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Absorption of $CO_2$by Amine Blends Solution: An Experimental Evaluation

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ABSTRACT: Carbon capture and storage (CCS) using post-combustion technology is the most mature CO_2 capture technology. Post-combustion process reference is based on the absorption/desorption process with a solution of monoethanolamine (MEA) 30wt% in water. However, this benchmark molecule has some drawbacks and especially the high regeneration energy which is around 4 GJ/ton CO_2. For this reason, there is a need to innovate and optimize solvents for CO_2 capture in order to minimize the regeneration energy and to improve the solvent capture efficiency. The choice of the promising molecules depends on many physical and chemical characteristics (like absorption capacity, kinetics reaction between amine, reaction enthalpy and solvent stability and toxicity). This work focuses on the absorption capacity and the reaction rates of single and blended amines. Five commercially available amines with 30wt% and 50wt% concentrations in water (monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), 2-amino-2-methylpropanol (AMP) and piperazine (PZ)) were screened experimentally based on equilibrium CO_2 absorption capacity and CO_2 absorption rate data; the results show that experimental data for single amines are in good agreement with literature values. From the solvent combinations, four piperazine-based blends show strong indication of better performance than 30wt% MEA reference. These are:
- 10wt%-MEA/20wt%-PZ
- 10wt%-DEA/20wt%-PZ
- 10wt%-AMP/20wt%-PZ
- 10wt%-MDEA/20wt%-PZ

10wt%-DEA/20wt%-PZ system shows the highest rate of 1.68mmol/mol-s with 0.88mol_{CO2}/mol_{amine} capacity while 10wt%-AMP/20wt%-PZ blend recorded the highest CO_2 absorption capacity of 0.99mol_{CO2}/mol_{amine}. 10wt%-DEA/20wt%-PZ and 10wt%-AMP/20wt%-PZ blends are respectively75% and 98% higher than CO_2 absorption capacity of 0.50mol_{CO2}/mol_{amine} for 30wt% MEA. Also, these blends are respectively 54% and 34% higher than CO_2 absorption rate of 1.09mmol/mol-s for 30wt% MEA. Equilibrium solubility data for 10wt%-AMP/20wt%-PZ blend is higher twice than the cyclic loading capacity reported for 30wt% MEA reference under CO_2 partial pressure of 12kPa. This experimental work showed that solvents with high performance can be obtained through amine blends. This will be of importance towards improving the post-combustion capture technology.

KEY WORDS: monoethanolamine, piperazine, CO_2 absorption capacity, CO_2 absorption rate

I. INTRODUCTION

Carbon dioxide (CO_2) is the most principal greenhouse gases emitted in comparison with the other greenhouse gases. In the future, the concentration in the atmosphere will increase and CO_2 will continue to pose significant danger to the climatic system [1]. Many solutions are realized or investigated to trap carbon dioxide. Post-combustion CO2capture technology is the most mature solution. It is based on absorption through chemical absorbents. Chemical absorption is suitable to capture CO_2 from gases which are highly diluted (~ 10-15%). Absorption with amine-based solvents has been extensively studied and regarded as the most effective technology for CO2 capture [2, 3]. Amine-CO_2 reaction can be reversed by increasing the temperature. CO2 capture is based on using various alkanolamines solutions like monoethanolamine (MEA), N-methyldiethanolamine (MDEA), Diethanolamine (DEA) or 2-amino-2-methyl-1-propanol (AMP). Primary, like MEA, and secondary amines, like DEA, have a high kinetics reaction with CO_2 and high regeneration energy. Tertiary amines, like MDEA, have a high CO_2 loading capacity, a low regeneration cost and low reaction kinetics with CO_2. There is another kind of amine which is called sterically hindered amine, like AMP, which has the same characteristics than tertiary amine (high CO_2 loading capacity). The benchmark amine, 30wt% MEA solution, has a good characteristics reaction with CO_2. Indeed, this amine reacts rapidly with CO_2 and has

a high CO_2 absorption capacity. However, its commercial deployment is still limited by a number of techno-economic factors as discussed elsewhere [4-8].

The high energy requirement for the MEA solvent regeneration is the main drawback of this technique. Many alternatives to MEA have been reported in literature like the use of physical absorbents, membranes, cryogenic. Also, the main challenge for post-combustion capture technology is to prospect new amine solvents performance. Many characteristics should to be evaluated to look for an optimal solvent. Ideal solvent will have a high absorption capacity and low regeneration energy (especially low absorption enthalpy). Research should be directed towards development and characterization of new solvents based on these key properties. In our study, we focus on amine blends where the combination of amine with high CO_2 loading capacity and amine with high reactivity with CO_2 will be a solution to decrease the drawbacks of MEA reference. These will provide better absorption characteristics than monoethanolamine (MEA). Blending amines belonging to various classes such as tertiary, primary, secondary amines, sterically hindered and cyclic amines have been shown to have better absorption properties than MEA alone [9-14]. For example, absorption capacity of MEA and 2-amino, 2-methylpropanol (AMP) blend is significantly higher than the stoichiometric limit of 0.5 mole of CO_2 per mole of MEA. This improvement observed in absorption properties for such amine blends has been attributed to the synergistic effect of high CO_2 reaction kinetics of primary amine and the high CO_2 absorption capacities of sterically hindered amines [10-12, 15].Also, another amine, piperazine (PZ) which contains two primary nitrogen, has been reported as a new reference solvent of prime importance for amine blends. The rate of piperazine is raised twice than 30wt% MEA under similar experimental conditions with negligible amine volatility, suitable carbamate stability constant and significantly lowers thermal degradation [16-18]. It is also expected to have good absorption capacity in addition to its CO_2 absorption rate.

Specifically, the subjects of many research works on amine blends are aimed at understanding the enhancement rate of lower MEA and low PZ concentrations in relatively higher concentrations of other classes of amines(usually at 30% total mass concentrations) [6, 19-23]. However, this study extends the above experiments by considering low, equal and high concentrations of two solvents involved in the blends using 30% and 50% total mass concentration. The objective is to identify promising blends based on the equilibrium CO_2 absorption capacities and CO_2 initial absorption rates using solvent screening approach.

