

# Technical Assessment of direct air capture using piperazine in an advanced solvent-based absorption process

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## ABSTRACT

Climate and environmental problems caused by increasing CO<sub>2</sub> concentration in the atmosphere make the direct air capture (DAC) technology having great prospects for development. As the widely used solvent in carbon capture based on chemical absorption processes, MEA still fails to address the issues of high energy consumption and high costs when used in DAC process. In this study, piperazine (PZ) was used as the new solvent for DAC process. The new configuration was simulated in Aspen Plus® V11 and the model was validated through experimental data and model comparison. It is followed by investigation of the potential for energy efficiency and cost reduction. The standard DAC-PZ configuration could reduce the reboiler duty from 10.7 GJ/tCO<sub>2</sub> to 8.9 GJ/tCO<sub>2</sub> for DAC-MEA process. Economic analysis will be carried out through Aspen Process Economic Analyzer®. Further analysis (e.g. sensitivity analysis for different parameters and optimisation) will be performed to further reduce the energy consumption and cost for the DAC-PZ process with different configurations.

**Keywords:** direct air capture, chemical absorption, process simulation

## INTRODUCTION

### Background and motivation

The concentration of CO<sub>2</sub> in the atmosphere is increasing for several decades. In November 2024, it has reached 423 ppm [1]. Carbon capture is essential to combat the ecological problems such as global warming associated with increased carbon emissions. Among all the carbon capture technologies, direct air capture (DAC), as a negative emission technology, has great potential for development to capture 980Mt CO<sub>2</sub> in 2050 according to the IEA Net Zero Emissions Scenario.

In the conventional solvent-based carbon capture process, MEA is the most commonly used solvent [2]. Nevertheless, MEA has a series of disadvantages which affects the improvement of the performance for carbon capture process. In comparison, PZ offers better performance and is more economical. Replacing MEA with PZ in the DAC process provides a new alternative for the DAC process to reduce energy consumption and costs.

### Literature review

The solvent-based carbon capture process is widely used. The process is based on chemical reactions between solvent and carbon dioxide which enables selective capture of specific components from the flue gas. In Canepa et al. [3], a solvent-based carbon capture process using MEA solvent was integrated with a combined cycle gas turbine (CCGT) power plant. Exhaust gas recirculation (EGR) technology was proposed to reduce the energy consumption for solvent regeneration. Luo and Wang [4] combined the solvent-based carbon capture process with nature gas combined cycle (NGCC) power plant. In addition to the traditional power plants, Hu et al. [5] applied the carbon capture process using MEA for treating flue gas from thermal cracking furnace in ethylene manufacturing. By recovering the excess heat from the gasoline fractionator, the energy consumption and capture cost could be reduced.

With minor modification of solvent-based carbon

capture, it can be used for DAC. Kiani et al. applied a conventional carbon capture process using MEA solvent for DAC. An economic performance analysis of the whole system confirmed the potential of this approach to reduce the cost of DAC [6]. Michailos integrated the air absorber with a traditional post-combustion carbon capture (PCC) absorber column to reduce the energy consumption for DAC. [7].

PZ is a better replacement of MEA in carbon capture studies due to its higher absorption capacity and heat degradation resistance. The performance parameters of two different concentrations of PZ comparing with MEA are presented in Table 1. Otitoju et al. used PZ in PCC process for NGCC power plant. PZ with higher performance could reduce the total energy consumption from 5.34GJ/tCO<sub>2</sub> with 30wt% MEA to 3.56GJ/tCO<sub>2</sub> with 30wt% PZ [8]. Ma et al. also used PZ instead of MEA in the carbon capture process for the ethylene plant. With flue gas heat recovery, the energy consumption could be reduced by 37.71% compared to the standard MEA configuration, while costs can be lowered by 36.76% [9]. These highlighted the significant potential of PZ solvents in the carbon capture field.

