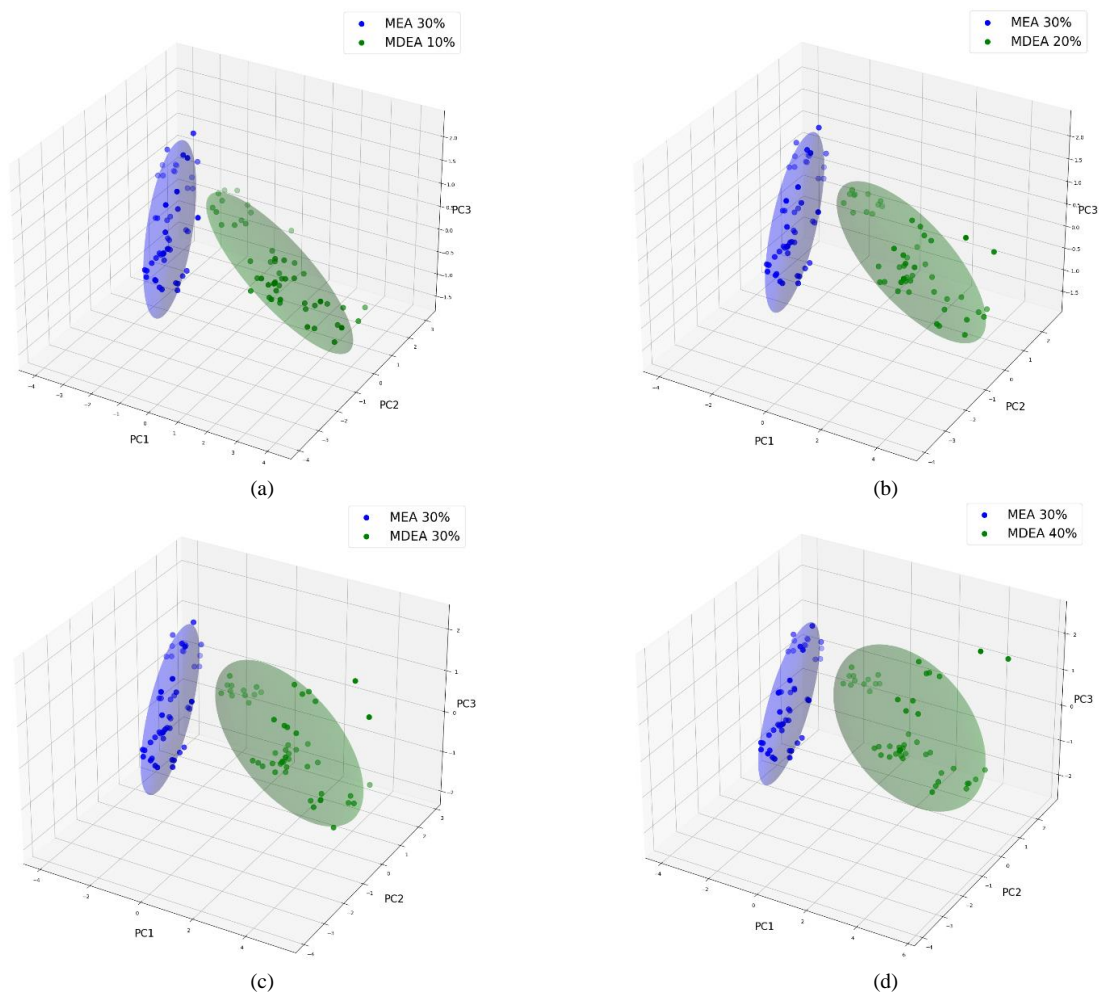


Fig. 4. PCA plot comparing MEA 30 wt% and (a) MDEA 10 wt%, (b) MDEA 20 wt%, (c) MDEA 30 wt%, and (d) MDEA 40 wt%.

