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## The 8th Trondheim Conference on CO2 Capture, Transport and Storage

# Multivariable Optimization of the Piperazine CO<sub>2</sub> Post-Combustion Process

Jozsef Gaspar<sup>a</sup>, Nicolas von Solms<sup>a</sup>, Kaj Thomsen<sup>a</sup>, Philip Loldrup Fosbøl<sup>a</sup> \*

<sup>a</sup>Technical University of Denmark, Department of Chemical Engineering, Center for Energy Resource Engineering (CERE), Søltofts Plads, 2800, Kgs. Lyngby, Denmark

## Abstract

8 molal piperazine (PZ) is a promising solvent for developing an energy efficient  $CO_2$  post-combustion capture process. However, it has a limited operating range due to precipitation. The operating range can be extended by decreasing the piperazine concentration and/or increasing the  $CO_2$  loading of the lean solvent. However, optimal solvent composition must be determined taking into account the solvent circulation rate and the heat demand of the solvent regeneration.

In this paper, we determine and generalize trends of performance for a broad range of operating conditions: 1.8 to 9 mol PZ/ kg water, 0.2 to 0.6 lean loading, and for two flue gas sources: natural gas combined cycle power plant (NGCC, 3.9 mol% CO<sub>2</sub>) and a coal based power plant (ASC, 13.25 mol% CO<sub>2</sub>). Special attention is given to the boundaries where precipitation may occur. The results are created by the hybrid CAPCO2 rate-based model which accounts for precipitation when estimating the heat and mass transfer rates. The results show that the 7 molal piperazine gives the lowest specific reboiler duty at 0.40 CO<sub>2</sub> lean loading:  $3.32 \text{ GJ/t CO}_2$  and  $4.05 \text{ GJ/t CO}_2$  for the ASC case and NGCC cases. The analysis also reveals that the capture process needs to be operated up to 7.8 % above the minimum duty to avoid the risk of clogging due to solid formation. Note, this analysis assumes a 25 °C minimum solvent temperature. The energy requirement of the capture process can be further improved by assuming a minimum solvent temperature of 30 °C which gives a specific reboiler duty of 3.23 GJ/t CO<sub>2</sub> (ASC case) and 3.80 GJ/t CO<sub>2</sub> (NGCC case).

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Keywords: CO2 capture; piperazine; rate-based simulation and optimization; solubility; extended UNIQUAC; specific reboiler duty; L/G ratio.

\* Corresponding author. Tel.: +45 45252868, ; fax: +45 45882258 . *E-mail address:* plf@kt.dtu.dk

## 1. Introduction

Flexibility is a core benefit of the post-combustion  $CO_2$  capture technology. It offers adaptabilities through scaleup possibilities, part-load operation during peak electricity price periods, and retrofit to existing power plants. Currently it is an energy efficient and mature solution. Thus, post-combustion capture is the most promising short and mid-term solution for decreasing the  $CO_2$  emissions.

The focus of this study is the piperazine (PZ) based  $CO_2$  post-combustion capture process. Recent modeling and experimental studies have shown that 8 m PZ has double the  $CO_2$  absorption rate and capacity compared to 7 m MEA [1]. There are other benefits of PZ such as moderate heat of absorption and thermal stability. However, the 8 m PZ solution has a limited operating range due to solubility issues. It precipitates at both lean and rich process conditions [2-4].

The operating range can be extended by decreasing the piperazine concentration of the solvent. 5 molal PZ is a promising alternative to eliminate the limitations but still retain the benefits of 8 m PZ. Chen et al. [1] demonstrates that the absorption rate of 5 m PZ is approximately 30% higher than 8 m PZ. However, the absorber must be operated at a higher L/G ratio to achieve 90% CO<sub>2</sub> removal. Furthermore, precipitation can be avoided by using a higher lean loading. Fosbøl et al. presents how the precipitation-free operational range grows exponentially with CO<sub>2</sub> loading indifferent of piperazine composition [4]. They show that an 8 molal PZ solution does not precipitate above  $0.40 \text{ CO}_2$  loading at 25°C.