**Table 1:** Performance parameters of different solvents [8]

Parameter	30wt% MEA	30wt% PZ	40wt% PZ
$K_L$ @313K (mol/s Pa m <sup>2</sup> )	4.3	11.3	8.5
Viscosity (Pa s) @313K	0.0025	0.003	0.011
CO <sub>2</sub> capacity (mol <sub>CO2</sub> /mol <sub>amine</sub> )	0.5	0.63	0.79
Thermal stability $T_{max}$ (K)	393	436	436
Max. regeneration Pressures (bar)	2.2	14.3	14.3

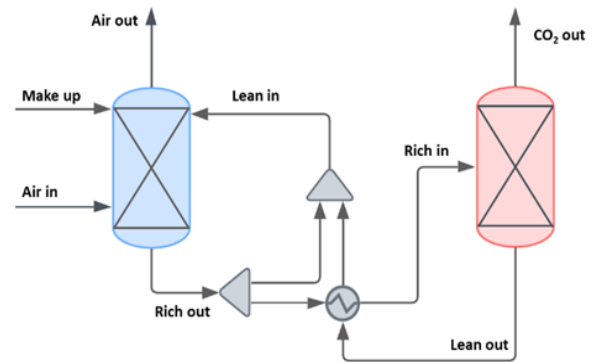
### Novelty of this study

Several studies on the DAC process use packed bed column as shown in the literature review part. High energy consumption and high cost remain significant challenges to the commercial deployment of DAC technology. However, use of PZ solvent in DAC process offers the possibility to optimize the process. In this study, PZ was selected as solvent for DAC process inside a packed bed column. Through simulation, new results on energy consumption and capture cost will be obtained. In future work, sensitivity analysis for different process parameters and optimisation will be performed to further reduce the energy consumption and cost for the DAC.

### PROCESS DESCRIPTION

The process of standard solvent-based absorption process for DAC process using PZ solvent is shown in Fig.

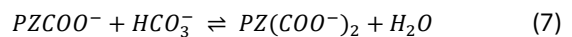
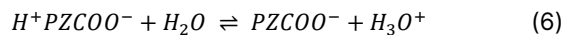
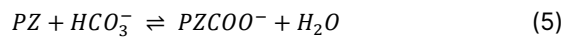
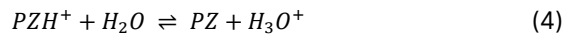
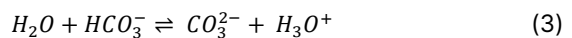
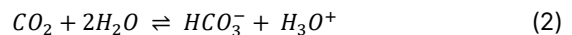
1. The process contains absorber, stripper, splitter, pump and heat exchanger. The absorber and stripper are all packed bed column using Mellapak 250X packing. In contrast to the PCC process, since CO<sub>2</sub> concentration in the air is much lower than in the flue gas from power plants or chemical plants, the rich solvent from absorber needs to be diverted by a splitter. Majority of the solvent is returned to the top of absorber for re-absorption. This is to increase the liquid/gas ratio in absorber to meet the design requirements of a conventional packed bed column. The remaining small portion goes to the stripper for solvent regeneration. The regenerated solvent from stripper then undergoes a heat exchange process with the small portion rich solvent to decrease the energy penalty.



**Figure 1.** The process of standard DAC process using PZ.

### MODEL DEVELOPMENT

In this study, the DAC process using PZ was developed in Aspen Plus® V11. The absorber and stripper are all rate-based models using RadFrac Block in the software. The rate-based model was used for reactions and physical properties. The liquid phase was calculated with Electrolyte Non-Random Two-Liquid (ElecNRTL) method. The vapour phase was calculated with the Redlich-Kwong equation of state. Equations (1) -(7) are equilibrium reactions for describing chemistry of CO<sub>2</sub> absorption with PZ solvent.

