

Available online at www.sciencedirect.com

Energy Procedia 4 (2011) 1–8

**Energy
Procedia**

www.elsevier.com/locate/procedia

GHGT-10

Pilot Plant Experiments for Post Combustion Carbon Dioxide Capture by Reactive Absorption with Novel Solvents

Hari Prasad Mangalapally, Hans Hasse*

Laboratory of Engineering Thermodynamics (LTD), University of Kaiserslautern, Germany

Abstract

The main challenge for CO₂ post combustion capture from power plant flue gases is reducing the energy demand of the process. Application of novel solvents will substantially contribute to this. The present work describes the testing of such novel solvents in a pilot plant (column diameters 0.125 m, absorber packing height 4.25 m, flue gas flow 30-110 kg/h, CO₂ partial pressure 35-135 mbar). Two novel amine solvents from EU-project CESAR were systematically studied and compared to Monoethanolamine (MEA). For each solvent, at a constant CO₂ removal rate of 90 % the regeneration energy is determined for different solvent flow rates. From the results the optimal solvent flow rate and the minimum regeneration energy are found. The resulting numbers for the different solvents can directly be compared. Both new solvents show improvements compared to MEA with a reduction of about 20 % in the regeneration energy and 45 % in the solvent flow rate for the most promising one.

© 2011 Published by Elsevier Ltd. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

Keywords: amines; carbon dioxide; flue gas; novel solvents; reactive absorption

* Corresponding author. Tel.: +49-631-205-3497; Fax: +49-631-205-3835.
E-mail address: hans.hasse@mv.uni-kl.de

1. Introduction

Carbon dioxide capture and sequestration is an important option for reducing greenhouse gas emissions and fighting the global climate change [1]. Aqueous absorption/desorption is the state-of-the-art technology for the post combustion capture (PCC) of CO₂ from coal-fired power plants [2, 3]. PCC is a mature process that could be implemented faster than competing technologies like pre combustion capture and oxy-fuel [4, 5]. The main challenge facing the implementation of aqueous absorption/desorption process on a large scale for PCC is high capital cost (columns, pumps, heat-exchangers and initial solvent) and the high operating cost (mainly reboiler duty but also electrical power for machinery and solvent makeup) [6]. The established reference solvent for this process is 0.3 g/g Monoethanolamine in aqueous solution and will be referred here simply as MEA. For a

standard absorption/desorption process running with MEA the regeneration energy requirement is reported to be about 4.2 GJ/t_{CO₂}, leading to an efficiency penalty of 12-14 % points in fossil fuelled power plants [7-9]. Current efforts for reducing the operating cost include the implementation of intercooling, flue gas cooling, lean vapor compression and operating the rich-lean heat exchanger at a lower temperature difference [3, 10, 11].

An important other option for reducing both the capital and operating cost include the development of improved solvents. They should have suitable gas solubility equilibrium data and fast reaction kinetics. Furthermore, stability, corrosion and environmental aspects are important. Up to now, Mitsubishi Heavy Industries together with Kansai Electric, commercially employ other solvents than MEA. Their solvent “KS-1TM” is known to be an aqueous solution of a sterically hindered amine. Besides the new solvent in their process these companies use various types of proprietary equipment. The regeneration heat of that process with the KS-1TM is said to be ~ 3 GJ/t_{CO₂}, i.e. 20 % lower than that of MEA ~ 3.7 GJ/t_{CO₂} [4, 12]. KS-1TM is also said to have advantages compared to MEA regarding degradation and corrosion by the supplier. In addition, Siemens together with E.on, employ another solvent than MEA. Their solvent “Siemens AAS” is known to be an aqueous solution of an amino acid salt. The energy demand for their improved process with Siemens AAS solvent for a full-scale capture plant is reported to be 2.7 GJ/t_{CO₂}. This would lead to an efficiency drop of only 8.5 % points compared to a state of the art hard coal power plant with 600 °C technology [18].

To achieve further progress in the development of economic PCC, new solvents are developed and tested in the European project CESAR [11]. The present paper reports on testing two of these solvents in a gas-fired PCC absorption/desorption pilot plant. Before testing the new solvents, a base line with the reference solvent MEA was established. The present paper focuses on the tests carried out with two novel solvents CESAR1 and CESAR2. The results are compared to MEA, to study the potential of improvement in regeneration energy for new solvents.

