

## PILOT PLANT EXPERIMENTS WITH MEA AND NEW SOLVENTS FOR POST COMBUSTION CO<sub>2</sub> CAPTURE BY REACTIVE ABSORPTION

Hari Prasad Mangalapally, Hans Hasse

Laboratory of Engineering Thermodynamics (LTD), University of Kaiserslautern, Erwin-Schroedinger-Strasse 44, D-67663 Kaiserslautern, Germany, Email: hari.mangalap@mv.uni-kl.de

### Abstract

Carbon dioxide is a greenhouse gas with a major impact on global climate change. One of the options for reducing CO<sub>2</sub> emissions is post combustion CO<sub>2</sub> capture from power plant flue gases. The main challenge for this process is the reduction of energy requirement for solvent regeneration. In order to reduce the costs of the absorption/desorption process, new tailored solvents for that process are needed. LTD operates a gas-fired pilot plant (column diameters 0.125 m, absorber packing height 4.25 m, flue gas flow 30-100 kg/h, CO<sub>2</sub> partial pressure 35-110 mbar) in which such new solvents were studied in the frame of the EU project CESAR. To obtain a baseline for testing the new solvents, first systematic studies were carried out with MEA in that plant with two different structured packings: Sulzer Mellapak 250.Y and BX 500. The most important process parameters CO<sub>2</sub> removal rate  $\Psi_{\text{CO}_2}$ , fluid dynamic load and solvent flow rate were systematically varied. Besides MEA, two new solvents were studied in the pilot plant. It is shown that a direct comparison of results for different solvents obtained in such pilot plant experiments is not trivial. The comparison of only a few operating points for the new solvents with seemingly corresponding results for MEA can lead to wrong conclusions, since for each solvent an optimisation of the operating conditions is necessary. Only systematic studies allow a meaningful comparison. The technique that was used in the present work for this purpose was measuring data sets at constant CO<sub>2</sub> removal rate of 90% (by adjustment of the regeneration energy in the desorber) and systematically varying the solvent flow rate. A minimal energy requirement for the given removal rate is found from these studies. Only the optima for different solvents should be compared. By this procedure, solvents were identified that show a clear improvement in regeneration energy requirement when compared to MEA.

**Keywords:** CO<sub>2</sub> capture, reactive absorption, flue gas, amines, new solvents

### 1. Introduction

Post-combustion capture (PCC) is the capture of CO<sub>2</sub> from conventional coal-fired power plants by scrubbing the flue gas with chemical solvents. The PCC process depends on the flue gas composition. Power plant flue gas consists of 3-16 mol% CO<sub>2</sub> depending on the type of plant (gas or coal). Besides carbon dioxide the main compounds of the flue gases are nitrogen, oxygen, water vapor, NO<sub>x</sub> and SO<sub>x</sub>. Table 1 shows typical power plant flue gas compositions.

**Table 1.** Flue gas composition<sup>3</sup>

	mol%						
	N <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	water vapor	NO <sub>x</sub>	SO <sub>x</sub>	ash
Coal-fired power plant	70-75%	12-16%	3-4%	6-7%	400ppm	150ppm	≥ 30ppm
Gas-fired power plant	70-75%	3-5%	10-12%	7-10%	< 50ppm	< 10ppm	-

