

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

Energy Procedia 1 (2009) 963–970

**Energy  
Procedia**[www.elsevier.com/locate/procedia](http://www.elsevier.com/locate/procedia)

GHGT-9

## Pilot plant experimental studies of post combustion CO<sub>2</sub> capture by reactive absorption with MEA and new solvents

Hari Prasad Mangalapally<sup>a\*</sup>, Ralf Notz<sup>b,c</sup>, Sebastian Hoch<sup>a</sup>, Norbert Asprion<sup>c</sup>,  
Georg Sieder<sup>c</sup>, Hugo Garcia<sup>c</sup>, Hans Hasse<sup>a</sup>

<sup>a</sup>Laboratory of Engineering Thermodynamics (LTD), Technische Universitaet Kaiserslautern, Germany

<sup>b</sup>Institute of Thermodynamics and Thermal Process Engineering (ITT), Universitaet Stuttgart, Germany

<sup>c</sup>BASF SE, Ludwigshafen, Germany

### Abstract

The main challenge for the CO<sub>2</sub> post combustion capture from power plant flue gases is the reduction of the energy requirement for solvent regeneration. The required reduction can only be achieved by application of new solvents. For the validation of new solvents in the absorption/desorption process, a pilot plant (column diameters 0.125 m, absorber packing height 4.2 m, flue gas flow 30-110 kg/h, CO<sub>2</sub> partial pressure 35-135 mbar) was built in the EU-project CASTOR. To obtain a baseline for testing of new solvents, first systematic studies were carried out with MEA in that plant. All important process parameters, i.e. CO<sub>2</sub> content in the flue gas, CO<sub>2</sub> removal rate  $\Psi_{\text{CO}_2}$ , fluid dynamic load, and solvent flow rate were varied. These studies allow detailed insight into the process, e.g., a quantification of the different contributions to the overall regeneration energy (namely: desorption enthalpy, stripping steam, heating up of solvent feed and condensate recycle) as a function of the chosen process parameters. A rate-based model of the process based on a detailed physico-chemical model was implemented in the process simulator CHEMASIM. It is shown that the model is able to predict the experimental results for MEA. Besides MEA, two new solvents were studied in the pilot plant. A direct comparison of different solvents 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 (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, one solvent candidate was identified that shows an advantage compared to MEA.

© 2009 Elsevier Ltd. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

**Keywords:** CO<sub>2</sub> capture; Reactive absorption; Desorption; Flue gas; Amines; Rate-based model; Simulations; New solvents

\* Corresponding author. Tel.: +49-631-205-2761; fax: +49-631-205-3835.

E-mail address: [hari.mangalap@mv.uni-kl.de](mailto:hari.mangalap@mv.uni-kl.de)

## 1. Introduction

Carbon dioxide is a greenhouse gas and substantially contributes to global warming and climate change. One of the options for reducing CO<sub>2</sub> emissions is the post combustion capture from power plant flue gases. Reactive absorption is the only technology that can be implemented quickly on a large scale at existing power plants for that purpose. The reference solvent for processes of this type is a 30 mass% aqueous solution of monoethanolamine (referred to simply as MEA in the following) which, however, has major drawback of high energy requirement for solvent regeneration, leading to an efficiency penalty up to 15 % points in fossil fuelled power plants. For better process economics it is essential to find more efficient solvents, tailored for post combustion capture. This was the task of the work that was carried out in the frame of the integrated European project CASTOR [1]. The paper reports on the achieved progress in this process.

Another major challenge for the carbon dioxide removal using post combustion capture is the amount of the flue gas. In typical applications flue gas flow rates are of the order of thousands of tons per hour corresponding to millions of cubic meters per hour, and hundreds of tons of carbon dioxide per hour [2]. At present there are several commercial processes available for CO<sub>2</sub> capture in post combustion systems. The maximum capacity of CO<sub>2</sub> capture of operational plants is not more than 32 tCO<sub>2</sub>/h. So far, there is no application of full scale CO<sub>2</sub> capture in power plants, even though test facilities using flue gas slipstreams exist [1]. In most commercial processes an aqueous solution of MEA is used. Only 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 heat 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> [3, 4].