2. Pilot plant and process description

The basic scheme of the absorption/desorption process for CO₂ capture from flue gases and a picture of the pilot plant are shown in Figure 1. The flue gas is produced by a gas burner; SO₂ and other components can be added. The operation of this burner with two different stages as well as a CO₂ recycle from the plant allow a wide variation of the CO₂ partial pressure in the flue gas between 35 mbar and 135 mbar. The flue gas is fed into the pre-washer column by a blower. The flue gas flow rate can be set between 30 kg/h and 150 kg/h. The maximum gas flow rate through the absorber is limited to approximately 100 kg/h (F-Factor ≈ 2.1 Pa^{0.5}) due to fluid dynamic restrictions. The pre-washer which is equipped with 0.84 m of the structured packing Mellapak 250.Y, is built as a direct contact cooler to set the temperature of the flue gas at the absorber inlet and at the same time to make sure that the flue gas is saturated with water. The absorber has five sections equipped with the structured packing BX 500 (Sulzer Chemtec). The total packing height is 4.25 m; the diameter is 0.125 m. To reduce solvent loss by flue gas, there is a washing section at the absorber top above the solvent inlet. The washing section is equipped with the 0.42 m of the structured packing Mellapak 250.Y. A low amount of fresh deionized water is added into the washing water recycle stream to avoid a prohibitive accumulation of amine in the washing water.

For steady state operation the liquid level in the absorber bottom is controlled by a pump. The rich solvent is pumped into the desorber through the rich lean heat exchanger. The desorber is equipped with three sections of BX 500 similar to the absorber. The total packing height in the desorber is

2.55 m; the diameter is again 0.125 m. The bottom of the desorber contains electrical heating elements for partial evaporation of the solvent. The vapor at the top of the desorber consists of water, CO₂ and some traces of amine. To retain the amine, also at the desorber top a washing section is installed, which is similar to that of the absorber. The vapor at the desorber top is led into a condenser where most of the water is removed so that almost pure CO₂ is obtained. A part of the condensate is used in the washing section of the desorber and another part if necessary is withdrawn to fulfill the water balance of the process. More detailed description of the pilot plant and its operation is given in reference [13].

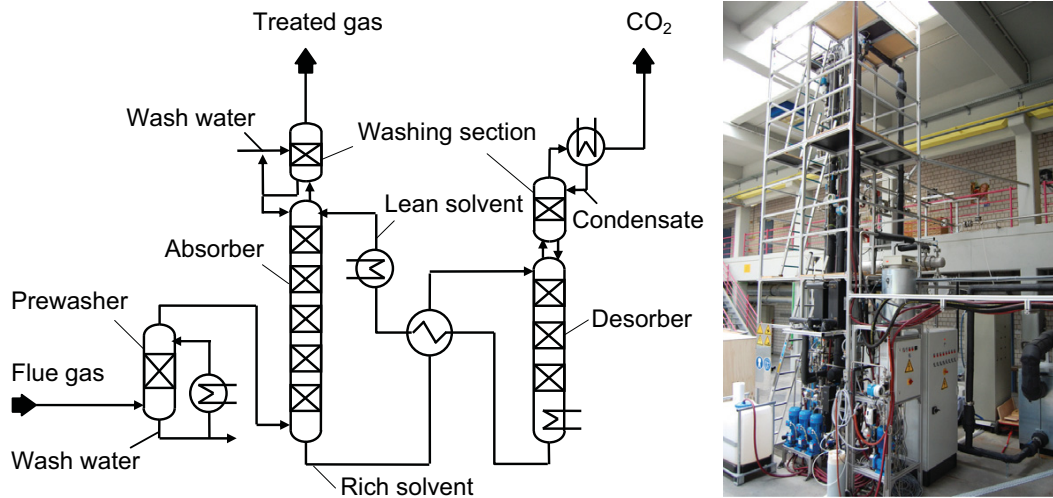


Figure 1 Basic scheme of the absorption/desorption PCC process and picture of the LTD pilot plant.

3. Pilot plant experiments with new solvents

The search of new solvents for CO₂ capture in CESAR was focused on aqueous solutions of pure amines and amine blends. CESAR1 is a mixture of primary and secondary amine, whereas CESAR2 is a primary amine with two amine groups. Table 1 specifies the details of the solvents. Having passed a pre-selection based on an evaluation of their equilibrium data of the CO₂ solubility, kinetic experiments, volatility, stability and toxicity, they were tested in the pilot plant and compared to MEA.