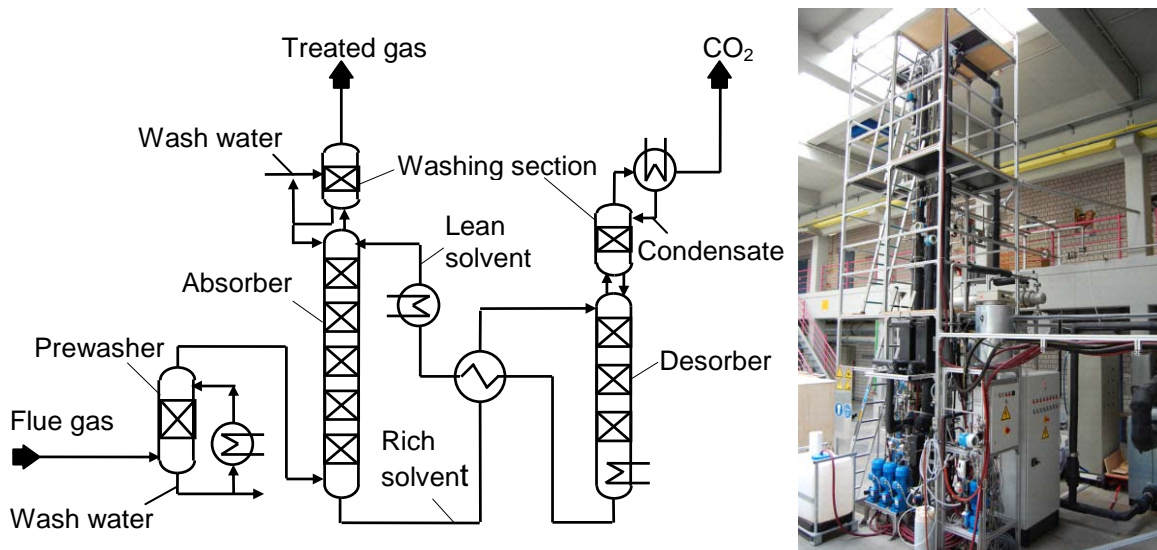
PCC can be based on established technology already applied on industrial scales in hydrogen production or natural gas sweetening processes. The reference solvent for processes of this type is a 30 mass% aqueous solution of monoethanolamine (referred to simply as MEA in the following). The

major drawback of PCC with MEA is that it requires much energy for regenerating the solvent. This results in a reduction of overall thermal efficiency of the power plant, which is so important that it rules out competitive application<sup>4</sup>. Mitsubishi Heavy Industries together with Kansai Electric, employ other patented chemical solvents – sterically hindered amines called KS-1, KS-2 or KS-3. The regeneration energy demand of KS solvents is said to be ~ 3 GJ/t CO<sub>2</sub>, i.e. 20% lower than that of MEA with ~ 3.7 GJ/t CO<sub>2</sub><sup>2, 9</sup>. Besides improved solvents, optimized equipment and operation, modification of the absorption/desorption process with intercooling and lean vapor compression can contribute to reduce the thermal efficiency-loss due to PCC<sup>4</sup>.

To achieve progress in the development of economic PCC, the EU project CESAR aims at developing and testing of new solvents. For the selection of promising solvents, several criteria have to be taken into account like equilibrium data of the CO<sub>2</sub> solubility, mass transfer data, reaction kinetics, volatility, stability and toxicity. Solvent selection was one of the main tasks within the CESAR project. After a pre-selection of solvents based on lab experiments, in which the criteria mentioned above were analyzed, successful solvent candidates need to be studied in pilot plant experiments. For this purpose a gas-fired pilot plant is operated at the Laboratory of Engineering Thermodynamics (LTD), at University of Kaiserslautern, Germany. To obtain a baseline for testing new solvents, first systematic studies were carried out with MEA in that plant with two different structured packings: Sulzer Mellapak 250.Y and BX 500. The important process parameters CO<sub>2</sub> removal rate  $\Psi_{\text{CO}_2}$ , fluid dynamic load, and solvent flow rate were systematically varied. Finally, two new solvents CESAR1 and CESAR2 were tested and compared to MEA.

## 2. Pilot plant

The basic scheme of the PCC absorption/desorption process and a picture of the pilot plant are shown in Figure 1. The flue gas is produced by a gas burner; SO<sub>2</sub> and other flue gas components can be added. The operation of this burner with two different stages as well as a CO<sub>2</sub> recycle from the plant allow a wide variation of the CO<sub>2</sub> partial pressure in the flue gas between 35 mbar and 110 mbar. The flue gas is fed into the pre-washer column by a blower. The flue gas flow rate can be set approximately between 30 kg/h and 150 kg/h. The maximum gas flow rate through the absorber is limited to approximately 100 kg/h ( $F\text{-Factor} \approx 2.4 \sqrt{\text{Pa}}$ ) due to fluid dynamic limitations.