The optimum solvent composition needs to be determined based on a circulation rate and energy demand, considering the solubility limit of PZ. It is worth noting that process conditions needs to be (re)optimized for each concentration value to assure a consistent and fair comparison of the solvent capacity and energy demand of the process. This analysis requires a systematic and thorough study showing the performance of PZ for a broad concentration and  $CO_2$  loading range.

The aim of this study is to perform a systematic and comprehensive evaluation of the absorption capacity and mass transfer benefits of a 1.8, 3, 5, 7, 8 and 9 m PZ solution, for two flue gas sources: natural gas combined cycle (3.9 mol%  $CO_2$ ) and a coal based power plant (13.25 mol%  $CO_2$ ). In this work, optimum process conditions, e.g. L/G ratio, lean loading, column specifications are determined for each PZ concentration. The results are created using the DTU in-house hybrid CAPCO2 rate-based model for  $CO_2$  absorption and desorption calculations [3]. Hybrid CAPCO2 is to our knowledge a first-of-its-kind rate-based model which includes solid precipitation in the mass and heat transfer estimation.

## 2. The rate-based model of a precipitating CO<sub>2</sub> capture process

In this work, the hybrid CAPCO2 in-house rate-based model is implemented to simulate  $CO_2$  absorption and desorption. Compared to traditional rate-based models, hybrid CAPCO2 includes solid-liquid phase change when predicting the  $CO_2$  mass and heat transfer rate between the gas phase and the liquid phase. This model was compared to pilot plant data. The analysis reveals a good agreement between the model and experiments [3].

The hybrid rate-based model is built on the core of the original CAPCO2 model. It is formulated as a boundary value problem with specified inlet conditions and calculated outlet conditions. The lean temperature, pressure, composition and flow rate are specified at the top of the column. The temperature, pressure, composition and flow rate of the gas are fixed at the bottom of the column. In case of a desorber, the gas stream results from an integrated reboiler unit and only the reboiler temperature and pressure have to be specified. The rate-based model is built on mass and energy balances for the liquid phase and gas phase. They are solved simultaneously with algebraic equations for mass and hydraulic properties, mass and heat transfer fluxes, and the extended UNIQUAC thermodynamic model. Extended UNIQUAC is a rigorous model which is able to accurately predict solid precipitation [4-6]. This model gives the phase equilibria and thermal properties. The numerical approach and the equation system of CAPCO2 are presented in previous works [7,8].

The mass and heat transfer fluxes are determined in a film theory approach, using the General Method (GM) enhancement factor model [3,9]. GM connects the Onda's approximation for reversible reactions with the van

Krevelen's approach for instantaneous irreversible reactions. Therefore, it is valid for both, absorber and desorber conditions, and for high driving forces and pinch conditions. It eliminates many of the limitations of existing enhancement factor models. Note that this is of crucial importance since absorption of carbon dioxide involves finite rate reactions [10].

Parameter	Expression/Source	Validation data
Density	$\rho = \rho_{H_{2}O} + 0.04796 \cdot w_{PZ}$	[11-16]
Viscosity	Dugas, 2009 [17]	[11-16]
Surface tension	$\sigma = 71.8623 - 0.1255(T - 293.15) - 17.9983 \cdot w_{PZ}$	[12,14,15]
Diffusivity of CO <sub>2</sub> and PZ in unloaded solution	Dugas and Rochelle, 2011 [18]	[10,11,19,20]

In this work, the Rocha et al. model predicts the mass transfer coefficients, the liquid hold-up and the interfacial area [21,22]. The necessary physical property parameters, e.g. diffusivities, surface tension, viscosity, conductivity, density and etc. entering this model has been evaluated and validated against experimental data. The physical properties describing the gas phase are presented in [7]. Table 1 gives an overview of these correlations for the liquid phase.

#### 3. Process boundaries and design specifications

The absorber and the desorber are designed for a nominal theoretical 250 MWe capacity advanced supercritical pulverized coal power plant (ASC) respectively a 250 MWe capacity natural gas combined cycle power plant (NGCC). The ASC plant produces 238 kg/s flue gas, with a  $CO_2$  concentration of 13.25 mol%. The NGCC plant produces 386.33 kg/s flue gas with 3.90 mol%  $CO_2$ . We assume that the gas from ASC respectively NGCC passes through a DeNOx plant, a wet limestone based desulphurization plant and a direct contact cooler for the control of combustion products. Therefore, the flue gas contains only  $CO_2$ , inert gases and it is saturated with water at the absorber inlet temperature, 40 °C.