Table 1 Tested PCC solvents.

Name	Composition
MEA	0.3 g/g Monoethanolamine + 0.7 g/g Water
CESAR1	0.28 g/g 2-Amino-2-methyl-1-propanol (AMP) + 0.17 g/g Piperazine (PIP) + 0.55 g/g Water
CESAR2	0.32 g/g 1,2-Ethanediamine (EDA) + 0.68 g/g Water

3.1. Equilibrium data comparison

Figure 2 shows the equilibrium data of CO₂ solubility at 40 °C and 120 °C for MEA using the Electrolyte-NRTL model [14] in comparison to experimental data for CESAR1 and CESAR2 [11]. The temperatures were chosen so as to represent typical values for the absorber and desorber respectively. The CO₂ loading is given in mol CO₂ per kg solvent. This unit was chosen, so that the influence of the solvent mass flow pumped around in the absorption/desorption process can be seen easily. The regeneration energy needed in the desorber can be separated into the following contributions [4]: the energy needed for desorption of CO₂ (desorption enthalpy), the energy to heat up the solvent and the reflux, and the energy needed for supplying the stripping stream. The distance between the equilibrium curves at high and low temperature is closely related to the solvent flow rate as well as the stripping stream. A large distance, even in certain cases resulting in a larger number for the desorption enthalpy, is desired as it will often lead to a lower regeneration energy and lower solvent flow rate as the separation task becomes easier [13, 15].

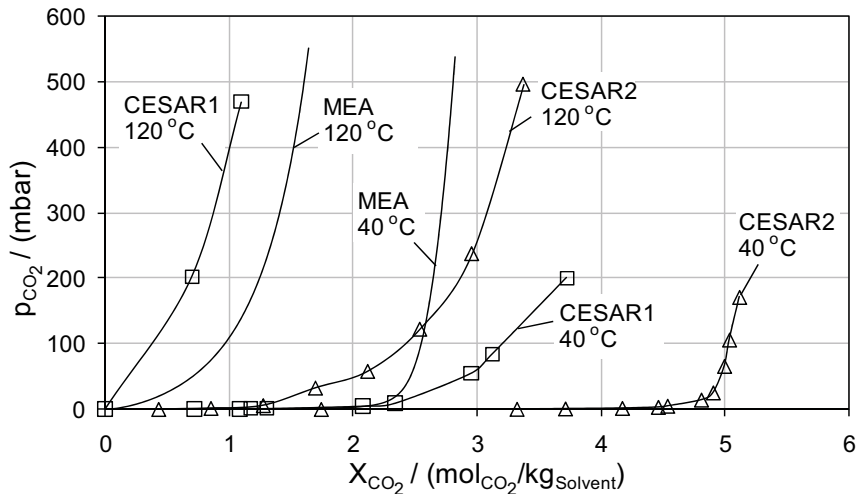


Figure 2 Calculated equilibrium data of CO₂ solubility at 40 °C and 120 °C for MEA (—) in comparison to experimental data for CESAR1 (□) and CESAR2 (Δ).

Figure 2 show that CESAR1 and CESAR2 have larger distances between the equilibrium curves than MEA. Hence, for CESAR1 and CESAR2 lower optimal solvent flow rates as well as somewhat lower regeneration energies compared to MEA can be expected. Especially, CESAR1 looks most promising due to the availability of largest distance between the equilibrium curves. It must be kept in mind that these expectations from equilibrium data, which were discussed above, do not take into account the mass transfer kinetics. Slow kinetics lead to a need for high columns and/or efficient packings.

3.2. Method for solvent comparison in the pilot plant and experimental results

For testing solvents in the pilot plant, a consistent method was defined and applied to all solvents, here to MEA, CESAR1 and CESAR2. For each set of experiments the CO₂ partial pressure in the flue gas is fixed. Two levels are studied, 54 mbar, corresponding to gas fired power plants, and 102 mbar, corresponding to coal fired power plants [11, 16].