II. MATERIALS AND EXPERIMENTAL METHODS

2.1 Chemical and solvent preparation

Monoethanolamine (MEA≥99%), diethanolamine (DEA=99%), methyldiethanolamine (MDEA≥99%), 2-amino-2-methylpropanol (AMP≥99%) and Piperazine (PZ=99%) were all purchased from Sigma Aldrich. Amines are used based on the given purity values by the supplier. Amine blends are prepared without any purification or further validations of the amine blends concentrations. The solvents evaluated through experiments are listed in Table 1 with their respective concentrations. All amines were chosen to represent various classes of amine. 30wt% concentration basis was used for all Piperazine blends due to observed precipitation at higher concentration. Other classes of amines were evaluated at 50wt% concentrations in order to benefit from their low corrosivity, low volatility and to enhance their performance. 30wt% MEA concentration was used as reference for comparing the experimental results. Each sample was prepared by using Cole Parmer mass balance with ±0.01% accuracy using the corresponding weight. CO_2 (≥99.5%) and N_2 (≥99%) were used to simulate the flue gas at specific CO_2 partial pressure for the experimental works.

Table 1: Amines and their concentrations

Solvent	Concentration (wt. %)
MEA	30
DEA	50
MDEA	50
Piperazine	30
MEA/MDEA	10/40; 25/25; 40/10
MEA/AMP	10/40; 25/25; 40/10
MEA/Piperazine	10/20; 15/15; 20/10
DEA/MDEA	10/40; 25/25; 40/10
DEA/AMP	10/40; 25/25; 40/10
DEA/Piperazine	10/20; 15/15; 20/10
AMP/MDEA	10/40; 25/25; 40/10
AMP/Piperazine	10/20; 15/15; 20/10
MDEA/Piperazine	10/20; 15/15; 20/10

2.2 Experimental set-up

2.2.1 Solvent screening experimental set-up

Figure 1 shows the schematic illustration of the experimental set-up. The solvent screening set-up is bench-scale laboratory equipment which is made up of six batch process reactors, enabling multiple investigations of solvents at the same time. Carbon dioxide and nitrogen gases are mixed and humidified to simulate gas stream of desired partial pressure. The CO_2 inlet partial pressures are measured by a pressure sensor calibrated at 100 kPa and working in the CO_2 pressure range of 0-20kPa with ±2% accuracy. The absorption characteristics are estimated based on time and CO_2 outlet partial pressures. A desktop computer equipped with signal processing capability automatically acquires the electrical data from the sensors. It converts the electrical data to CO_2 outlet pressure and generates time-pressure data. Due to the capacity limit of 20% CO_2 partial pressure of the sensors and the desire to work at flue gas stream pressure of 100kPafor a typical coal-fired power plant, the maximum CO_2 pressure evaluated in the experiments is 20kPa.

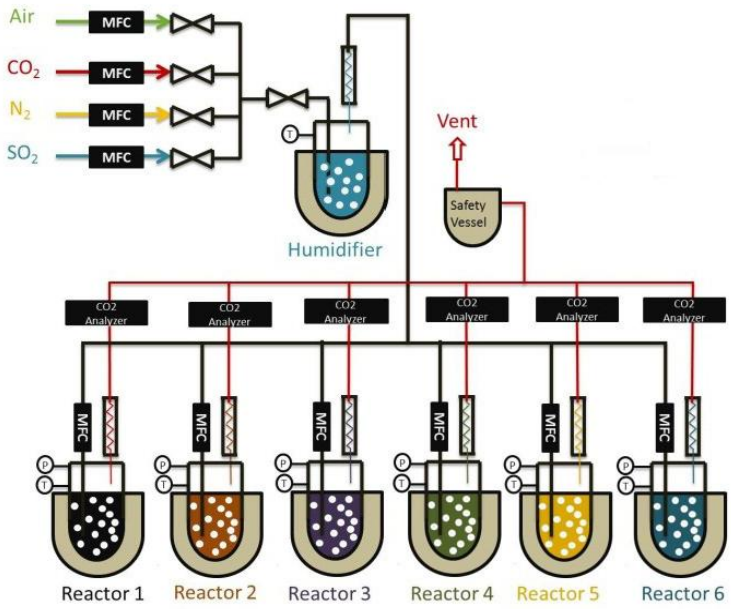

Figure 1: Schematic representation of solvent screening experimental set-up

2.2.2 CO_2 equilibrium solubility experimental set-up.

The CO_2 equilibrium solubility experimental set-up is used to obtain vapour-liquid equilibrium (VLE) data. It is essentially similar to the solvent screening apparatus but with a larger solvent capacity and higher operational for temperature and gas pressure. The volumetric size is 500ml with a 3000 rpm mixing capacity. Its temperature range is from 20°C to 200°C and operational pressure range of 10kPa to 1000kPa. This wider range of operation conditions allow for solubility data generation and absorption capacity evaluation at different temperatures and CO_2 partial pressures.

2.3 Procedure

2.3.1 Solvent screening and vapor-liquid equilibrium methods

Preparation of 100g of solution for every single amine and amine blend was transferred into the batch reactors using deionized water. Each reactor has an oil bath coupled with a 1200±10rpm magnetic stirrer. The magnetic stirrer is used to maintain perfect mixing of solution by creating a uniform central vortex. Each reactor has a volumetric capacity of 250ml, with a temperature limit of 150±1°C and a pressure limit of 600±10kPa. A continuous stream of pure nitrogen gas was passed through each reactor to strip off any CO_2 or oxygen that might be present in the air space above the solvent. The temperature of the oil bath was set at higher temperature than the reaction set point. The higher oil bath temperature ensures sufficient heat transfer to maintain the reactor at the set experimental conditions. The oil bath has a temperature accuracy of ±1.0°C.Humidified inlet simulated flue gas stream is bubbled through the solvent by a stainless steel gas distributor with 0.5mm internal diameter. Only CO_2 (≥99.5%) and N2 (≥99%) pure gas streams are used for the flue gas simulation (i.e. no air or sulfur dioxide gas streams in the flue gas). The CO_2 gas flow rate is kept at 12kPa using flow rate of 12.0±0.1 L/hr, with N_2 gas flow rate of 88.0±0.1 L/hr with a total gas stream pressure of 100kPa. All sensors provide real-time measurements.

Also, sufficient gas pressure must be built in the make-up vessel to ensure equal and continuous flow of gas streams into all reactors. Depending on the absorption properties of the solvents, gas stream leaving the solvent after reaction with amine solution will have lower CO_2 concentration compared to the inlet gas stream. The outlet gas stream flowed through a condenser operating at 8°C in order to prevent solvent loss. Real time experimental data were logged on the computer. The solvent absorption process is said to reach equilibrium when the outlet CO_2 partial pressure equals the inlet CO_2 partial pressure and the pressure maintained constant over a time period. This pressure is taken as the gas phase CO_2 partial pressure which is in equilibrium with the liquid state. The VLE experimental method is similar to the solvent screening procedure.300g of solvent was prepared and transferred into the reactor. Gas stream consisting of carbon dioxide with partial pressure of 10kPa, 12kPa and 20kPa in nitrogen was used. The experiment was repeated for 40°C and 120°C, corresponding to absorption column and stripper temperature in a typical post-combustion capture.