To achieve progress in the development of low-cost post combustion CO<sub>2</sub> capture CASTOR aimed at developing and pilot plant testing of new solvents. For this purpose a gas-fired absorption/desorption pilot plant for removal of carbon dioxide from flue gases was built. It was initially operated at Universitaet Stuttgart, and has recently been transferred to TU Kaiserslautern, Germany. Before testing the new solvents, a base line with the standard solvent MEA had to be established. Therefore, systematic parameter studies were carried out with MEA. A rate-based model of the MEA process was developed, implemented in CHEMASIM and successfully tested. Finally two new solvents CASTOR1 and CASTOR2 were tested and compared to MEA.

## 2. Pilot plant

The basic scheme of the absorption/desorption process for CO<sub>2</sub> 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; 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> make-up from gas bottles and 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 135 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 110 kg/h ( $F\text{-Factor} \approx 2.4 \sqrt{\text{Pa}}$ ) due to fluid dynamic limitations.

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 four elements of the structured packing Mellapak 250.Y (Sulzer Chemtec). The total packing height is 4.2 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.

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 four elements of Mellapak 250.Y similar to the absorber. The total packing height in the desorber is 2.52 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 is withdrawn to fulfill the water balance of the absorption/desorption process.

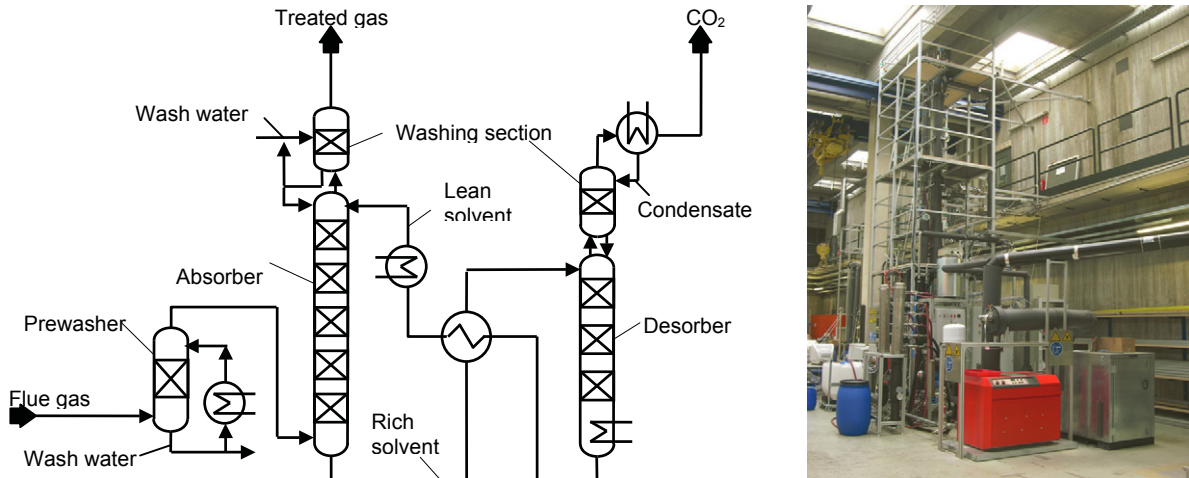


Figure 1: Basic scheme of the absorption/desorption process for post combustion carbon dioxide capture and picture of the pilot plant for CO<sub>2</sub> capture from flue gases by reactive absorption.

### 3. Pilot plant experiments with MEA

#### Parameter study

In this paper only some results of parameter studies carried out with MEA are reported. The full data set will be given in reference [5].

Table 1: Overview of process parameter studies that are discussed in the present work.

Varied parameter	Range of variation	Constant parameters
CO <sub>2</sub> partial pressure	$p_{CO_2} = 35 - 135$ mbar	$\dot{Q}_{Evaporator}$ , $\dot{m}_{Solvent}$ , $\dot{m}_{Fluegas}$
CO <sub>2</sub> removal rate	$\Psi_{CO_2} = 40 - 88$ %	$p_{CO_2}$ , $\dot{m}_{Solvent}$ , $\dot{m}_{Fluegas}$
Flue gas flow rate	$\dot{m}_{Fluegas} = 55 - 100$ kg/h	$\Psi_{CO_2}$ , $\frac{\dot{m}_{Solvent}}{\dot{m}_{Fluegas}}$ , $p_{CO_2}$
Solvent flow rate	$\dot{m}_{Solvent} = 100 - 350$ kg/h	$\Psi_{CO_2}$ , $p_{CO_2}$ , $\dot{m}_{Fluegas}$