Furthermore, the CO₂ removal rate (Ψ_{CO_2}) is specified. For post combustion capture of CO₂ from power plants, the target is often a CO₂ removal rate of 90 %. Therefore, the experiments were

carried out at that rate. As a direct setting of the CO₂ removal rate is not possible it has to be adjusted by suitably choosing the reboiler duty in an iterative process during each experiment. The reboiler duty at the desired removal rate is the most important result of the experiment. The experimental number needs to be corrected for heat losses which can be accurately assessed [13]. That assessment shows that, it is sufficient to subtract an average heat loss of 1.5 kW. All numbers reported here are corrected numbers after the subtraction. They are given in terms of regeneration energy per ton of captured CO₂. Other detailed results like concentration, temperature and mass transfer profiles are available but are not reported in the frame of the present short survey. Full information will be given in reference [17].

The operating conditions of the experiments of the present work are summarized in Table 2. The results from these experiments are analyzed in plots of the regeneration energy versus the ratio of the liquid to the gas mass flow. These plots allow finding an optimum solvent flow rate and the corresponding minimum regeneration energy. The optima for the different solvents are then compared. The numerical results will depend on the specified removal rate and the CO₂ partial pressure as well as on the plant design. But, for a given suitable design of the pilot plant and for a suitable choice of the other process parameters, a first assessment of the potential of new solvents is possible and the ranking of the solvents should be reliable.

Figure 3 shows the regeneration energy as a function of the solvent flow rate (L/G ratio) for the experiments at low CO₂ partial pressure (Set I, cf. Table 2). Three solvents are compared: MEA, CESAR1 and CESAR2. Figure 4 shows the same plot for the high CO₂ partial pressure (Set II, cf. Table 2).

Table 2 Operating conditions of the two sets of experiments at low and high CO₂ partial pressure.

Process Variables	Set I	Set II
Flue gas mass flow / kg/h	76	80
Flue gas temperature at absorber inlet / °C	47	47
Variation range of solvent mass flow / kg/h	35 – 200	75 – 275
Solvent temperature at absorber inlet / °C	40	40
Solvent to flue gas mass flow ratio (L/G) / kg/kg	0.45 – 2.7	0.94 – 3.5
CO ₂ partial pressure in flue gas / mbar	54	102
CO ₂ mass flow in flue gas / kg/h	6.2	12
CO ₂ mass flow captured / kg/h	5.5	10.5
CO ₂ removal rate / %	90	90

4. Discussion

The results for MEA at the low CO₂ partial pressure given in Figure 3 indicate an optimum L/G ratio of about 1.2 corresponding to regeneration energy of about 3.8 GJ/t_{CO₂}. The corresponding numbers for CESAR1 are L/G = 0.65 with regeneration energy of about 3.0 GJ/t_{CO₂} and L/G = 0.95 with regeneration energy of about 3.45 GJ/t_{CO₂} for CESAR2. This is a considerable improvement compared to MEA. The comparison is summarized in Table 3.

Figure 4 shows the comparison for the results at the high CO₂ partial pressure. The results for MEA indicate an optimum L/G ratio of about 2.5 corresponding to regeneration energy of about 4.1 GJ/t_{CO₂}. The corresponding numbers for CESAR1 are L/G = 1.4 with regeneration energy of about

3.3 GJ/t_{CO₂} and L/G = 1.9 with regeneration energy of about 3.8 GJ/t_{CO₂} for CESAR2. Again, a considerable improvement compared to MEA is observed. The comparison is again summarized in Table 3.

Table 3 Comparison of optimal operation points for the different solvents for two sets of experiments at low and high CO₂ partial pressure.

p_{CO_2} / mbar	Regeneration Energy / GJ/t _{CO₂}		L/G ratio / kg/kg	
	54	102	54	102
MEA	3.8 (100 %)	4.1 (100 %)	1.2 (100 %)	2.5 (100 %)
CESAR1	3.0 (79 %)	3.3 (80 %)	0.65 (54 %)	1.4 (56 %)
CESAR2	3.45 (91 %)	3.8 (93 %)	0.95 (79 %)	1.9 (76 %)

This Table allows a comparison of both data sets. The relative improvements observed at the high and low CO₂ partial pressure are similar, both for the regeneration energy and the solvent flow rate. In comparing the numbers, the uncertainties of the determination of the minima from the data reported in Figures 3 and 4 should be kept in mind. The improvements are in line with expectations from the equilibrium data, cf. Figure 2 and Section 3.1.