Parameter	Unit	ASC	NGCC
Flue gas flow rate	kg/s	238.46	386.33
Flue gas temperature	°C	40	40
Flue gas pressure	kPa	101.6	101.6
Flue gas CO <sub>2</sub> composition	mol%	13.25	3.90
Flue gas H <sub>2</sub> O composition	mol%	12.11	8.20
Lean inlet temperature	°C	40	40
Lean loading	mol/mol	0.2 - 0.6	0.3 - 0.6
Rich loading	mol/mol	0.65 - 0.8	0.6 - 0.7
Piperazine concentration	mol/kg water	1.8 - 9	1.8 - 7
L/G ratio	mol/mol	2 - 12	0.5 - 5
Reboiler pressure	kPa	190	190

Table 2. Main inlet and outlet specifications for the absorber and the desorber

In the absorber the flue gas is washed with lean piperazine solution. The concentration of the lean solvent for the ASC case is varied between 1.8 and 9 mol PZ/kg  $H_2O$  and 0.20 to 0.60  $CO_2$  loading. The covered PZ concentration range for the NGCC case is from 1.8 to 7 mol PZ/kg  $H_2O$ . Higher piperazine concentrations are not feasible and

results in insufficient wetting of the column due to the low solvent flow rate. Note that the lean loading and the operating temperature range are chosen taking into account the solubility window of the loaded piperazine solution. Table 2 summarizes the main operating conditions for the absorber and the desorber.

The absorber and the stripper are packed columns equipped with Sulzer Mellapak 2X structured packing. This packing offers low pressure drop and can be used for wide range of liquid loads. The carbon capture plant is designed for 90% CO<sub>2</sub> removal percentage. The diameter of the columns is calculated for an operating velocity of 70% flooding and it varies between 10 and 15 m. A minimum diameter of 10 m is required to accommodate the gas flow resulting from the ASC and NGCC plant. In this work, an 18 m tall absorber column is used. A sensitivity study has shown that the CO<sub>2</sub> capture efficiency increases with the column height up to 18 m, and then it remains unchanged. A similar behavior is shown in [23]. Based on the approach for the absorber, the height of the stripper is set to 14 m.

### 4. Results and discussion

This section shows a parametric sensitivity study to determine the effect of the lean solvent PZ and  $CO_2$  concentration on energy demand and solvent recirculation flow rate. Moreover, it presents the effect of pressure on the energy performance of stripping and compression and it underlines the operating conditions where precipitation may occur. The present analysis demonstrates how the  $CO_2$  capture process must be operated above optimal conditions to avoid clogging due to solid formation.

#### 4.1. Thermodynamic analysis

We perform a thermodynamic analysis to determine the precipitation boundary and the maximum capacity of the solvents. This analysis gives the upper and the lower limit for the  $CO_2$  loading range. The approach of this work is to determine the  $CO_2$  loading at which the first solid particle appears for a given piperazine concentration at 25 °C. It corresponds to the minimum loading value required for solid-free operation. Here it is determined using the extended UNIQUAC thermodynamic model [4-6]. Note that 25 °C is chosen as the minimum temperature and any colder condition will results in solid formation at lower loadings. In this work, the loading is defined as moles of  $CO_2$  per 1 mol of piperazine.

Table 3 shows the results for various PZ concentrations. In general the concentrations 3 molal piperazine or above will precipitate a solid. A high loading removes precipitation. This is reflected in the thermodynamic analysis which reveals how the minimum  $CO_2$  loading exponentially increases with respect to piperazine concentration. A 1.8 molal solution will not precipitate at 25 °C, while a 9 molal needs 0.42 loading or else it will precipitate piperazine.

