Simulation of CO_2 Absorption Using the System K_2CO_3-Piperazine

Muazzam Arshad*, Walter Wukovits, Anton Friedl

Vienna University of Technology, Institute of Chemical Engineering, Getreidemarkt 9/166-2, 1060 Vienna, Austria
muazzam.arshad@tuwien.ac.at

CO_2 is one of the main sources of global warming affecting the environment. It is one of the biggest challenges of future to reduce CO_2 emissions in addition to capture and disposal of CO_2 produced as a result of burning of fossil fuels. In this work, CO_2 removal from biogas by absorption process is studied. For CO_2 absorption from biogas, aqueous K_2CO_3 and piperazine solvents are used independently and then ultimately in a combination. Equilibrium studies are done to calculate capabilities of simulation tool Aspen Plus® towards the component systems $CO_2/H_2O/PZ$, $CO_2/H_2O/K_2CO_3$ and finally $CO_2/H_2O/PZ/K_2CO_3$. Validation and comparisons of equilibrium studies were made with literature data. Furthermore, all the mentioned systems were then compared using typical parameter ranges for biogas composition and conditions. The effect on absorption loading capacity of CO_2 was studied by varying parameters of temperature, pressure and biogas composition.

1. Introduction

Main causes of greenhouse effect are emissions of harmful gases and oxides of different components such as oxides of carbon. Clean and sustainable energy is an important demand of future. Thus, worldwide a lot of effort is being put into production of clean energy. Investigations include improving already employed processes as well as developing new processes of producing clean and sustainable energy. Large emphasis is put in the use of biofuels to substitute fossil energy carriers. In the course of rising oil and gas prices as well as global warming, biofuels are gaining further attention.

Producing biogas out of biomass and agricultural residues is a widespread and simple option of biofuel production. During the last years, a trend towards utilization of pure CH_4 can be observed instead of production of just heat and power from biogas. To obtain pure CH_4 from biogas, CO_2 has to be removed. In this way purified CH_4 can be obtained to be fed to an existing natural gas grid or to be used as chemical for synthesis or use as vehicle fuel (Niesner, 2013).

Several processes are available for CH_4/CO_2 separation such as adsorption, membrane separation or absorption. In this work, removal of CO_2 by absorption will be studied. There have been several works done in the development of processes to remove CO_2 from exhaust gases of industries as well as from furnaces burning fossil fuels. Several solvents have been studied for the removal of CO_2. Most important solvent for commercial use in absorption of CO_2 on large scale is MEA or comparable amines. However, these solvents are not suitable for CO_2 removal in small scale biogas facilities. Here, other solvents have been suggested, e.g. pressurized water or cold potassium carbonate solution. Unfortunately, potassium carbonate has a low CO_2 absorption rate at low temperatures. However rate of absorption can be enhanced by piperazine as an activator (Cullinane, 2005). Several previous studies investigate the effect of piperazine on the solubility of CO_2 for mixtures with other amines like MDEA.

In this work, potassium carbonate and piperazine solutions are studied individually and later on in a combination of both for their performance in biogas upgrading. Based on experimental investigations, process simulation in the commercial simulation environment Aspen Plus® will be used to develop and design a dedicated absorption-desorption cycle for biogas upgrading in small scale.

In a first step, equilibrium studies are performed to investigate solubility of carbon dioxide in potassium carbonate, piperazine and the mixture of potassium carbonate and piperazine at equilibrium conditions as basis for process development.

2. Absorption systems

2.1 K$_2$CO$_3$

The use of K$_2$CO$_3$ as CO$_2$ absorbent has been recognized since early 1900's. Commonly absorption by potassium carbonate can be represented by the following overall reaction (Kothandaraman, 2010):
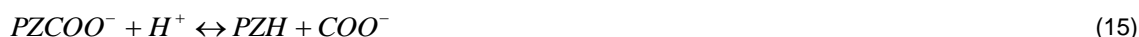
$$CO_2 + K_2CO_3 + H_2O \leftrightarrow 2KHCO_3 \tag{1}$$