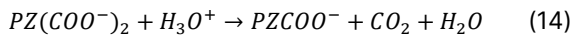
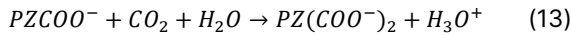
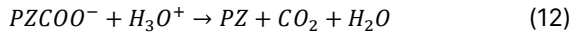
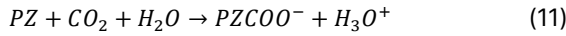


The equilibrium constants ( $K_{eq}$ ) was calculated by equation (8) based on molar concentration scale. All

these chemical reactions and coefficients of the equilibrium constant are coming from reference studies [8].

$$\ln K_{eq} = A + \frac{B}{T} + C \ln T + DT \quad (8)$$

Equations (9) -(14) are kinetically controlled reactions for describing the rate of absorption.



The power law is described in equation (15) which determines the reaction rates ( $k_j$ ). All parameters pre-exponential factor  $k_j^o$  and activation energy  $E_j$  for calculating the reaction rates of kinetically controlled reactions (9)-(14) are shown in Table 2.

$$k_j = k_j^o \exp\left(-\frac{E_j}{RT}\right) \prod_{i=1}^n C_i^{a_{ij}} \quad (15)$$

**Table 2:** Kinetic parameters for reactions (9) -(14)

Reaction No.	$k_j^o$ (m <sup>3</sup> /kmol s)	$E_j$ (kJ/kmol)
9	4.32 e + 13	5.55 e + 4
10	2.38 e + 17	1.23 e + 5
11	4.14 e + 10	3.36 e + 4
12	7.94 e + 21	6.69 e + 4
13	3.62 e + 10	3.36 e + 4
14	5.56 e + 25	7.69 e + 4

## MODEL VALIDATION AND COMPARISON

Model validation is essential to verify the accuracy of the model. For this case, there is no experimental data for DAC process using PZ solvent. The model validation and comparison is divided into two parts: (a) The accuracy of PZ solvent for CO<sub>2</sub> capture is validated using experimental data from pilot plant at the University of Texas at Austin as presented in [10]. (b) The accuracy of the DAC process simulation using MEA is verified by comparing the simulation results of a DAC process using MEA solvent with those presented in [6].

### Model validation for Carbon Capture process using PZ solvent

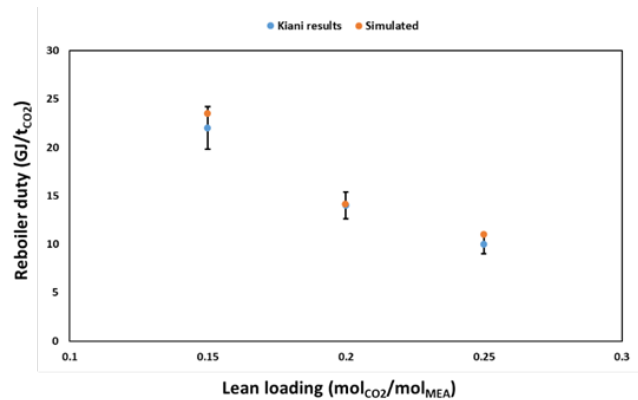
The validation part for PZ used pilot plant data to test the model prediction accuracy for the absorber-only process. The pilot plant data is from the University of Texas at Austin. The flue gas mass flow rate is 0.165 m<sup>3</sup>/s. The CO<sub>2</sub> concentration in flue gas is 12vol%. The height

of absorber is 6.1m, diameter is 0.427m and packing material is chosen as Mellapak 2X [10].

In this part, 5 cases were chosen with different concentration of PZ, L/G ration and lean loading as input. Two model prediction outputs: rich loading and capture level are compared with the experimental results. The relative error for different cases are shown in Table 3. By comparing model prediction results with experimental data, the errors across different cases were all kept within 10%. It proved that the model can simulate the performance of CO<sub>2</sub> absorption by PZ in the absorber.