2.3.2 Phosphoric acid titration methods

Liquid phase loaded with CO_2 at partial pressure equilibrium obtained from solvent screening and CO_2 equilibrium solubility experimental set-ups is analyzed to determine absorption capacity value. Titration method with 85% phosphoric acid concentration is used. The phosphoric acid titration set-up is illustrated schematically in Figure 2. It consists of a round-bottom reactor flask which is filled with 350ml of 85% phosphoric acid solution and placed in a heating mantle fitted with temperature regulator. At a constant heating mantle temperature of 240±2°C, the phosphoric acid in the round bottom flask can be maintained at 150±2°C. This supplies the needed heat for the endothermic desorption process of carbonated amines with phosphoric acid towards CO_2. Nitrogen is needed for dilution and as a sweeping gas for analyzing CO_2concentration in the carbonated amine from either the solvent screening or vapor-liquid equilibrium set-ups. The top-central opening of the set-up is fitted with a condenser, kept at 8°C to remove water vapor content before carbon dioxide gets to the CO2 infrared analyzer.

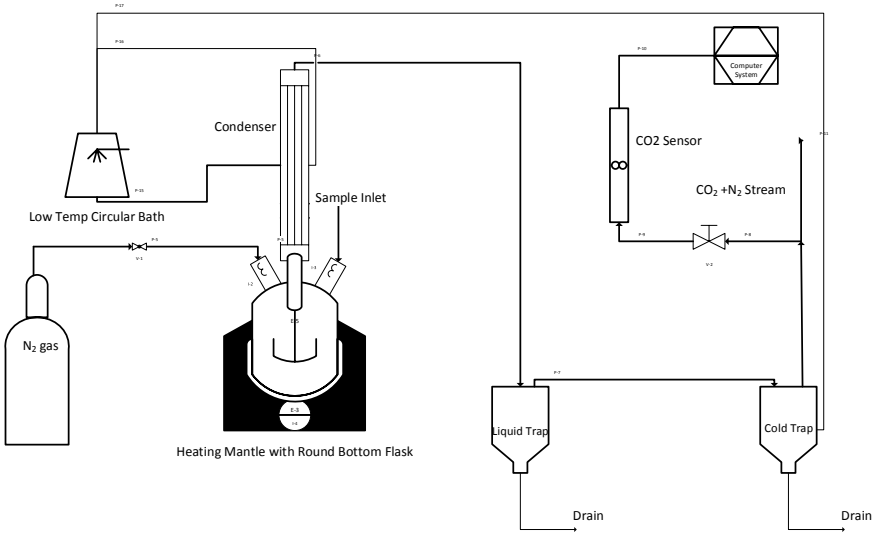

Figure 2: Schematic diagram of phosphoric acid titration set-up

The CO_2 concentration obtained from the infrared gas analyzer and gas flow rate are then logged on the computer system for analysis. Samples from solvent screening and vapor-liquid equilibrium experiments are introduced into the set-up. CO_2 desorption from the amine is as a result of the esterification reaction between boiling phosphoric acid and amine, forming either phosphoric ester complexes at elevated temperature. This is illustrated in the general chemical reaction as given in equation 1 where R1 and R2 can be any alkyl groups. The CO_2 evolved is carried in a nitrogen stream through a condenser to an infrared CO_2 analyzer which detects and records changes in voltage. The resulting voltage peaks are correlated automatically to CO_2 partial pressure. The CO_2 mole dissolved is obtained using the CO_2 partial pressure data that are logged automatically on the computer system using ideal gas equation. With the mass of carbonated amine sample, M_{amine}, introduced into the phosphoric acid solution, the molecular weight of the amine blend, M_W blend, the volume of the CO_2 desorbed logged on the computer, V_{CO2}, and the molar volume of ideal gas, M_{VGa}s, the absorption capacity of the solvent under equilibrium condition is obtained by dividing the obtained CO_2 mole with the mole of amine used as given in equation 2.

$$PO_4^{3-} + n(R_1R_2N^+COO^-) + N_2 \rightarrow [(R_1R_2N^+)_nPO_4^{3-} + nCO_2 + N_2 \quad (1)$$

$$\alpha_{CO2} = \left(\frac{{}^{V_{CO2}}/_{MV_{Gas}}}{{}^{M_{amine}}/_{MW_{blend}}} \right) \quad (2)$$

III. RESULTS AND DISCUSSION

3.1 Individual solvent

Solvent screening experiments were performed for blends containing MEA, DEA, MDEA, AMP and piperazine. Performance output parameters evaluated are the CO_2 equilibrium absorption capacities and the CO_2 initial absorption rates. This work considered blending systems of two amines solvent. The concentration of each amine was expected to be critical parameters in determining the absorption rate and capacity. Other parameters that might influence the absorption characteristics are reaction temperature, total gas pressure and CO_2 partial pressure. In this case, these different parameters were kept constant. Therefore, performance in the CO_2 absorption capacities and the CO_2 initial absorption rates will be affected by the variation of concentrations of the blends amines systems. Reactor temperature was kept at 40°C with total gas pressure of 100kPa (CO_2 partial pressure was 12kPa). Results for single amines evaluated are presented in Table 2. The absorption capacity data are found to be of ±0.05 in experimental error. AMP was not studied because of coagulation at concentrations equal or above 30wt% under the experimental conditions.