The above reaction can be broken down in the following steps:

$$K_2CO_3 \rightarrow CO_3^{-2} + 2K^+ \tag{2}$$

$$KHCO_3 \rightarrow HCO_3^- + K^+ \tag{3}$$

$$KOH \rightarrow OH^- + K^+ \tag{4}$$

$$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+ \tag{5}$$

$$H_2O + HCO_3 \leftrightarrow H_3O^+ + CO_3^{-2} \tag{6}$$

$$2H_2O \leftrightarrow H_3O^+ + OH^- \tag{7}$$

For treatment of gas at high temperatures, K$_2$CO$_3$ is effective. It has been used previously in hot potassium carbonate process (Benfield) for removal of CO$_2$ and acid gases from ammonia synthesis gas and natural gas etc. (Cullinane, 2005). Solubility of KHCO$_3$ can be increased by high temperature of absorber, which allows operation with highly concentrated solution. K$_2$CO$_3$ solutions offer advantages for absorption of CO$_2$.of having low heat duty in reboiler as it requires less energy to regenerate. But low solubility and slow rate of absorption at a lower temperature, make the solvent unsuitable in cases where higher purity is required. However, these limitations can be solved by adding amines such as piperazine, which act as an activator or promoter to increase rate of CO$_2$ absorption.

2.2 Piperazine

Equilibrium reaction of piperazine with carbon dioxide can be described by the following mechanism (Hilliard, 2008):

$$CO_2 + H_2O \leftrightarrow H_2CO_3^- + H^+ \tag{8}$$

$$HCO_3 \leftrightarrow CO_3^{-2} + H^+ \tag{9}$$

$$H_2O \leftrightarrow H^+ + OH^- \tag{10}$$

$$PZ + H^+ \leftrightarrow PZH^+ \tag{11}$$

$$PZH^+ + H^+ \leftrightarrow PZH_2^{+2} \tag{12}$$

$$PZ + HCO_3^- \leftrightarrow PZCOO^- + H_2O \tag{13}$$

$$PZCOO^- + HCO_3- \leftrightarrow PZ(COO^-)^2 + H_2O \tag{14}$$

$$PZCOO^- + H^+ \leftrightarrow PZH + COO^- \tag{15}$$

Piperazine is a cyclic diamine (Bougie, 2011) making it capable of reacting twice with CO$_2$ forming carbamate and bicarbamate species shown in reactions, Eq(12) and Eq(13). Reaction, Eq(13), formation of bicarbamate might be slower than former reaction, but it increases the capacity to capture CO$_2$. Piperazine has a high rate of absorption and can thus be used as a promoter with K$_2$CO$_3$ to increase rate of absorption.

3. Model

Simulation models were developed in Aspen Plus® based on Aspen example files using Aspen Plus example files for independent systems of piperazine (AspenTech, 2010) and K$_2$CO$_3$ (AspenTech, 2012), respectively, using ENRTL thermodynamic model with apparent component approach. Flash column was used for performing equilibrium calculations. For the combined system, piperazine model was taken as a base for manual modification since Aspen Plus® Electrolyte Wizard was not able to properly generate the electrolyte system for aqueous piperazine. Besides manual addition of components in the system, such as,

K_2CO_3, $KHCO_3$ and KOH, additional reactions for K_2CO_3 were manually added to the chemistry section of the model. Furthermore, some binary interaction parameters such as Henry coefficients and electrolyte pair parameters were altered. These parameters were taken from K_2CO_3 example model (AspenTech, 2012). Design specifications were used to achieve a certain partial pressure of CO_2 by varying total pressure of the flash column to observe corresponding CO_2 loading in liquid stream. Also design specifications were included to maintain original concentration of piperazine and K_2CO_3 in liquid streams to ensure equilibrium conditions.

4. Results

As prerequisite for a proper simulation of the upgrading process, correct representation of physical and thermodynamic properties in Aspen Plus® has to be ensured. In a first step, equilibrium studies are done to investigate solubility of carbon dioxide in potassium carbonate, piperazine and the mixture of potassium carbonate and piperazine at equilibrium conditions as basis for process development.

Different data sets from literature were analysed and compared before selecting trustable data to validate Aspen Plus® simulations. In Figure 1, comparison of Aspen Plus® simulations with literature is done for a fixed concentration of 0.6 mol/kg piperazine at different temperatures to show the trend of equilibrium curves. It can be observed, that for a fixed concentration, higher loading capacity is obtained for lower temperatures. Similarly, in Figure 2, Aspen Plus® simulations are compared with literature data at a fixed temperature of 298 K for different concentrations of piperazine, showing a good fit, with exception of a few outliers at low partial pressure of CO_2.
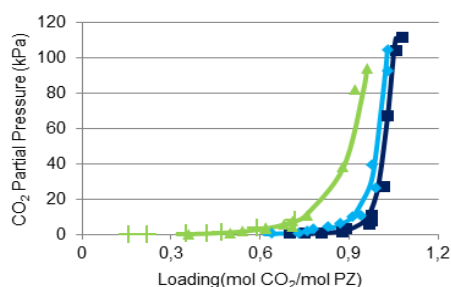