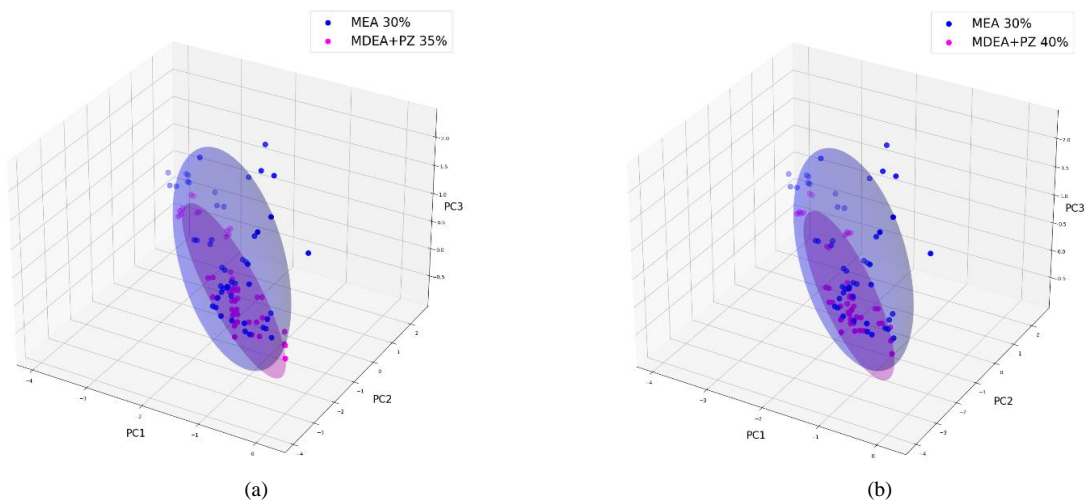


Fig. 5. PCA plot comparing MEA 30 wt% and (a) MDEA+PZ 30+5 wt% and (b) MDEA+PZ 30+10 wt%.

#### 4.2. MOO of the CO<sub>2</sub> capture plant

MOO is conducted for the CO<sub>2</sub> capture plant using the selected amine solvent candidates to generate a Pareto front that highlights the trade-off between CO<sub>2</sub> capture cost (USD/tonne CO<sub>2</sub>) and CO<sub>2</sub> capture percentage (%). This optimization aims to minimize CO<sub>2</sub> capture cost while maximizing CO<sub>2</sub> capture percentage, based on the given input variables. The CO<sub>2</sub> capture cost is defined as the operational cost of the CO<sub>2</sub> capture plant divided by the amount of CO<sub>2</sub> captured, as expressed in Eq. 1. Operational cost comprises the sum of utility costs and make-up amine costs, detailed in Eq. 2. The unit cost basis underlying these calculations are summarized in Table 3. CO<sub>2</sub> capture percentage is calculated as the ratio of the amount of CO<sub>2</sub> captured to the total CO<sub>2</sub> in the flue gas stream, as described in Eq. 3.

$$CO_2 \text{ capture cost} \left( \frac{\text{USD}}{\text{tonne } CO_2} \right) = \frac{\text{Operational cost} \left( \frac{\text{USD}}{\text{h}} \right)}{\text{Amount of } CO_2 \text{ captured} \left( \frac{\text{kg}}{\text{h}} \right) \times \frac{1 \text{ tonne}}{1,000 \text{ kg}}} \quad (1)$$

$$\text{Operational cost} \left( \frac{\text{USD}}{\text{h}} \right) = \text{Utilities cost} + \text{make up amine cost} \quad (2)$$

$$CO_2 \text{ capture percentage} (\%) = \frac{CO_2 \text{ in rich amine} - CO_2 \text{ in lean amine}}{CO_2 \text{ in flue gas}} \times 100\% \quad (3)$$

Table 3. Unit cost basis for calculating CO<sub>2</sub> capture cost.