The mentioned single amines are considered as reference data to compare the performance of the solvent blends. Value of absorption capacity of MEA is consistent with literature where it is between 0.5 molCO_2/mol amine and 0.6 molCO_2/mol amine for 12kPa CO_2 partial pressure [24-26]. Experimental data for Piperazine and MDEA also are in good accordance with literature as mentioned in Table 3. For all amines presented in Table 2, 30wt% Piperazine showed the highest CO_2 absorption capacity with 1.06molCO_2/mol amine. This is about 66% higher than 30wt% MEA reference. Piperazine is a diamine with two nitrogen atoms per molecule. The presence of these two nitrogen atoms was found to double its CO_2 uptake in comparison to MEA with one nitrogen atom per molecule. Absorption capacity of 50wt% DEA-based solvent, which is a secondary amine, outperformed 30wt% MEA. This result can be explained by the difference of amine concentration and structural effect. MDEA showed the lowest CO_2 absorption capacity for CO_2 partial pressure applied here. Since there is no hydrogen atom attached to the amino group on MDEA, there cannot be a direct reaction between MDEA and CO_2. This structural property reduces the function of MDEA to a base catalyst, which enhances the formation of bicarbonate through hydration reaction of water and CO_2 [25]. Also, the lower absorption capacity is due to the fact that CO_2 absorption in MDEA is greatly influenced by the CO_2 partial pressure in the stream. Significant CO_2 absorption will only be obtained in a gas stream with high CO_2 partial pressure [25]. It is also noted that the breakthrough curve for 50wt% MDEA deviated from the maximum value of 1 for the CO_2 output/CO_2 input pressure ratio. This observation implied that the desorption rate is faster than the absorption rate as the equilibrium state is approached at constant CO_2 partial pressure and temperature.

Table 2: Solvent screening results for amines at 40°C and 12kPa CO_2 pressure

Solvent	Concentration	Absorption Capacity mol_{CO2}/mol_{amine}	Absorption Rate mmol/mol.s
MEA	30wt%	0 .50	1.09
DEA	50wt%	0.63	0.74
MDEA	50wt%	0.38	0.04
PZ	30wt%	1.06	1.81

Table 3: Equilibrium absorption capacity results in comparison with literature

Solvent	Concentration	This work mol_{CO2}/mol_{amine}	literature mol_{CO2}/mol_{amine}	reference
MEA	30wt%	0 .50	0.50-0.60	[25]
MDEA	50wt%	0.38	0.30-0.40	[33]
PZ	30wt%	1.06	0.90-1.00	[34]

CO_2 output/input concentration profile is believed to give good indications of solvent reactivity [27] and was used to evaluate the initial absorption rate of the amines. CO_2 absorption rate was evaluated using the slope of the absorption curve from the CO_2 output/input concentration profile. The slope of the breakthrough

curve gives the initial CO_2 absorption rate as established in literature [28, 29]. The absorption curves from the solvent screening data for the amines at 40^0C and CO_2 partial pressure of 12kPa are plotted in Figure 3. The absorption rate data are found to be of ±0.5 in experimental error. From Figure 3, MDEA have the lowest reaction rate in comparison with the others amines and his absorption curve is almost horizontal. For 50wt% MDEA absorption curve, the CO_2 partial pressure in the output stream was very high at the beginning of the experiment. This implied that less amount of CO_2 was absorbed by MDEA. As a result of its poor reaction kinetics and the dependence of its performance on high CO_2 partial pressure in the inlet gas stream. The CO_2 absorption rate value is 0.04 mmol/mol-s. In comparison, 50wt% MDEA rate is 28.59 times slower than 30wt% MEA and 47.50 times slower than 30wt% Piperazine. However, 30wt% Piperazine shows complete absorption of all CO_2 in the inlet gas stream at the start of the experiment. It also produced a consistently steep and smooth absorption curve. From Table 2, 30wt% Piperazine has the highest rate with value of 1.81mmol/mol-s. It is 1.66 times higher than 30wt% MEA. However, 30wt% MEA, a primary amine, was found to be 1.47 times more reactive than DEA, a secondary amine, as expected.

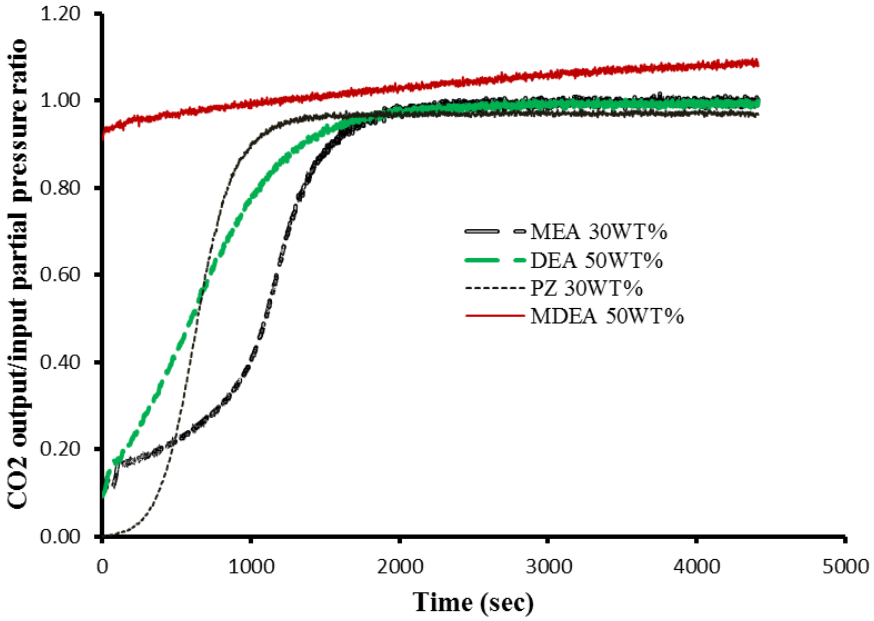

Figure 3: Absorption curve for amines at 40°C and 12 kPa CO_2 pressure

3.2 Amine blend

Table 4 provides data on the equilibrium absorption capacities of all blends evaluated at 40°C and 12kPa CO_2 partial pressure. Results of the experiments for blends with 40wt% AMP could not be obtained due to the coagulation of AMP under the experimental conditions. It is found that blends involving Piperazine at 20wt% concentration have better absorption capacities than other evaluated combinations. This shows that Piperazine are benefiting because of the presence of two nitrogen atoms in the molecule which increase the CO_2 loading. AMP, as a sterically hindered amine, and MDEA, as a tertiary amine, in combination with Piperazine shows the highest absorption capacities among all the blends. This is consistent with expectations with respect to the sterically hindered amine and tertiary amines which involve bicarbonate formation.