Figure 1: Comparison of Aspen Plus® simulations with different literature data for 0.6 mol/kg aq. Piperazine solution; ■ Derk (298 K); ♦ Derk (313 K); ▲ Derk (343 K); + Bishnoi (343 K); ━ Aspen Plus® (298 K,313 K,343 K)
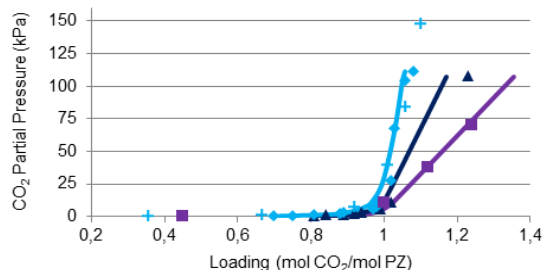
Figure 2: Comparison of Aspen Plus® simulations with literature data for different aq. Piperazine concentrations at 298 K; ♦ Derk (0.6 mol/kg); + Francis (0.6 mol/kg); ▲ Derk (0.2 mol/kg);■ Francis (0.1mol/kg); ━ Aspen Plus® (0.1 mol/kg,0.2 mol/kg,0.6 mol/kg)
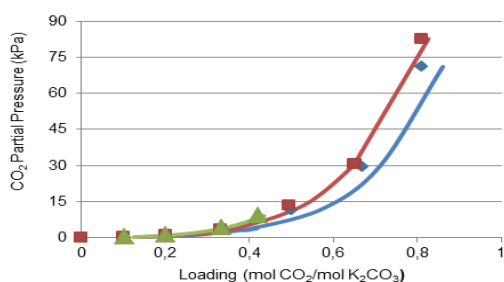

Figure 3: Aspen Plus® simulations vs literature data for different concentrations of aq. K_2CO_3 solution at 343 K; ♦ Tosh (20 wt%); ■ Tosh (30 wt%); ▲ Tosh (40 wt%); ━ Aspen Plus® (20 wt%,30 wt%,40 wt%)
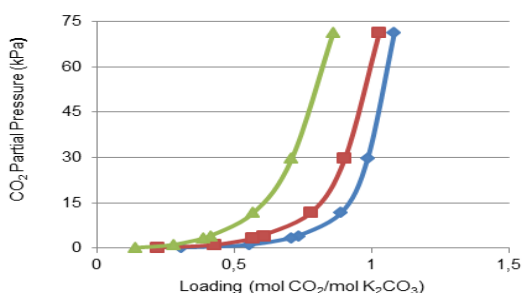
Figure 4: Comparison of Aspen Plus® simulations for 20 wt% aq. K_2CO_3 solution at different temperatures; ♦ 298 K; ■ 303 K; ▲ 343 K
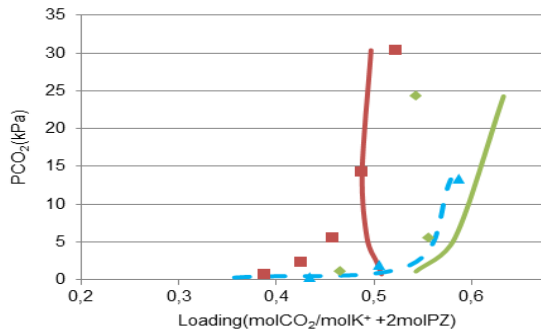
Figure 5: Aspen Plus® simulation vs literature data of Hilliard NTNU for 3 mol/kg K2CO3/1.2 mol/kg PZ at different temperatures; ♦ Hilliard NTNU at 120 °C; ▲ Hilliard NTNU at 100 °C; ━ Aspen Plus® (120 °C,100 °C)
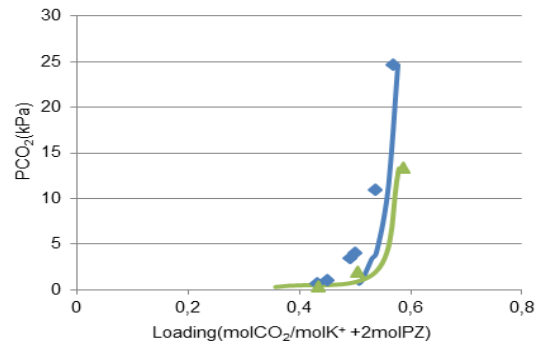
Figure 6: Aspen Plus® simulation vs literature data of Hilliard NTNU for different concentrations of solvents at 100 °C; ♦ 1.8 mol/kg K2CO3/0.6 mol/kg PZ; ▲ 3 mol/kg K2CO3/1.2 mol/kg PZ; ■ 2.5 mol/kg K2CO3/2.5 mol/kg PZ; ━ Aspen Plus® (1.8 mol/kg K2CO3/0.6 mol/kg PZ, 3 mol/kg K2CO3/1.2 mol/kg PZ; 2.5 mol/kg K2CO3/2.5 mol/kg PZ)