Additional experiments were carried out to study the overall mass transfer kinetics, which are not reported in the present paper. They show that the mass transfer kinetics of CESAR1, CESAR2 and MEA are similar so that the comparison presented above is valid.

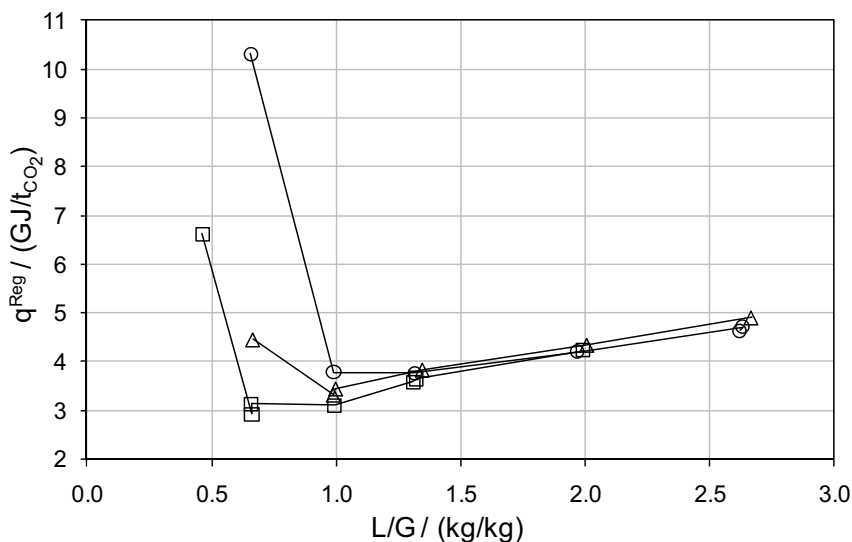


Figure 3 Comparison of pilot plant results for experiments carried out with different solvents at low CO₂ partial pressure (Set I, cf. Table 2): regeneration energy as a function of L/G for MEA (○), CESAR1 (□) and CESAR2 (Δ).

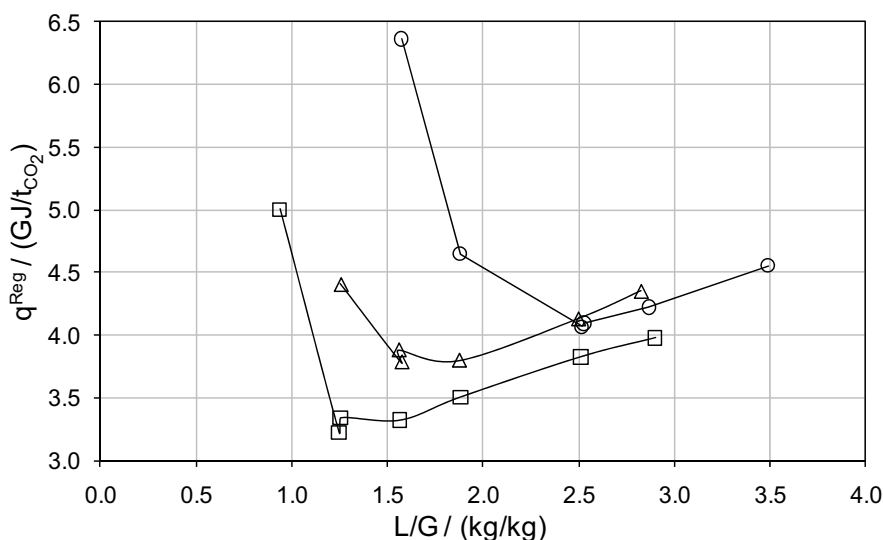


Figure 4 Comparison of pilot plant results for experiments carried out with different solvents at high CO₂ partial pressure (Set II, cf. Table 2): regeneration energy as a function of L/G for MEA (○), CESAR1 (□) and CESAR2 (Δ).

5. Conclusions

Two new PCC solvents, CESAR1 and CESAR2, as well as MEA as a reference were studied in the pilot plant using a systematic approach. For each solvent, at a constant CO₂ removal rate of 90 % the regeneration energy is determined for different L/G ratios. From the plot of the results, the optimal L/G ratio and the minimum regeneration energy are found. Both new solvents show a clear improvement compared to MEA.

Acknowledgment

This work was carried out under the European Commission's 7th Framework Program Integrated Project CESAR (FP7/2007-2011) under grant agreement n° 213569.