#### 3.1. Variation of CO<sub>2</sub> partial pressure

In order to study the influence of the CO<sub>2</sub> content on the process behavior, the CO<sub>2</sub> partial pressure in the flue gas was varied between 35 mbar and 135 mbar while maintaining the other parameters like solvent flow rate and evaporator energy constant, see Table 1. Figure 2a shows that with increasing CO<sub>2</sub> partial pressure the amount of

captured CO<sub>2</sub> increases asymptotically and finally reaches a constant value. Figure 2a also contains data on the total CO<sub>2</sub> flow in the flue gas, comparing both lines in Figure 2a therefore gives information on the capture rate. The increase of the captured CO<sub>2</sub> amount with increasing partial pressure of CO<sub>2</sub> is expected as the driving force for the mass transfer increase. However the amount cannot be increased above the saturation of the solvent, which explains the asymptotic behavior. Approaching the saturation limit leads to a decrease in the capture rate. This behavior can also be seen in Figure 2b. With the increase of driving force the loading difference between rich and lean solvent first increases and finally remains constant after reaching equilibrium.

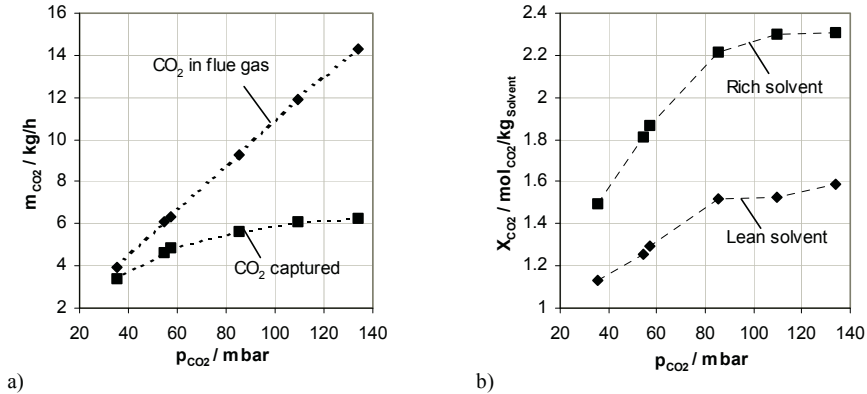


Figure 2: Influence of partial pressure of CO<sub>2</sub> on: a) CO<sub>2</sub> mass flow (total amount in the flue gas compared to captured amount), and b) CO<sub>2</sub> loading in rich and lean solvents. All other process parameters are kept constant see Table 1.

### 3.2. Variation of CO<sub>2</sub> removal rate

The CO<sub>2</sub> removal rate was varied by varying the evaporator energy while maintaining other parameters like the solvent flow rate and CO<sub>2</sub> partial pressure in the flue gas constant, see Table 1. Figure 3a shows that with an increase of the CO<sub>2</sub> removal rate, the regeneration energy requirement also increases. But after reaching a certain CO<sub>2</sub> removal rate there is a drastic increase in the regeneration energy requirement. This behavior can be explained by Figure 3b. With increasing CO<sub>2</sub> removal rate the loading difference between rich and lean solvent increases and for high removal rates the lean loading shifts to very low values such that CO<sub>2</sub> separation in the desorber for a particular packing height becomes difficult resulting in a very high regeneration energy requirement.

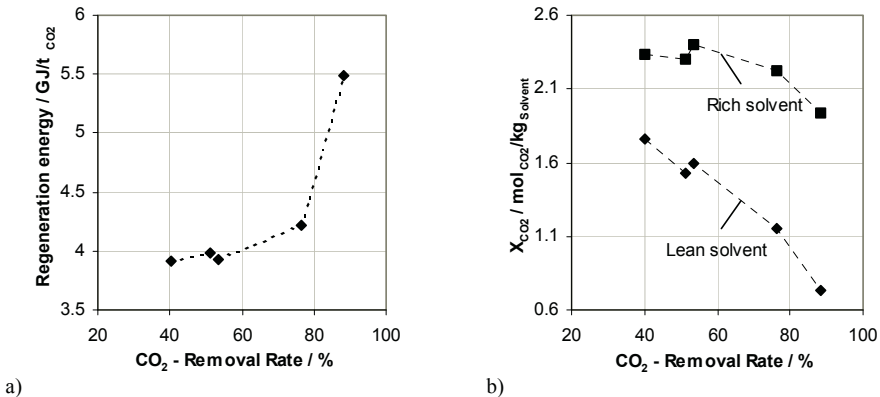


Figure 3: Influence of CO<sub>2</sub> removal rate on a) regeneration energy, and b) CO<sub>2</sub> loading in rich and lean solvents. All other process parameters are kept constant see Table 1.