Tuble 5. Dower and upper mint of the CO2 founds range for the FISC and the FISCE case						
Solvent concentration (mol PZ/kg water)	1.8	3	5	7	8	9
Solvent concentration (wt. %)	13.4	20.5	30.1	37.6	40.8	43.7
Minimum CO <sub>2</sub> loading at 25 °C (mol/mol)	0	0.169	0.339	0.400	0.414	0.422
Maximum rich loading - ASC at 50 °C (mol/mol)	0.833	0.808	0.804	0.796	0.792	0.781
Maximum rich loading - NGCC at 50 °C (mol/mol)	0.720	0.716	0.712	0.707	0.735	0.670

Table 3. Lower and upper limit of the CO<sub>2</sub> loading range for the ASC and the NGCC case

Furthermore, a thermodynamic analysis is carried out which shows the maximum rich loading, corresponding to an isothermal absorber at 50 °C. It is reached when equilibrium prevails in the bottom of the absorber. The value, called rich loading, is an expression of the solvent capacity. A low rich loading results in less captured  $CO_2$  and a high rich loading gives more removal of  $CO_2$  per solvent. Table 3 gives the value for both the ASC and the NGCC cases for different piperazine concentrations. It outlines that the solvent capacity (rich loading) linearly decreases with respect to the piperazine concentration. It underlines how the rich loading for the NGCC case is smaller than for the ASC case. It is approximately 0.80 mol/mol for the ASC case and it is roughly 0.70 mol/mol for the NGCC case. The decrease of the maximum rich loading is due to the lower partial pressure of  $CO_2$  in the flue gas.

There is a clear link between the piperazine concentration and the  $CO_2$  loading of the solvent for determining the solid-free operation window. The risk of clogging due to solid formation is higher in concentrated piperazine solutions. The minimum loading, to avoid solid formation above 25 °C, increases from 0 to 0.42 mol  $CO_2$ /mol PZ, when the concentration increases from 1.8 to 9 mol PZ/kg water. Basically, the solid-free loading range shrinks when increasing the piperazine concentration due to the lower maximum rich loading values. The specific ranges are smaller for the NGCC case compared to the ASC case.

#### 4.2. Effect of lean composition on L/G ratio

This section utilizes a thorough rate-based calculation strategy. It shows the importance of lean composition on the L/G ratio, required for 90 %  $CO_2$  capture. The focus is on evaluating the benefits of increasing the PZ concentration and/or decreasing the  $CO_2$  loading of the lean. The 90%  $CO_2$  capture is reached by adjusting the lean solvent flow rate. It is important to note that a higher L/G ratio results in greater pump work and it requires a wider column to keep a constant 70% of flooding.

Fig. 1A and Fig. 1B show the L/G ratio and the lean solvent flow rate at 90% CO<sub>2</sub> capture for the ASC and NGCC cases using 3, 5, and 7 molal piperazine as function of the lean CO<sub>2</sub> loading. Note that the flue gas flow rate for the ASC case is 238.46 kg/s respectively 386.33 kg/s for the NGCC case. These figures outline that both, PZ concentration and the CO<sub>2</sub> lean loading, have a great impact on the L/G ratio, independent of the flue gas source. The L/G ratio slowly increases up to 0.40 lean CO<sub>2</sub> loading, followed by a sudden rise up to 0.50 CO<sub>2</sub> load. Furthermore, Fig. 1A underlines that the L/G ratio reduces significantly when increasing the solvent concentration. An increase of the PZ content from 3 to 5 molality decreases the L/G ratio with approximately 2 units (ASC case) respectively 0.5 units (NGCC case).



Fig. 1. (A) L/G ratio at 90% CO<sub>2</sub> capture and (B) lean solvent flow rate as function of lean loading for different solvent concentrations for the ASC and the NGCC case

In addition, Fig. 1A shows that the L/G ratio is more than double for the ASC case compared to the NGCC case. However, looking at the solvent flow rate, Fig. 1B, it can be seen that, at high lean loadings, the lean solvent flow is comparable between the ASC and the NGCC scenarios. Fig. 1B underlines that the solvent flow required for 90 %  $CO_2$  capture increases suddenly from 0.40 to 0.50 loading. This sudden change in the flow rate is more visible for the NGCC case. This unexpected behavior was analyzed by Plaza et al. [24] and Darshan et al. [25]. They show how mass transfer pinch occurs at the location of the temperature bulge for intermediate lean loadings and it results in capture capacity penalties. It has to be noted that the temperature bulge is located near to the top of the column at the low lean loadings. This phenomenon can be avoided by implementing intercooling. At high lean loading, the L/G ratio is sufficiently large to reduce the magnitude of the temperature bulge. Therefore, temperature related mass transfer limitations are avoided at low and high loadings for these conditions.