**Figure 1.** Basic scheme of the absorption/desorption process for post combustion carbon dioxide capture and picture of the LTD pilot plant for CO<sub>2</sub> capture from flue gases by reactive absorption

The pre-washer 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 is built of five sections, which are each equipped with five elements of the structured packing BX 500 (Sulzer Chemtec, Winterthur Switzerland). The total packing height is 4.25 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 two elements 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. And the water balance over the absorber is fulfilled by adjusting the temperature of the flue gas at the outlet of the absorber.

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 built of three sections, which are each equipped with five elements of BX 500 similar to the absorber. The total packing height in the desorber is 2.55 m. Both the absorber and desorber columns have a diameter of 0.125 m. The bottom of the desorber contains electrical heating elements for partial evaporation of the solvent. For aqueous amine solutions, mainly water is evaporated. The vapor at the top of the desorber consists of water, CO<sub>2</sub> and some traces of amine. To retain the amine, also at the desorber top a washing section is installed. This washing section is equipped with two elements of the structured packing Mellapak 250.Y. The vapor at the desorber top is led into the condenser where most of the water is removed so that almost pure CO<sub>2</sub> 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 absorption/desorption process.

### 3. Pilot plant experiments with MEA for different column internals

In order to study the influence of column internals on absorption capacity when replaced by a more efficient internals, parameter studies with the variation of removal rate were carried out while maintaining CO<sub>2</sub> partial pressure, flue gas flow, solvent mass flow and all other process parameters constant. Table 2 shows typical operating conditions for the two different types of packing that were studied. Despite the fact that the flue gas volume flow was equal for all experiments, mass flow in the experiments carried out with Mellapak 250 Y is slightly lower than for the experiments with BX 500. This is due to a different composition of the supplied natural gas.

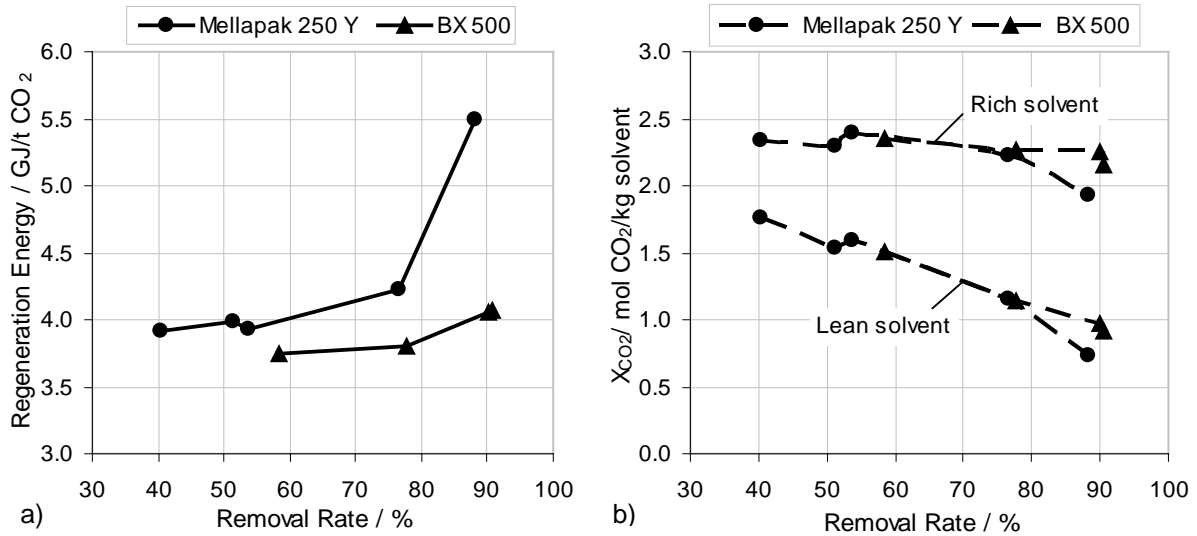
**Table 2.** Typical operating conditions in the pilot plant experiments