Table 4: Equilibrium absorption experiment results for amine blends at 40°C and 12kPa CO_2 pressure

Amine blend	Concentration	Absorption Capacity mol_{CO2}/mol_{amine}
DEA/MDEA	10wt%/40wt%	0.52
DEA/MDEA	25wt%/25wt%	0.50
DEA/MDEA	40wt%/10wt%	0.61
MDEA/PZ	10wt%/20wt%	0.92
MDEA/PZ	15wt%/15wt%	0.92

MDEA/PZ	20wt%/10wt%	0.74
DEA/PZ	10wt%/20wt%	0.88
DEA/PZ	15wt%/15wt%	0.85
DEA/PZ	20wt%/10wt%	0.79
MEA/PZ	10wt%/20wt%	0.75
MEA/PZ	15wt%/15wt%	0.73
MEA/PZ	20wt%/10wt%	0.69
MEA/MDEA	10wt%/40wt%	0.69
MEA/MDEA	25wt%/25wt%	0.73
MEA/MDEA	40wt%/10wt%	0.69
MEA/AMP	10wt%/40wt%	0.57
MEA/AMP	25wt%/25wt%	0.59
MEA/AMP	40wt%/10wt%	0.74
DEA/AMP	10wt%/40wt%	-
DEA/AMP	25wt%/25wt%	0.66
DEA/AMP	40wt%/10wt%	0.60
AMP/PZ	10wt%/20wt%	0.99
AMP/PZ	15wt%/15wt%	0.90
AMP/PZ	20wt%/10wt%	0.92
AMP/MDEA	10wt%/40wt%	0.65
AMP/MDEA	25wt%/25wt%	-
AMP/MDEA	40wt%/10wt%	-

Results from solvent screening absorption rate are evaluated for all blends involving MEA, DEA and MDEA. Data are compared with 30wt% MEA reference. Figure 4, Figure 5 and Figure 6 present the absorption rate results based on performance of all blends. MEA/piperazine blends performed better than 30wt% MEA as shown in Figure 4. However, MEA/AMP and MEA/MDEA blends have lower rates than 30wt% MEA under all concentrations considered. This is essentially due to the less reactive nature of AMP and MDEA with CO_2. Therefore, the combination of MEA with AMP and MDEA leads to a trade-off between the reaction rate and absorption capacity when compared to MEA at equal concentration. MEA will give higher CO_2 absorption reaction rate and lower CO_2 absorption capacity than MEA/AMP and MEA/MDEA blends.

From Figure 5, DEA/PZ blend has the highest kinetics among all blends involving DEA. 30wt% MEA is found to outperform 50wt% DEA. CO_2 absorption rate is dependent on the chemical nature of a solvent as well as its concentration. 30wt% MEA shows higher rate than all other blends except for DEA/PZ blend. Piperazine is able to kinetically activate DEA as evident in the reaction rate. However, kinetic activation by DEA in DEA/MDEA and DEA/AMP blends is not of significant impacts on reaction rate. The authors also found that higher rate is measured for DEA/AMP blends in comparison to DEA/MDEA blends, except at 40wt% DEA in 10wt% MDEA. This is attributed to the higher reactivity of AMP. For all MDEA-containing blends, 30wt% MEA is better in terms of CO_2 absorption reaction rate. Though MDEA/Piperazine blends shows better reactivity at 15wt% and 20wt% Piperazine composition, the poor reactivity of MDEA led to MDEA 20wt%/piperazine-10wt% blend having lower rate value of 1.04mol/mol-s while 30wt% MEA recorded 1.09mol/mol-s.

With a focus on both absorption rate and capacity, four promising blends amines have been selected: 10wt%-MEA/20wt%-PZ

10wt%-DEA/20wt%-PZ
10wt%-AMP/20wt%-PZ
10wt%-MDEA/20wt%-PZ

10wt%-DEA/20wt%-PZ blend showed the highest rate of 1.68mmol/mol-s with 0.88mol/mol capacity. However, its CO_2 absorption capacity is significantly lower than MEA/PZ blend with a value of 0.75. In terms of absorption rate, there is no significant difference between 10wt%-MEA/20wt%-PZ and 10wt%-DEA/20wt%-PZ blends.10wt%-AMP/20wt%-PZ blend has the highest CO_2 absorption capacity of 0.99mol/mol and a relatively high rate of 1.47mmol/mol-s which is 87.3% of DEA-10wt%/PZ-20wt% blend (the blend with the highest overall rates). Therefore, 10wt%-AMP/20wt%-PZ blend could be regarded as the most promising blend among the Piperazine-containing blends evaluated.