Note in Fig. 1A and Fig. 1B how the lines are not drawn below approximately 0.3 and 0.4 lean loading due to precipitation issues, see Table 3.

#### 4.3. Effect of pressure on energy performance

The effect of the reboiler operating pressure on energy performance is evaluated in this section. The performance of the system is described in terms of equivalent work which shows the work lost from the turbine upstream of the power plant plus the work needed to compress the pure  $CO_2$  product stream. Thus, it contains the heat used in the stripper and the electricity needed by the compressors.

The focus is on exemplifying the correlation between pressure and equivalent work as function of piperazine concentration using the specifications of the ASC and the NGCC cases. In this analysis, the operating pressure of the reboiler is chosen (190 and 250 kPa) and the steam input to the reboiler is varied to reach 0.30 respectively  $0.42 \text{ CO}_2$  lean loading. These loadings correspond to the minimum CO<sub>2</sub> loading for solid-free operation of a 4.5 molal respectively 9 molal piperazine solution at 25 °C. Note that all of the other variables, e.g. diameter, feed flow rate, rich loading, etc. are kept constant to purely isolate the effect of pressure on the performance of the system.

The equivalent work is given by eq. (1). A typical value for the Carnot cycle efficiency with a turbine cycle efficiency of  $\eta = 75\%$  is assumed. In addition, we use  $\Delta T=5K$  temperature difference and the temperature of the sink,  $T_{sink}$ , is taken as 313 K. The compression work,  $W_{compression}$ , is estimated using the correlation from [26].

$$W_{eq} = \eta \left( \frac{T_{source} + \Delta T - T_{sink}}{T_{source} + \Delta T} \right) Q_{reboiler} + W_{compression}$$
(1)

Fig. 2 shows the equivalent work as function of solvent concentration at 190 kPa and 250 kPa for 0.30 and 0.42 loadings. The results outline the benefits of increasing the piperazine concentration. The equivalent work exponentially decreases all the way up to 7 molality for all reboiler pressures and lean loadings. Further increase of the concentration to 9 molal only leads to minor reduction of the energy demand.



Fig. 2. . Equivalent work as function of solvent concentration at 190 and 250 kPa for the ASC and NGCC cases.

In addition, this figure emphasizes that the energy demand of  $CO_2$  stripping and compression is generally lower at 0.30 loading compared to 0.42  $CO_2$  load. However, the difference between the isobars diminishes for more concentrated solutions and they overlap above 8 molality. Furthermore, this figure outlines that the equivalent work is 7 to 20% less at 190 kPa compared to 250 kPa. Based on the experience with monoethanolamine (MEA), the opposite would be expected. However the same behavior was shown experimentally by van Wagener et al. for 8 molal PZ [27].

It can be concluded that it is less energy intensive running the stripper at 190 kPa than at 250 kPa. In addition, the 5 molal piperazine case seems to be the most promising solvent since further concentrating the solvent results in minor energy improvement but exponential increase of the minimum  $CO_2$  loading due to solid formation.

#### 4.4. Effect of lean composition on energy performance

We now investigate the performance of the stripper for various operating conditions using solvents with different piperazine concentrations. The performance of the stripper is quantified in terms of specific reboiler duty (SRD), the heat (GJ) needed to strip out 1 ton of  $CO_2$ . In this analysis, the steam input to the reboiler is varied at fixed rich loading and reboiler pressure of 190 kPa. Other parameters which influence the performance of the system, e.g. pressure, height, diameter, are kept constant to isolate the effect of lean composition on the heat demand. Note that the rich loading for the ASC case is 0.8 mol  $CO_2$ /mol PZ and it is 0.7 for the NGCC case. These values correspond to the maximum rich loading. Therefore, the heat demand of the stripper may be slightly higher for integrated simulations. However, we adopt this approach to isolate the effect of the absorber from the desorber.