Process variables	Mellapak 250 Y	BX 500
Flue gas flow $\dot{m}_{Fluegas}$ / kg/h	~ 75	~ 79
Solvent flow $\dot{m}_{Solvent}$ / kg/h	200	200
CO <sub>2</sub> partial pressure $p_{CO_2}$ / mbar	~ 109	~ 102
CO <sub>2</sub> mass flow in flue gas $\dot{m}_{CO_2}^{abs, G, in}$ / kg/h	~ 12	~ 12
CO <sub>2</sub> mass flow captured $\dot{m}_{CO_2}^{captured}$ / kg/h	4.8 – 10.6	6.7 – 10.6
CO <sub>2</sub> removal rate $\Psi_{CO_2}$ / %	40 - 88	58 - 90

Figure 2a shows the comparison of the regeneration energy for Mellapak 250 Y and BX 500 for experiments with different CO<sub>2</sub> removal rates. The increase of the regeneration energy demand with increasing CO<sub>2</sub> removal rate is drastic for the experiments with Mellapak 250 Y packing for removal rates above 80%. For BX 500 packing, because of its much higher surface area, lower numbers of the regeneration energy are found even at removal rates above 80%.

This behaviour can be explained by Figure 2b which shows the comparison of CO<sub>2</sub> loading of the rich and lean solvents for Mellapak 250 Y and BX 500 for different CO<sub>2</sub> removal rates. Upon increasing the CO<sub>2</sub> removal rate the loading difference between rich and lean solvent increases for both Mellapak 250 Y and BX 500. For high removal rates there are differences between Mellapak 250 Y and BX 500. For Mellapak 250 Y, lower values of the rich loading are observed. This is due to the lack of sufficient surface area for the mass transfer in the absorber, which causes that the equilibrium is not reached. For a given solvent flow, flue gas flow and removal rate the loading difference is fixed. Therefore lean loadings are also shifted to low values for Mellapak 250 Y. For attaining these low lean loadings in the

stripper, high regeneration energies are needed. Contrarily to Mellapak 250 Y sufficient surface area for mass transfer is provided by the BX packing so that the rich loading remains almost constant even at high removal rates.



**Figure 2.** Comparison of a) regeneration energy, b) CO<sub>2</sub> loading of rich and lean solvents for experiments with Mellapak 250 Y and BX 500 at different CO<sub>2</sub> removal rates

#### 4. New solvents

The search of new solvents for CO<sub>2</sub> capture in CESAR is mainly focused on aqueous amine solutions. Both pure amine and amine blends were studied. CESAR1 and CESAR2 are such amine blends. Having passed the pre-selection described above, they were tested in the pilot plant and compared to MEA. The packing used for this study was BX.