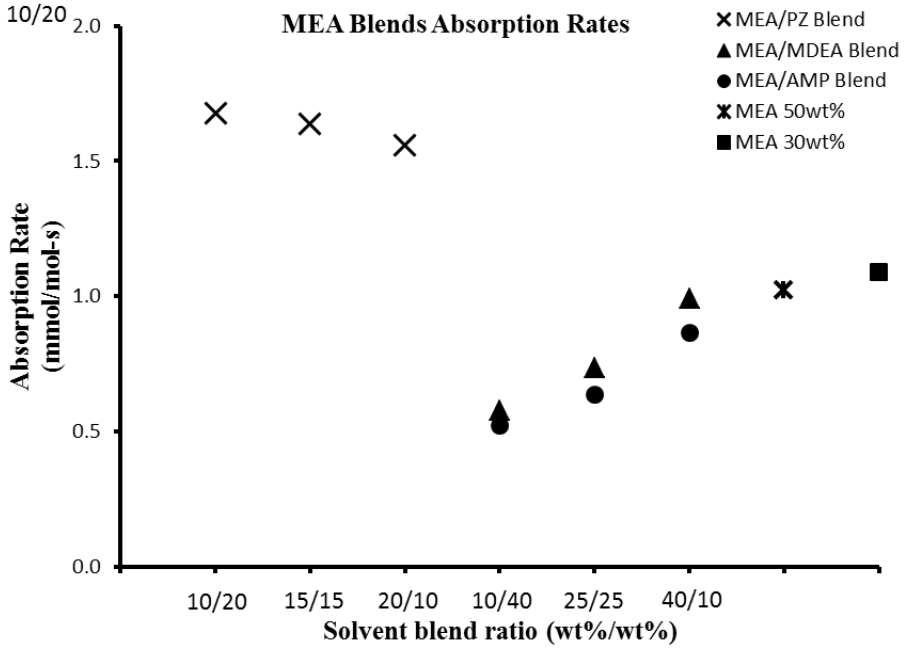

Figure 4: Plot of absorption rates for all MEA blends

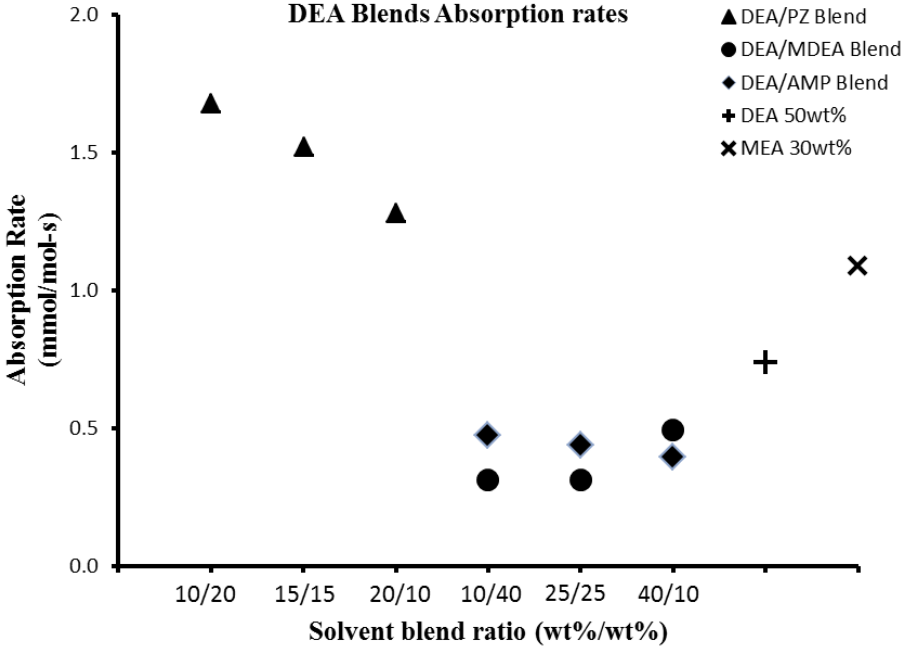

Figure 5: Plot of absorption rates for all DEA blends

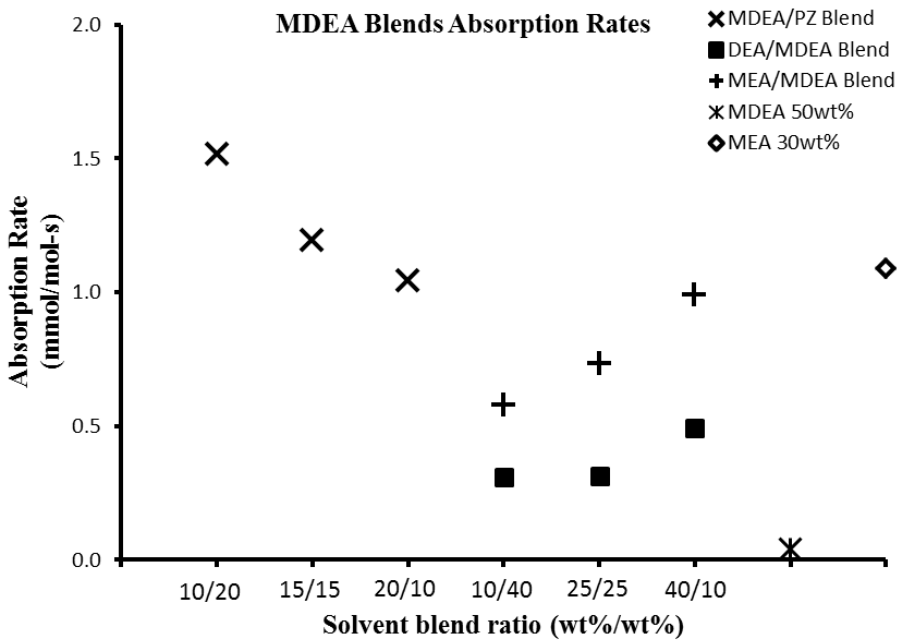

Figure 6: Plot of absorption rates for all MDEA blends

Figure 7 shows a comparison of the absorption capacity results of 30wt% Piperazine with the four promising blends and the single amines is done and a comparison of absorption rate results are shown in Figure 8. Absorption capacity results shows that 30wt% piperazine have the better performance with rate of 1.81mmol/mol-s which is about 8% faster than DEA-10wt%/PZ-20wt% blend (which have the highest rates among the blend evaluated). In addition, stand-alone 30wt% piperazine has CO_2 absorption capacity of 1.06mol/mol. This value is also higher than that of 10wt%-AMP/20wt%-PZ blend (the blend with the highest capacity among the solvent list evaluated).Though 30wt% piperazine outperformed all single amines studied here, the promising blends of 20wt% piperazine with 10wt% MEA, 10wt% DEA or 10wt% AMP can be good substitutes for the 30wt% piperazine based on their relatively high rates and capacities. This is due to precipitation in high concentration of piperazine.

Also, the proportion of MEA, DEA or AMP can be increased to 20wt% composition with 20wt% piperazine to obtain 40wt% total amine concentration. Such increase of the second amine concentration in blends with piperazine is expected to give improved results. However, increasing piperazine concentration to 40wt% poses precipitation challenges at the experimental conditions.

Furthermore, the CO_2 solubility data for 10wt%-AMP/20wt%-PZ blend (taken as the most promising system) at total gas pressure of 100kPa with CO_2 partial pressure between 10 and 20 kPa is measured. The result is presented in Table 5 with rich loadings obtained at 40°C and lean loadings at 120°C. As expected, lean and rich loading increased with higher CO_2 pressure, rising by about 112% and 56% for 20kPa in comparison with 10kPa respectively. Also, another important thermodynamics property is the cyclic capacity. It is the difference between the rich and lean loading (mole of CO_2/mole of amine) and provides the performance of amine solution for CO_2 capture. Results show that cyclic capacities of 10wt%-AMP/20wt%-PZ blend at 12 and 20kPa partial pressures are twice the average reported value of 0.24molCO_2/molamine for 30wt% monoethanolamine at similar CO_2 partial pressure [30-32]. So, within the range of CO_2 partial pressure for coal-fired power plants, 10wt%-AMP/20wt%-PZ blend is a promising system for CO_2 capture. Further works on enthalpy and excess enthalpy characterizations, thermal solvent regeneration requirement and degradation are ongoing. The conclusions of such further experimental works will determine the suitability of the 10wt%-AMP/20wt%-PZ blend for post-combustion capture applications.