Fig. 3 presents the specific reboiler duty (SRD) versus the lean loading for the ASC and NGCC case using 3, 5 and 7 molal piperazine solutions. This figure highlights that the heat demand of the solvent regeneration reduces exponentially with respect to lean loading. It reduces until it reaches a minimum around 0.25  $CO_2$  loading. This minimum corresponds to the optimum operating conditions and it is reached when the water condensation balances the heat required for solvent regeneration. Below the optimum lean loading, the heat input to the stripper is too high and the excess of heat is mostly consumed by evaporation of water. Above the optimum point, the steam flow to the reboiler is insufficient and it results in a low  $CO_2$  recovery rate. This case corresponds to a low energy input system. Even though it requires a low energy input it is not feasible as seen in Fig. 3 by the higher SRD compared to the minimum.



Fig. 3. Specific reboiler duty as function of lean loading for the ASC and the NGCC case.

Furthermore, Fig. 3 demonstrates that the reboiler duty varies with respect to piperazine concentration and flue gas type. It shows how the energy demand of the NGCC case is roughly 0.7 GJ/t  $CO_2$  higher compared to the ASC case. This is due to the lower rich  $CO_2$  loading of the desorber feed.

The figure demonstrates that the 7 molal solution has the best energy performance for both cases (ASC and NGCC) and it is approximately 15 - 20 % smaller compared to the 3 molal case. The optimum lean loading and optimum SRD for 3, 5 and 7 molal solutions are shown in Table 4. The feasible SRD can be further reduced to 3.15 GJ/t CO<sub>2</sub> for the ASC case when using a 9 molal PZ solution. However, the risk of solid formation becomes considerably higher and the safe operation range shrinks to the 0.42 - 0.78 loading range. Moreover, the full benefit of highly concentrated solutions can be reached only using intercooling. A 0.18 GJ/t CO<sub>2</sub> saving seems to be insignificant compared to the capital and operational cost of an absorber with intercooling.

Flue gas source	Piperazine concentration	Optimum lean loading	Optimum SRD	Minimum lean loading	Feasible SRD	Energy penalty
	mol PZ/kg water	mol CO <sub>2</sub> /mol PZ	$GJ/ \ ton \ CO_2$	GJ/ ton CO <sub>2</sub>	GJ/ ton CO <sub>2</sub>	(%)
	3	0.221	3.855	0.169	3.854	0
ASC	5	0.242	3.389	0.339	3.519	3.7
	7	0.258	3.173	0.400	3.327	4.6
	3	0.229	4.545	0.169	4.545	0
NGCC	5	0.269	4.025	0.339	4.484	10.2
	7	0.271	3.736	0.400	4.051	7.8

Table 4. Optimum and feasible energy performance of the stripper for 3, 5 and 7 m PZ solution for the ASC and the NGCC scenario

\* Energy penalty(%) = (Feasible SRD – Optimum SRD)/ Feasible SRD · 100

It can be seen by comparing the optimum lean loading, Table 4, with the minimum lean loading, Table 3, that generally the minimum lean loading is greater than the optimum value. Note the minimum lean loading is the limit at which the first precipitate appears at 25 °C. The optimum lean loading corresponds to the best SRD, as shown in Fig. 3. For example, a 5 molal solution has an optimum lean loading of 0.24 but the minimum lean loading is 0.34. Therefore, the stripper must be operated above the optimum loading to avoid solid formation. This energy penalty is quantified as the relative difference between the feasible SRD and optimum SRD and it is given in Table 4. The feasible SRD corresponds to the specific reboiler duty in the solid-free domain. The solid free domain is above the minimum lean loading.

Table 4 shows the energy penalty for 3, 5 and 7 molal solution for the ASC and NGCC cases. It illustrates that the energy penalty is greater for the NGCC scenario. It can be seen that the lowest feasible specific duty is 3.32 GJ/t CO<sub>2</sub> and 4.05 GJ/t CO<sub>2</sub> for the ASC and NGCC case respectively. This value corresponds to the 7 molal PZ for both cases. A possible approach to expand the safe and precipitation-free domain is to assume a minimum solvent temperature (precipitation boundary) of 30 °C. However, additional heating of the storage and buffer tanks and appropriate control structures are needed. Operational challenges may appear especially in Nordic countries or during winter. However, a greater minimum solvent temperature allows the operation of the plant at 3.13 GJ/t CO<sub>2</sub> respectively 3.74 GJ/t CO<sub>2</sub> reboiler duty for the ASC and NGCC cases.