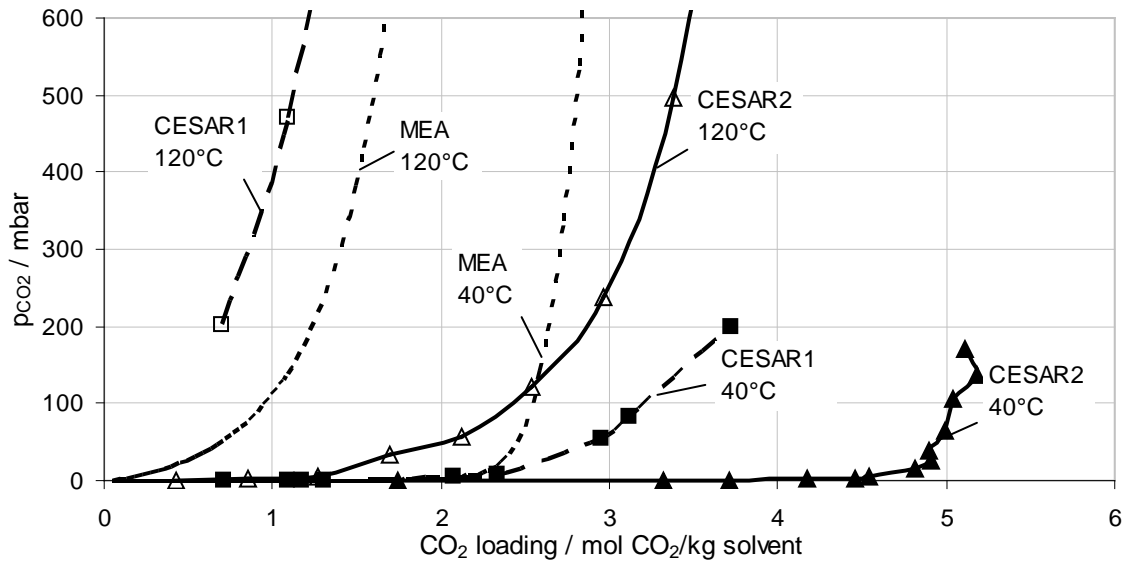
##### 4.1 Equilibrium data comparison

Figure 3 shows the comparison of equilibrium data for MEA, CESAR1 and CESAR2 at 40 °C and 120 °C. The temperatures were chosen so as to represent typical values for the absorber and desorber respectively. The CO<sub>2</sub> loading is given in mol CO<sub>2</sub> / 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.

Equilibrium data for MEA have been calculated by using the Electrolyte-NRTL model with CHEMASIM<sup>6, 8, 10, 11</sup>, data for CESAR1 and CESAR2 have been measured by the project partners Norwegian University of Science and Technology (NTNU) / The Foundation for Scientific and Industrial Research (SINTEF) and Netherlands Organisation for Applied Scientific Research (TNO Science & industry).

The regeneration energy needed in the desorber can be separated into the following contributions<sup>1</sup>. The energy needed for desorption of CO<sub>2</sub> (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 high difference leads to a lower regeneration energy<sup>5, 8</sup>.

Figure 3 show that CESAR1 and CESAR2 have higher distances between the equilibrium curves than MEA. Hence, for CESAR1 and CESAR2 lower regeneration energies at lower solvent flow rates should be expected compared to MEA. CESAR1 looks a little more promising than CESAR2. 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.



**Figure 3.** Equilibrium data for the CO<sub>2</sub> solubility in an aqueous solution of MEA, CESAR1 and CESAR2 at 40°C and 120°C

#### 4.2 Methodology for solvent comparison in the pilot plant<sup>1</sup>

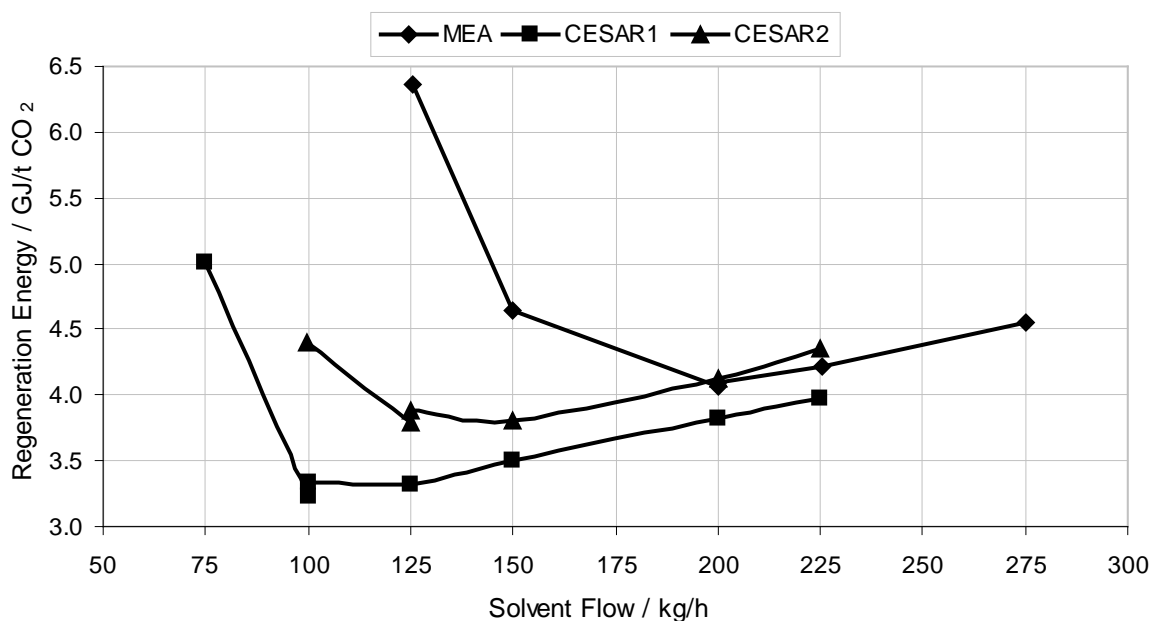
For solvent comparison in the pilot plant, a consistent methodology was defined and applied to all solvents, hence, in the present work to MEA, CESAR1 and CESAR2. Experiments are carried out at different solvent flow rates with constant CO<sub>2</sub> removal rate of 90%. The removal rate is set by adjusting the regeneration energy. The results of each set of these experiments are analyzed in plots of the regeneration energy versus the solvent flow rate. This allows finding an optimum solvent flow rate. The optima for the different solvents are then compared. Table 3 summarizes the operating conditions of these experiments.