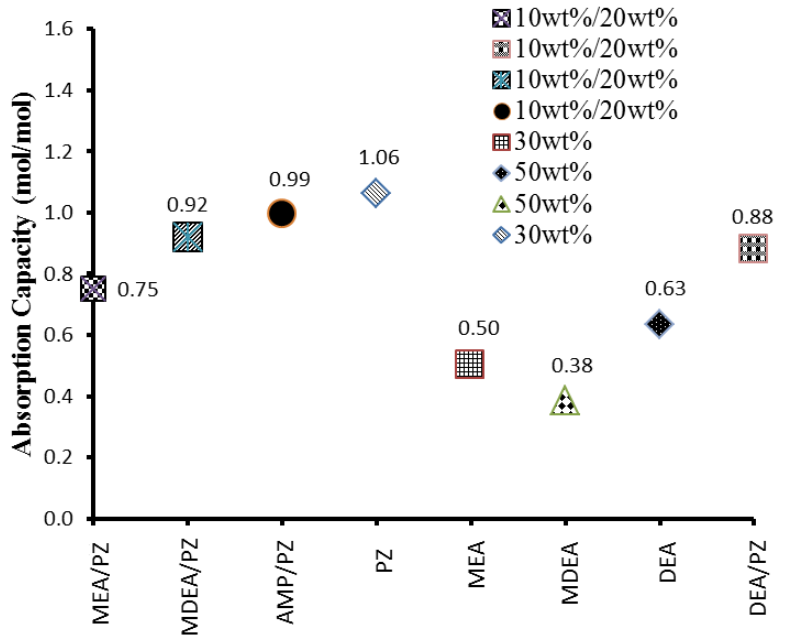

Figure 7: Absorption capacity values of the four promising blends in comparison to single amines

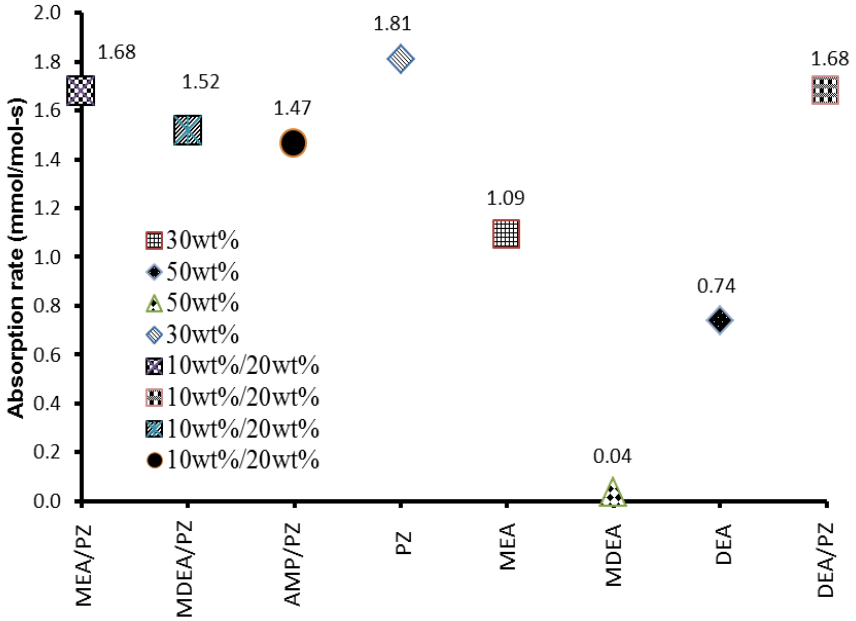

Figure 8: Initial absorption rates of the four promising blends in comparison to single amines

Table 5: Vapour liquid equilibrium data for AMP/PZ (10/20wt%) blends

CO_2 Partial Pressure kPa	Rich Loading (at 40°C) mol_{CO2}/mol_{amina}	Lean Loading (at 120°C) mol_{CO2}/mol_{amine}	Cyclic Loading mol_{CO2}/mol_{amine}
10	0.78	0 .34	0.44
12	0.99	0.51	0.48
20	1.22	0.72	0.50

IV. CONCLUSION

This research work considered the evaluation and characterization of amine blends-CO_2-H_2Osystems for CO_2 post-combustion capture. The objective was to evaluate amine blends as potential sorbent to finding the most promising systems for CO_2 post-combustion capture. Five solvents covering various and relevant classes of amine (MEA, DEA, AMP, MDEA and piperazine) are blended. Then, they were screened experimentally using CO2 absorption capacity and CO2 absorption rate as the output parameters under total gas pressure of 100kPa (with CO2 partial pressure of 12kPa) and temperature of 40°C (temperature in the absorber). Through the results, four promising blends were identified which outperformed other blends and 30wt% MEA reference:

10wt%-MEA/20wt%-PZ
10wt%-DEA/20wt%-PZ
10wt%-AMP/20wt%-PZ
10wt%-MDEA/20wt%-PZ

10wt%-DEA/20wt%-PZ blend showed the highest rate of 1.68mmol/mol-s with 0.88 mol_{CO2}/mol_{amine} capacity while 10wt%-AMP/20wt%-PZ blend recorded the highest absorption capacity of 0.99 mol_{CO2}/mol_{amine} with rate of 1.47mmol/mol-s. As indication, absorption capacity for 30wt% MEA reference is $0.50mol_{CO2}/mol_{amine}$ and absorption rate is 1.09mmol/mol-s. Furthermore, equilibrium solubility data for 10wt%-AMP/20wt%-PZ blend is twice higher than the cyclic loading capacity reported for 30wt% MEA reference under CO_2 partial pressure of 10kPa to 20kPa. This portends that there are great potentials in piperazine-containing blends. In summary, these experimental results have shown that novel solvent development through amine blends can play significantly role towards the deployment of post-combustion capture technology.

REFERENCES

[1] IPCC. IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change [Metz, B.,O. Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.)]. Cambridge University Press, in, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2005, pp. 442.

[2] A.B. Rao, E.S. Rubin, A technical, economic, and environmental assessment of amine-based CO_2 capture technology for power plant greenhouse gas control, Environmental science & technology, 36 (2002) 4467-4475.

[3] B. Mandal, A. Biswas, S. Bandyopadhyay, Absorption of carbon dioxide into aqueous blends of 2-amino-2-methyl-1-propanol and diethanolamine, Chemical Engineering Science, 58 (2003) 4137-4144.

[4] A. Bello, R.O. Idem, Comprehensive study of the kinetics of the oxidative degradation of CO_2 loaded and concentrated aqueous monoethanolamine (MEA) with and without sodium metavanadate during CO_2 absorption from flue gases, Industrial & Engineering Chemistry Research, 45 (2006) 2569-2579.

[5] B.A. Oyenekan, G.T. Rochelle, Energy performance of stripper configurations for CO_2 capture by aqueous amines, Industrial & Engineering Chemistry Research, 45 (2006) 2457-2464.