Utility	Cost	Cost (in USD per unit)	Remarks	Reference
Cooling water	USD 15.7 / 1,000 m <sup>3</sup>	USD 0.0157 / m <sup>3</sup>	-	[12]
Electricity	USD 0.0674 / kWh	USD 0.0674 / kWh	-	[12]
Steam	USD 9.54 / 1,000 kg	USD 0.00954 / kg	Medium pressure steam without credit for power	[12]
Process water	USD 0.177 / 1,000 kg	USD 0.000177 / kg	High purity water for process use	[12]
Solvent – MEA	€30.50 / L	USD 34.09 / L	-	[13,14]
Solvent – DEA	€25.70 / L	USD 28.73 / L	-	[13,14]
Solvent – MDEA	€51.60 / L	USD 57.67 / L	-	[13,14]
Solvent – PZ	€68.70 / L	USD 76.79 / L	-	[13,14]

The input variables for this optimization are consistent with those used in the DoE (see Table 2), except that the reboiler temperature is replaced with CO<sub>2</sub> recovery to facilitate faster convergence. The optimization is performed using the Non-dominated Sorting Genetic Algorithm II (NSGA-II), implemented in Python, to exchange simulation data with Aspen HYSYS. The Python-Aspen HYSYS integration code is adapted from Medina [15], while the NSGA-II implementation is sourced from the Pymoo library [16].

Fig. 6 illustrates the Pareto front, focusing on the CO<sub>2</sub> capture percentage range of 80–95%. The data clearly show that the CO<sub>2</sub> capture cost for MEA 30 wt% is substantially higher, ranging from USD 124–309 per tonne of CO<sub>2</sub>, compared to MDEA+PZ 30+5 wt% (USD 43–103 per tonne of CO<sub>2</sub>) and MDEA+PZ 30+10 wt% (USD 44–78 per tonne of CO<sub>2</sub>). This elevated cost for CO<sub>2</sub> capture process is primarily due to the low CO<sub>2</sub> mole fraction in the flue gas stream (4.5 mol%) [1,17], which results in a more expensive separation process. Additionally, the figure highlights that MDEA+PZ achieves a lower CO<sub>2</sub> capture cost than MEA 30 wt%, primarily due to its lower solvent regeneration energy requirement [3].

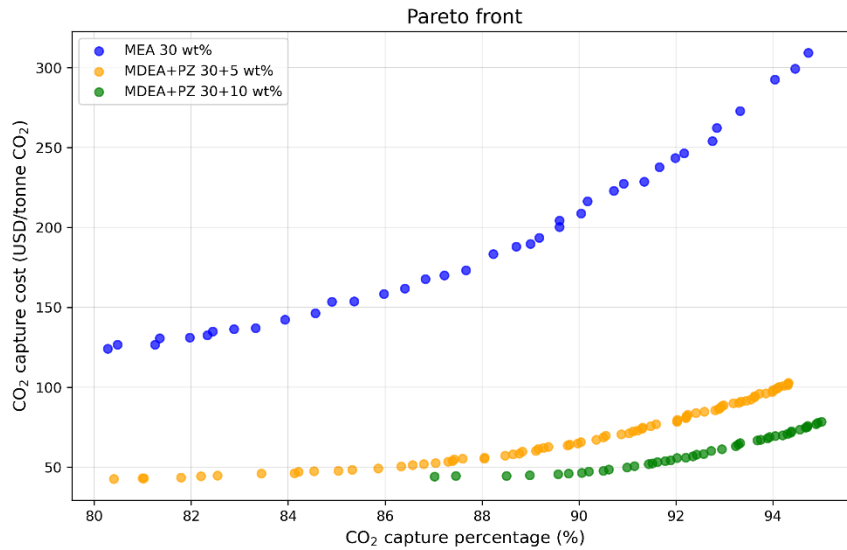


Fig. 6. Pareto front result for MEA 30 wt%, MDEA+PZ 30+5 wt%, and MDEA+PZ 30+10 wt%.

#### 4.3. Comparison matrix of amine solvent candidates

Table 5 presents the comparison matrix for the amine solvent candidates. The total impact includes both safety and environmental impact indicators, calculated using the metrics outlined in Table 4, which are derived from the Waste Reduction (WAR) algorithm [18]. In this analysis, the impact of each amine solvent is expressed as the impact per hour per kilogram of solvent.