**Table 3.** Operating conditions of the experiments for solvent comparison (BX packing)

Process variables	Set data
Flue gas flow $\dot{m}_{Fluegas}$ / kg/h	~ 79
Solvent flow $\dot{m}_{Solvent}$ / kg/h	75 – 275
CO <sub>2</sub> partial pressure $p_{CO_2}$ / mbar	~ 102
CO <sub>2</sub> mass flow in flue gas $\dot{m}_{CO_2}^{abs, G, in}$ / kg/h	~ 12
CO <sub>2</sub> mass flow captured $\dot{m}_{CO_2}^{captured}$ / kg/h	~ 10.6

#### 4.3 Comparison of new solvents with MEA

Figure 4 shows the comparison of measured regeneration energies for MEA, CESAR1 and CESAR2. The experiments with MEA show a minimum of the regeneration energy for a solvent flow rate of 200 kg/h (L/G: 2.5) with minimum energy of ~ 4.1 GJ/t CO<sub>2</sub>. For CESAR1 the optimum solvent flow rate is 100 kg/h (L/G: 1.25) with minimum regeneration energy of ~ 3.25 GJ/t CO<sub>2</sub>, for CESAR2 the optimum solvent flow rate is 125 kg/h (L/G: 1.56) with minimum regeneration energy of ~ 3.8 GJ/t CO<sub>2</sub>. Hence, the demand for regeneration energy is lowered by ~ 20% for CESAR1 and ~ 7% for CESAR2 respectively, when compared to MEA. As expected from equilibrium data (see Figure 3) both CESAR1 and CESAR2 showed optima at lower solvent flows (i.e. lower liquid to gas ratios (L/G)) when compared to MEA. Additional experiments carried out to study the overall mass transfer kinetics, which are not reported in this paper showed that CESAR1 and CESAR2 mass transfer kinetics are similar compared to MEA.



**Figure 4.** Comparison of pilot plat results: regeneration energy as a function of solvent flow rate for MEA, CESAR1 and CESAR2. The removal rate is 90%

## 5. Conclusions

To obtain a baseline for studies of new solvents, systematic investigations on CO<sub>2</sub> capture from flue gases were carried out with the standard solvent MEA in a pilot plant with two different structured packings: Sulzer Mellapak 250.Y and BX 500. A methodology for comparing new solvents with MEA was developed and applied to study two new solvents in the pilot plant. The results show that both the optimal solvent flow rate and regeneration energy are significantly reduced compared to MEA.

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## References

1. H. P. Mangalapally et.al., *Energy Procedia I* (2009) 963-970
2. T. Mimura et.al., *Energy Conversion and Management* 38 (1997) S57-S62
3. J. Rolker and W. Arlt, *Chemie Ingenieur Technik*. 78 (4) 2006 416-424
4. T.Wall, *Proceedings of the Combustion Institute* 31 (2007) 31-47
5. R. Notz et.al., *International Journal of Greenhouse Gas Control* (Accepted) (2010)
6. W. Böttinger et.al., *Fluid Phase Equilibria* 263 (2008) 131-143
7. M.R. Abu-Zahra et.al., *International Journal of Greenhouse Gas Control* 1 (2007) 37-46
8. R. Notz, PhD Thesis – Universitaet Stuttgart, Germany (2009)
9. T. Mimura et.al., *Energy Conversion and Management* 36 (1995) 397-400
10. N. Asprion, *Industrial & Engineering Chemistry Research* 45 (2006) 2054-2069
11. D.M. Austgen et.al., *Industrial & Engineering Chemistry Research* 28 (1989) 1060-1073