In Figure 3, calculated data show good agreement with literature data by Tosh et al (1959) for different concentrations of K_2CO_3 at 343 K. There are some outliers for 20 wt% K_2CO_3 but overall the match is quite reasonable. Comparisons were also made with literature data by Park et al (1997), not presented in this paper, showing reasonable fit except some deviation at 323 K. In Figure 4, Aspen simulations of equilibrium curves are shown for 20 wt% aqueous K_2CO_3 solution for different temperatures.

For combined system of K_2CO_3+Piperazine, literature data were taken from Hilliard (2008), in which results from two different sets of experiments were given. One set of experiments was performed in University of Texas, Austin (UT) and the other set of experiments was performed in Norges Teknisk-Naturvitenshapelige Universitet (NTNU). The results of the system for the ENRTL model show a good fit, with exception of a few outliers at low partial pressure of CO_2 as is observable in Figure 6.

Though Aspen simulations match very well with the literature data, there are some deviations at low partial pressures of CO_2 showing volatility of piperazine at low pressure. Furthermore, the combined model was validated by calculating equilibrium loadings for independent systems of K_2CO_3 and piperazine and verifying by literature (not shown in the paper). The equilibrium model simulations show a good agreement and can be used to predict the simulations at different process conditions.

4.1 Comparison of absorption systems

Comparisons were then made to study the different solvent systems and analyze them. A random concentration of 3 mol/kg K_2CO_3 and 1.2 mol/kg piperazine were used for the study. Analysis was made by varying different parameters to see their effect on the absorption capacity at equilibrium. To study the systems, parameter ranges were chosen which could be interesting for biogas upgrading (Table 1). The parameters which were used for the study were temperature, composition of feed gas (amount of CO_2 present in biogas), total pressure and equilibrium partial pressure of carbon dioxide. For instance, temperature range was taken considering the temperature range used for fermentation in production of biogas.

Table 1: Typical ranges of parameters for biogas and parameter ranges chosen for simulation study

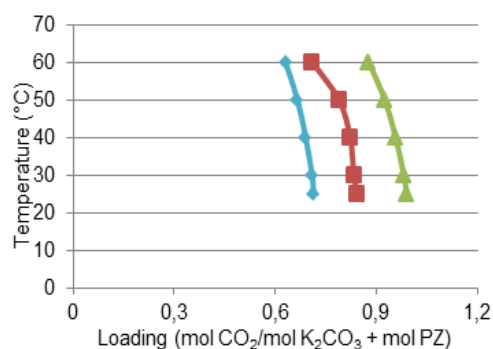| Parameter	Typical Range of biogas		Range chosen	Reference
Temperature	Thermophillic fermentation:	upto 298 K	298-333 K	Hilby (2014)
	Mesophillic fermentation:	305-315 K		Hilby (2014)
	Thermophyllic fermentation:	323-331 K		Hilby (2014)
Composition	CH4: 50-70 %		CH4: 50-70 %	Mursec (2009)
	CO2: 25-50 %		CO2: 28-50 %	Mursec (2009)
			N2: The rest	
Pressure			1-3 bar	

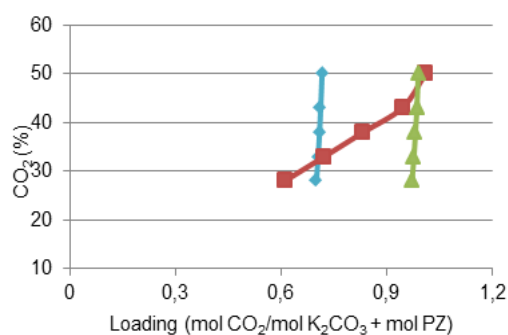*Figure 7: Change in loading with varying temperature of flash column; ♦ 3 mol/kg K_2CO_3/1.2 mol/kg PZ; ■ 3 mol/kg K_2CO_3; ▲ 1.2 mol/kg PZ*