### Model comparison for DAC process using MEA solvent

The DAC process using MEA solvent is simulated. The MEA concentration is chosen as 30 wt%. The capture level from air is set as 50%. The inlet air mass flowrate is 943t/h and CO<sub>2</sub> concentration in the air is assumed as 400 ppm. The ratio of rich solvent recirculation splitter is set the same to reach 2.54 L/G ratio (kg/kg) for absorber [6]. The impact of lean loading on the reboiler duty for DAC was considered and used as results for comparison. The simulation results compared with Kiani et al. [6] are shown in Figure 2. The simulation results have the same trend as Kiani et al. [6]. The relative error range is setting as 10% in the figure.



**Figure 2.** Comparison of simulation results with reference [6] on DAC process.

### CASE STUDY TO DETERMINE PZ SOLVENT CONCENTRATION

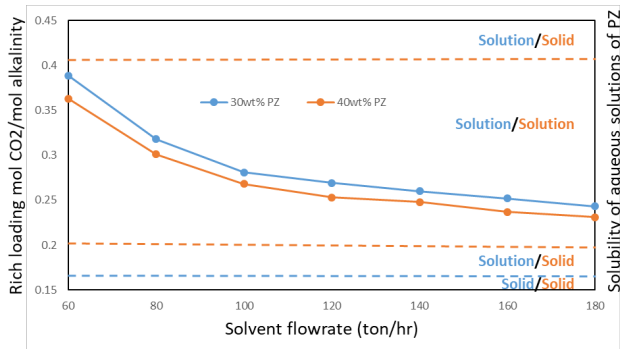
As we mentioned in the literature review, PZ has better performance as a replacement for MEA. Since the DAC-PZ process is different from other conventional PZ-based carbon capture studies, it is essential to determine the optimal PZ concentration.

This case study compared 30wt% PZ with 40wt% PZ in the absorber only DAC process. The lean loading was setting as 0.2 mol CO<sub>2</sub>/mol alkalinity, the capture level of CO<sub>2</sub> from air was setting as 50%. The sensitivity analysis

**Table 3:** Validation results of comparing 5 experimental cases to model prediction values with relative error

Input			Output 1			Output 2		
PZ wt%	L/G (mol/mol)	Lean loading	Experimental Rich loading	Prediction Rich loading	Relative error	Experimental Capture level %	Model prediction Capture level %	Relative error
30	5.5	0.257	0.360	0.391	8.6%	78.3	82.4	5.3%
30	6.8	0.274	0.360	0.386	7.2%	88.6	90.2	1.8%
40	5.5	0.285	0.340	0.355	4.4%	85.9	88.6	3.2%
40	6.7	0.267	0.340	0.334	1.9%	92.2	91.3	1.0%
40	5.5	0.308	0.370	0.358	3.2%	66.6	61.1	8.3%

of solvent flowrate on rich loading for 30wt% and 40wt% is shown in Figure 3. The solubility of aqueous solutions of PZ is also labelled in the right side. As indicated by the orange dashed line in Figure 3, excessively high or low loading can lead to solid formation in PZ solvent. 40wt% PZ has significantly narrow operational range compared to 30 wt% PZ although it has a higher CO<sub>2</sub> capacity. Meanwhile, the higher mass transfer rate and lower viscosity of 30 wt% PZ make it more suitable for the DAC-PZ process.