References

- [1] Plaza JM, Chen E, Rochelle GT. Absorber Intercooling in CO₂ Absorption by Piperazine-Promoted Potassium Carbonate. *AIChE Journal* 2010; 56:905-14.
- [2] Oyekan BA, Rochelle GT. Energy Performance of Stripper Configurations for CO₂ Capture by Aqueous Amines. *Industrial & Engineering Chemistry Research* 2006; 45:2457-64.
- [3] Abu-Zahra MR. Carbon Dioxide Capture from Flue Gas: Development and Evaluation of Existing and Novel Process Concepts. PhD Dissertation - Technische Universiteit Delft, the Netherlands 2009.
- [4] Mangalapally HP, Notz R, Hoch S, Asprion N, Sieder G, Garcia H, Hasse H. Pilot Plant Experimental Studies of Post Combustion CO₂ Capture by Reactive Absorption with MEA and New Solvents. *Energy Procedia* 2009; 1:963-70.

- [5] Notz R, Asprion N, Clausen I, Hasse H. Selection and Pilot Plant Tests of New Absorbents for Post Combustion Carbon Dioxide Capture. *Chemical Engineering Research and Design* 2007; 85:510-5.
- [6] Oyenekan BA, Rochelle GT. Alternative Stripper Configurations for CO₂ Capture by Aqueous Amines. *AIChE Journal* 2007; 53:3144-54.
- [7] Chapel D G, Mariz C L, Ernest J. Recovery of CO₂ from Flue Gases: Commercial Trends. In: *Conference Proceedings of the Canadian Society of Chemical Engineerings Annual Meeting*. Saskatoon, Saskatchewan, Canada 1999; Oct 4-6.
- [8] Sander M T, Mariz C L. The Fluor Daniel Econamine FG process: Past Experience and Present Day Focus. *Energy Conversion and Management* 1992; 33:341-8.
- [9] Sieder G. No Escape for CO₂: BASF's Solvent and Technology Development Program for PCC. *International Symposium on Post Combustion Capture*. Duesseldorf/Neuss 2009; Jul 30-31.
- [10] Reddy S, Johnson D, Gilmartin J. Fluor's Econamine FG plusSM Technology for CO₂ Capture at Coal-fired Power Plants. *Power Plant Air Pollutant Control "Mega" Symposium*. Baltimore 2008; August 25-28.
- [11] EU-Project, CO₂ Enhanced Separation and Recovery (CESAR). Integrated Research Project Partially Funded by the European Commission under the 7th Framework Program. Grant Agreement Number 213569. Project Duration from 01.02.2008 to 31.01.2011. <http://www.co2cesar.eu>.
- [12] Mimura T, Simayoshi H, Suda T, Iijima M, Mitsuoka S. Developments of Energy Saving Technology for Flue gas Carbon Dioxide Recovery in Power Plant by Chemical Absorption Method and Steam System. *Energy Conversion and Management* 1997; 38:S57-62.
- [13] Notz R. CO₂-Abtrennung aus Kraftwerksabgasen mittels Reaktivabsorption. PhD Dissertation - Universitaet Stuttgart, Germany. Logos Verlag Berlin GmbH 2010. ISBN 978-3-8325-2386-2.
- [14] Asprion N. Nonequilibrium Rate-Based Simulation of Reactive Systems: Simulation Model, Heat Transfer, and Influence of Film Discretization. *Industrial & Engineering Chemistry Research* 2006; 45:2054-69.
- [15] Notz R, Tönnies I, Mangalapally HP, Hoch S, Hasse H. A Short-cut Method for Assessing Absorbents for Post Combustion Carbon Dioxide Capture. *International Journal of Greenhouse Gas Control* 2010; (in press).
- [16] Rolker J, Arlt W. Abtrennung von Kohlendioxid aus Rauchgasen mittels Absorption. *Chemie Ingenieur Technik* 2006; 78:416-24.
- [17] Mangalapally HP. Post Combustion Capture of CO₂ by Reactive Absorption. PhD Dissertation - TU Kaiserslautern, Germany 2010; (in preparation).
- [18] Jockenhoevel T, Schneider R, Rode H. Validation of a Second-Generation Post-Combustion Capture Technology – Results from POSTCAP Pilot Plant Operation. *PowerGen Europe* 2010; June 08-10.