Figure 8: Change in loading with varying CO_2 concentration in biogas; ♦ 3 mol/kg K_2CO_3/1.2 mol/kg PZ; ■ 3 mol/kg K_2CO_3; ▲ 1.2 mol/kg PZ

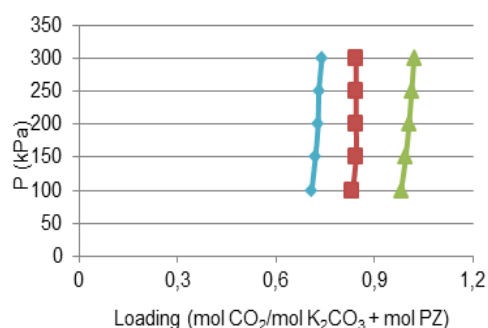*Figure 9: Change in loading with varying pressure of flash column; ♦ 3 mol/kg K_2CO_3/1.2 mol/kg PZ; ■ 3 mol/kg K_2CO_3; ▲ 1.2 mol/kg PZ*

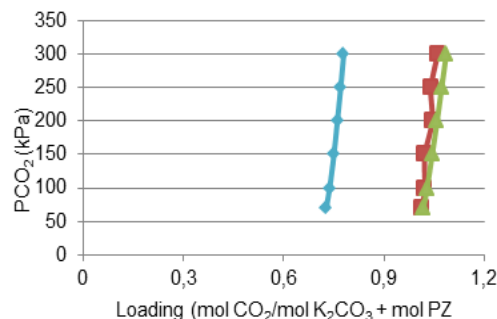*Figure 10: Change in loading with varying partial pressure of CO_2; ♦ 3 mol/kg K_2CO_3/1.2 mol/kg PZ; ■ 3 mol/kg K_2CO_3; ▲ 1.2 mol/kg PZ*

Figure 7 represents changes in loading of carbon dioxide in liquid stream with change in temperature of flash column. We can observe that as expected, at constant pressure and biogas concentration, increasing temperature reduces carbon dioxide loading capacity. In Figure 8, it can also be seen that for a constant temperature and pressure, an increase in CO_2 concentration in fed biogas leads to an increase in CO_2 loading and hence its removal. Thus, higher initial concentration of CO_2 results in higher loading. Furthermore, as expected, increase in equilibrium partial or total pressure leads to an increase in CO_2 loading capacity for constant temperature and initial concentrations of CO_2 in biogas as shown in Figure 9 and Figure 10.

It can be seen that equilibrium curve for the combined system is always to the left showing lower loading and the piperazine curve is always to the right showing higher loading confirming the presence of carbamate formed by piperazine. The excess CO_2 in piperazine curves can be explained by physically absorbed CO_2 with piperazine. It is the usual trend seen for amines that first CO_2 is absorbed chemically, but when all solvent is spent in chemical reactions, CO_2 cannot be anymore absorbed chemically but has to be dissolved physically (Ermatchkov, 2006). This results in higher loadings in liquid stream. The comparison and behavior has to be studied and analyzed further.

5. Conclusion

This work presents equilibrium data for CO_2 absorption in aqueous solutions of piperazine and K_2CO_3. Literature data are compared with results from calculations with Aspen Plus® ENRTL property method. Calculations are performed in a flash unit at equilibrium conditions considering the involved electrolyte system. Adjustment of property parameters gives a proper representation of the component system CO_2-K_2CO_3-Piperazine-H_2O.

Data from Aspen Plus® simulations match very well with literature data in case of solubility of piperazine solution with less than 4 % deviation. Deviations can however be observed at some temperatures with

some literature data probably related with experimental inaccuracies. Data calculated for K_2CO_3 match even better with less than 0.05 % deviation. For aqueous K_2CO_3-piperazine solutions, simulations show good match with literature data apart from some deviation at very low partial pressures of CO_2 probably due to vapor pressure (volatility) of piperazine. But at higher pressures, the calculated data fit well with the literature data. This shows that the Aspen Plus® model can be used to predict CO_2 absorption in equilibrium environment using K_2CO_3-piperazine as solvent.

The presented equilibrium calculations will form the basis for rate based absorption studies in Aspen Plus® and thus for a detailed design of the absorption and desorption steps in the biogas upgrading process with aqueous K_2CO_3-piperazine solutions.

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