Table 4. Amine safety and environmental impacts [18].

Solvent	HTPI <sup>a</sup>	HTPE <sup>b</sup>	TTP <sup>c</sup>	ATP <sup>d</sup>	GWP <sup>e</sup>	ODP <sup>f</sup>	PCOP <sup>g</sup>	AP <sup>h</sup>	Total
MEA 30 wt%	0.0550	0.0119	0.0550	$5.74 \times 10^{-5}$	0.0000	0.0000	0.6410	0.0000	0.7630
MDEA+PZ 30+5 wt%	0.0274	0.0000	0.0274	$2.89 \times 10^{-5}$	0.0000	0.0000	0.0000	0.0000	0.0549
MDEA+PZ 30+10 wt%	0.0312	0.0000	0.0312	$3.59 \times 10^{-5}$	0.0000	0.0000	0.0000	0.0000	0.0625

<sup>a</sup>HTPI = Human Toxicity Potential by Ingestion, <sup>b</sup>HTPE = Human Toxicity Potential by Inhalation or Dermal Exposure, <sup>c</sup>TTP = Terrestrial Toxicity Potential, <sup>d</sup>ATP = Aquatic Toxicity Potential, <sup>e</sup>GWP = Global Warming Potential, <sup>f</sup>ODP = Ozone Depletion Potential, <sup>g</sup>PCOP = Photochemical Oxidation Potential, and <sup>h</sup>AP = Acidification Potential.

Table 5. Comparison matrix of amine solvent candidates.

Solvent	Total impact (impact per hour per kg of solvent)	Amine set-up cost (USD/h)		CO <sub>2</sub> capture cost (USD/tonne CO <sub>2</sub> )	
		Min	Max	Min	Max
MEA 30 wt%	0.7630	$8.145 \times 10^7$	$1.860 \times 10^8$	124	309
MDEA+PZ 30+5 wt%	<b>0.0549</b>	$1.929 \times 10^8$	$5.871 \times 10^8$	43	103
MDEA+PZ 30+10 wt%	0.0625	$2.090 \times 10^8$	$4.048 \times 10^8$	<b>44</b>	<b>78</b>

The comparison matrix reveals that, in terms of safety and environmental impact, MDEA+PZ outperforms MEA significantly, with MDEA+PZ 30+5 wt% showing the lowest total impact. Regarding amine set-up cost, MEA 30 wt% is the most cost-effective option among the candidates. When it comes to CO<sub>2</sub> capture cost, MDEA+PZ again

performs better than MEA, with MDEA+PZ 30+10 wt% offering the lowest CO<sub>2</sub> capture cost—USD 44 per tonne of CO<sub>2</sub> at 87% capture and USD 78 per tonne CO<sub>2</sub> at 95% capture.

## 5. Conclusion

A general framework for selecting the most suitable amine solvent is proposed, combining process simulation with DoE and PCA. This approach is applied to a case study of an amine-based CO<sub>2</sub> capture process at a natural gas-fired power plant. PCA plots and cluster analysis are used for the initial screening of amine solvent candidates, revealing similar performance between MDEA+PZ 30+5 wt%, MDEA+PZ 30+10 wt%, and MEA 30 wt% as the benchmark solvent. MOO of the CO<sub>2</sub> capture plant highlights the trade-off between CO<sub>2</sub> capture percentage and CO<sub>2</sub> capture cost, offering valuable economic insights for each amine solvent. The results show that while MEA 30 wt% offers the lowest amine set-up cost, MDEA+PZ outperforms MEA 30 wt% in terms of safety, environmental impact, and CO<sub>2</sub> capture cost. Specifically, MDEA+PZ 30+5 wt% has the lowest total environmental impact, while MDEA+PZ 30+10 wt% offers the lowest CO<sub>2</sub> capture cost.

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