**Figure 3.** Sensitivity analysis of different solvent flowrate on rich loading with solubility area.

## CASE STUDY OF STANDARD DAC-PZ PROCESS

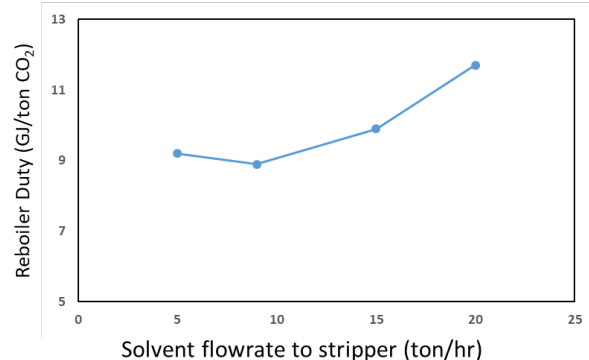
The standard DAC-PZ process was simulated as the closed-loop model. The operating parameters were listed in the Table 4. Due to the higher absorption capacity of PZ solvent compared to MEA, the rich solvent entering the stripper has a higher rich loading. The impact of solvent flowrate to stripper on the reboiler duty is shown in Figure 4 through sensitivity analysis. When the solvent flowrate is too low to the stripper, the rich loading of solvent will be above the highest operating range for PZ. When the solvent flowrate is too high, the reboiler duty will increase significantly because of the increasing heat

requirement for water in solvent. In this case, the separation ratio of the splitter controlling the solvent circulation is different to DAC-MEA, with a different L/G ratio as 2.03 and liquid flowrate to stripper as 8.81 ton/hr.

**Table 4:** Operating conditions

### Operating conditions

Inlet air temperature (K)	298
Air relative humidity (%)	100
CO <sub>2</sub> concentration in inlet air (ppm)	400
CO <sub>2</sub> captured (ton/hr)	0.291
CO <sub>2</sub> capture efficiency (%)	50
Flow rate of air (ton/hr)	943
PZ concentration (wt%)	30
L/G ratio in absorber (ton/ton)	2.03
Flooding capacity of absorber/stripper (%)	70/65
Packing type (Absorber and Stripper)	Mellapak 250X
Absorber pressure (bar)	1
Stripper pressure (bar)	2
Absorber diameter (m)	9.8
Absorber packing height (m)	4

**Figure 4.** Impact of solvent flowrate to the stripper on reboiler duty.

The simulation results were presented in the Table

5. At a CO<sub>2</sub> production rate of 0.289 ton/hr, the reboiler duty is 8.9 GJ/tCO<sub>2</sub>, which is 16.8% lower than the reboiler duty of 10.7 GJ/tCO<sub>2</sub> observed in the DAC process using MEA.

**Table 5:** Compare of simulation results between DAC-PZ and DAC-MEA process.

Simulation results	DAC-PZ	DAC-MEA
Absorption liquid flow to stripper (ton/hr)	8.81	9.12
Absorber recirculation liquid flow (ton/hr)	1905	2396
CO <sub>2</sub> lean loading (mol <sub>CO2</sub> /mol <sub>alk</sub> )	0.2	0.2
CO <sub>2</sub> rich loading (mol <sub>CO2</sub> /mol <sub>alk</sub> )	0.4	0.35
Reboiler temperature (K)	394	396.2
CO <sub>2</sub> production (ton/hr)	0.289	0.288
Reboiler duty (GJ/hr)	2.57	3.08
Reboiler duty (GJ/tCO <sub>2</sub> )	8.9	10.7

## CONCLUSION AND FUTURE WORK

Using PZ solvent to replace MEA solvent in standard configuration of DAC process, the reboiler duty could reduce 16.8%. As a more efficient solvent with lower energy consumption, this study demonstrates that the application of PZ in the DAC process is promising.

Due to page limitations, the economic analysis of the standard DAC-PZ process is not presented in this paper. This part will be addressed in future work which will be carried out through Aspen Process Economic Analyzer®. Building on the standard configuration, this study will conduct further analyses, such as examining the impact of the separation factor of the circulating solvent on this system and the effect of different CO<sub>2</sub> concentration in the atmosphere on DAC-PZ process. Through different configurations, such as utilizing advanced flash stripper (AFS) and rich-split process, this study will perform energy and economic optimizations for the DAC-PZ system. Optimal design and operation for DAC process using PZ can be achieved.

## ACKNOWLEDGEMENTS

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