[6] G. Pellegrini, R. Strube, G. Manfrida, Comparative study of chemical absorbents in postcombustion CO_2 capture, Energy, 35 (2010) 851-857.

[7] R. Strube, G. Pellegrini, G. Manfrida, The environmental impact of post-combustion CO_2 capture with MEA, with aqueous ammonia, and with an aqueous ammonia-ethanol mixture for a coal-fired power plant, Energy, 36 (2011) 3763-3770.

[8] B. Mandal, S. Bandyopadhyay, Absorption of carbon dioxide into aqueous blends of 2-amino-2-methyl-1-propanol and monoethanolamine, Chemical Engineering Science, 61 (2006) 5440-5447.

[9] L. Dubois, P. Kahasha Mbasha, D. Thomas, CO_2 absorption into aqueous solutions of a polyamine (PZEA), a sterically hindered amine (AMP), and their blends, Chemical Engineering & Technology, 33 (2010) 461-467.

[10] K. Osman, C. Coquelet, D. Ramjugernath, Absorption Data and Modeling of Carbon Dioxide in Aqueous Blends of Bis (2-hydroxyethyl) methylamine (MDEA) and 2, 2-Iminodiethanol (DEA): 25% MDEA+ 25% DEA and 30% MDEA+ 20% DEA, Journal of Chemical & Engineering Data, 57 (2012) 1607-1620.

[11] M.A. Pacheco, S. Kaganoi, G.T. Rochelle, CO_2 absorption into aqueous mixtures of diglycolamine and methyldiethanolamine, Chemical Engineering Science, 55 (2000) 5125-5140.

[12] A.T. Zoghi, F. Feyzi, S. Zarrinpashneh, Experimental investigation on the effect of addition of amine activators to aqueous solutions ofmethyldiethanolamine on the rate of carbon dioxide absorption, International journal of greenhouse gas control, 7 (2012) 12-19.

[13] J.-I. Baek, J.-H. Yoon, Solubility of Carbon Dioxide in Aqueous Solutions of 2-Amino-2-methyl-1,3-propanediol, Journal of Chemical & Engineering Data, 43 (1998) 635-637.

[14] F. Bougie, M.C. Iliuta, Analysis of regeneration of sterically hindered alkanolamines aqueous solutions with and without activator, Chemical Engineering Science, 65 (2010) 4746-4750.

[15] R. Rowland, Q. Yang, P. Jackson, M. Attalla, Amine mixtures and the effect of additives on the CO_2 capture rate, Energy Procedia, 4 (2011) 195-200.

[16] S.A. Freeman, R. Dugas, D. Van Wagener, T. Nguyen, G.T. Rochelle, Carbon dioxide capture with concentrated, aqueous piperazine, Energy Procedia, 1 (2009) 1489-1496.

[17] G. Rochelle, E. Chen, S. Freeman, D. Van Wagener, Q. Xu, A. Voice, Aqueous piperazine as the new standard for CO_2 capture technology, Chemical Engineering Journal, 171 (2011) 725-733.

[18] S. Bishnoi, G.T. Rochelle, Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility, Chemical Engineering Science, 55 (2000) 5531-5543.

[19] S. Paul, K. Thomsen, Kinetics of absorption of carbon dioxide into aqueous potassium salt of proline, International journal of greenhouse gas control, 8 (2012) 169-179.

[20] L. Dubois, & Thomas, D., Screening of aqueous amine-based solvents for postcombustion CO_2 capture by chemical absorption, Chemical Engineering and Technology, 35 (2012) 513-524.

[21] J. Zhang, D.W. Agar, X. Zhang, F. Geuzebroek, CO_2 absorption in biphasic solvents with enhanced low temperature solvent regeneration, Energy Procedia, 4 (2011) 67-74.
[22] K. Maneeintr, R.O. Idem, P. Tontiwachwuthikul, A.G.H. Wee, Synthesis, solubilities, and cyclic capacities of amino alcohols for CO2 capture from flue gas streams, Energy Procedia, 1 (2009) 1327-1334.
[23] N. McCann, M. Maeder, M. Attalla, Simulation of enthalpy and capacity of CO_2 absorption by aqueous amine systems, Industrial & Engineering Chemistry Research, 47 (2008) 2002-2009.
[24] G. Puxty, R. Rowland, A. Allport, Q. Yang, M. Bown, R. Burns, M. Maeder, M. Attalla, Carbon dioxide postcombustion capture: A novel screening study of the carbon dioxide absorption performance of 76 amines, Environmental science & technology, 43 (2009) 6427-6433.
[25] A.L. Kohl, R. Nielsen, Gas purification, Gulf Professional Publishing, 1997.
[26] F.-Y. Jou, A.E. Mather, F.D. Otto, The solubility of CO_2 in a 30 mass percent monoethanolamine solution, The Canadian Journal of Chemical Engineering, 73 (1995) 140-147.
[27] P. Singh, D. Brilman, M.J. Groeneveld, Evaluation of CO_2 solubility in potential aqueous amine-based solvents at low CO_2 partial pressure, International journal of greenhouse gas control, 5 (2011) 61-68.
[28] [28] P. Singh, Amine based solvent for CO_2 absorption "From molecular structure to process:, in, University of Twente, The Netherlands, 2011, pp. 200.
[29] P. Feron, Assessing Post-Combustion Capture for Coal-fired Power Stations in Asia-Pacific Partnership Countries. Final report to the Department of Resources, Energy and Tourism, in, CSIRO 2012.
[30] M. Abu-Zahra, Carbon Dioxide Capture from Flue Gas: Development and Evaluation of Existing and Novel Process Concepts, in, Print Partners Ipskamp B. V., Delft, 2009.
[31] U.E. Aronu, H.F. Svendsen, K.A. Hoff, O. Juliussen, Solvent selection for carbon dioxide absorption, Energy Procedia, 1 (2009) 1051-1057.
[32] P. Brúder, A. Grimstvedt, T. Mejdell, H.F. Svendsen, CO_2 capture into aqueous solutions of piperazine activated 2-amino-2-methyl-1-propanol, Chemical Engineering Science, 66 (2011) 6193-6198.
[33] F.Y. Jou, Mather, A.E., Otto, F.D., Solubility of acidic gases in aqueous methyldiethanolamine solutions, Ind. Eng. Chem. Process Des. Dev, 21 (1982) 539-544.
[34] R.E. Dugas, Carbon dioxide absorption, desorption, and diffusion in aqueous piperazine and monoethanolamine, in, The University of Texas at Austin, United States -- Texas, 2009, pp. 283.