### 5. Conclusions

This work shows a systematic evaluation of a  $CO_2$  post-combustion capture process for 1.8, 3, 5, 7, 8, and 9 molal piperazine solutions. It shows the results for two flue gas sources: an advanced supercritical pulverized coal power plant (ASC) with 13.25 %  $CO_2$  and a natural gas combined cycle power plant (NGCC) with 3.90 %  $CO_2$ . The results are created using the hybrid CAPCO2 in-house rate-based model for  $CO_2$  absorption and desorption. This model takes into account precipitation of piperazine in the description of mass transfer and in the calculation of the

equilibrium composition. They are determined using the extended UNIQUAC thermodynamic model. The mass and heat transfer fluxes are described in a film-theory approach, using the General Method (GM) enhancement factor model. This model is valid for both absorption and desorption conditions.

This study shows the optimum PZ concentration,  $CO_2$  loading and the corresponding solvent flow rate. It underlines that the L/G ratio and the reboiler duty strongly depend on the piperazine concentration and  $CO_2$  loading. Furthermore, it underlines that the energy demand of the process is a strong function of  $CO_2$  partial pressure of the flue gas due to the decrease of the solvent capacity (maximum rich loading). Higher partial pressure gives a greater maximum rich loading corresponding to greater solvent capacity. Furthermore, we demonstrate how the value of the rich loading greatly influences the performance of the stripper and it is an important criterion for the design of an absorber. A rich loading of 0.70 mol  $CO_2$ /mol PZ, corresponding to NGCC case, gives 0.7 GJ/t  $CO_2$  higher energy demand compared to a 0.80 rich loading, ASC case. Other important parameter for the performance of the system is the operating pressure of the reboiler. The simulations show how a greater pressure results in higher energy demand, especially at lower  $CO_2$  lean loading and piperazine concentration. The effect of pressure on energy demand diminishes when increasing the piperazine concentration above 7 molal.

This analysis demonstrates that the 7 molal solution has the best energy performance for both cases (ASC and NGCC) and it is approximately 15 - 20 % smaller compared to the 3 molal case. The lowest feasible specific reboiler duty can be reached at 0.40 CO<sub>2</sub> lean loading: 3.32 GJ/t CO<sub>2</sub> and 4.05 GJ/t CO<sub>2</sub> for the ASC case and NGCC cases. The analysis also reveals that the capture process needs to be operated up to 7.8 % above the minimum duty to avoid the risk of clogging due to solid formation. Note this analysis assumes a 25 °C minimum solvent temperature. The energy requirement of the capture process can be further improved by assuming a greater minimum temperature when the reboiler duty lowers to 3.17 GJ/t CO<sub>2</sub> (ASC case) and 3.73 GJ/t CO<sub>2</sub> (NGCC case). However, it may require additional heating of storage tanks and more complex control structure, especially in coldwinter conditions. The energy demand of stripping reduces to 3.15 GJ/t CO<sub>2</sub> for coal based cases when using a 9 molal solution and absorber with intercooling. However, the solid-free operation window of this system is significantly smaller compared to the 7 molal solution.

The SRD calculations performed in this work are deliberately based on process calculations without any particular optimization or heat integration in mind. This is purely set up with the strategy to perform a basic comparison of the process conditions, without too much interference from other types of optimization. There is still at great potential for further decreasing the SRD by more advanced heat integration. The local design optima found in this work will most likely remain optima in more advanced heat integration scenarios.

Since implementation of  $CO_2$  capture in a coal-fired power plant will introduce significant capital and operating cost, other process configurations as well as dynamic-optimal scheduling of a capture process should also be studied. This study provides the base to build on by emphasizing the benefits and drawbacks of piperazine for the relevant operating process conditions.

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