For a given design of the absorption / desorption plant, a given solvent flow and for a given flue gas specification, there is a certain CO<sub>2</sub> removal rate that best fits the given plant design. In the case of the present pilot plant for MEA and  $p_{\text{CO}_2} = 110$  mbar that removal rate is 54 %. Higher removal rates would require higher columns or more effective internals.

### 3.3. Variation of flue gas flow rate

To study the influence of the fluid dynamic load of the absorber on the regeneration energy, the flue gas flow rate (F-Factor) was varied while maintaining a constant removal rate and a constant liquid to gas ratio. If the process was equilibrium controlled, that variation should not have any influence on the regeneration energy. Figure 4a, however, shows that with the decrease of the flue gas flow rate also the regeneration energy demand decreases. At lower gas flow rates; the mass of CO<sub>2</sub> transferred between the phase's decreases, while the surface area remains almost constant. For kinetically controlled processes, this is favorable. Figure 4b gives more details. As the F-Factor decreases, the rich loading increases, and since the CO<sub>2</sub> removal rate and liquid to gas ratio are kept constant, also the lean loading increases. With the increase of the lean loading, the CO<sub>2</sub> separation in the desorber becomes easier, resulting in a decrease of the regeneration energy.

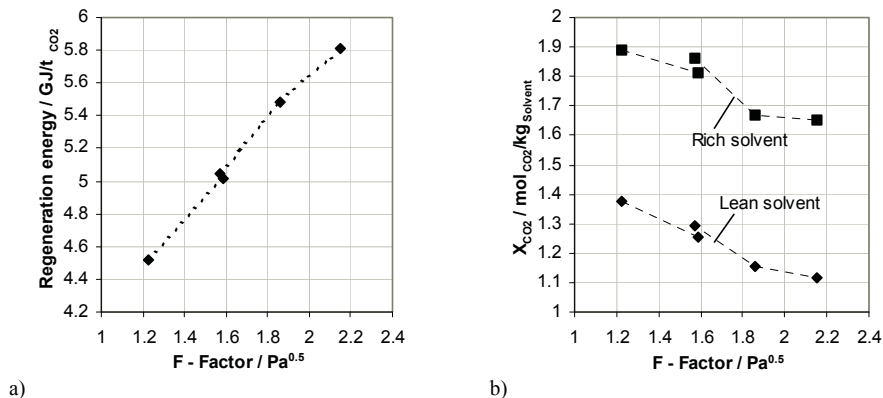


Figure 4: Influence of the gas-side fluid dynamic load of the absorber (F-factor) on a) regeneration energy, and b) CO<sub>2</sub> loading in rich and lean solvents. All other process parameters are kept constant see Table 1.

### 3.4. Variation of solvent flow rate

The solvent flow rate was varied maintaining a constant removal rate by adjusting the regeneration energy. Figure 5a shows the variation of the regeneration energy with the variation of the solvent flow rate for a constant removal rate and flue gas flow rate. For the shown operating conditions the optimum solvent flow rate at minimum regeneration energy was 200 kg/h. As shown in Figure 5b the increase in the regeneration energy to the left of the optimum solvent flow is related to the high amount of stripping steam needed to obtain the required low lean loading. The increase in the regeneration energy to the right of the optimum solvent flow can be explained by the energy requirement to heat up the higher solvent flows.

Figure 5b also shows that there are four major contributions to the regeneration energy, namely: desorption enthalpy, stripping steam, heating up of the solvent feed and the condensate reflux. The specific desorption enthalpy mainly depends on the temperature if the CO<sub>2</sub> loading is less than 0.5 mol<sub>CO<sub>2</sub></sub>/mol<sub>MEA</sub> [7] and thus is almost constant for the experimental conditions in this parameter study. In addition the reflux water flow at the top of the desorber is small, so that the optimum solvent flow rate depends mainly on the energy requirement for stripping steam and for heating up of the solvent. The four contributions to the regeneration energy shown in Figure 5b are mainly influenced by the heat of absorption and equilibrium data for the solubility of CO<sub>2</sub>. For solvent selection these

physical properties have to be taken into account. Because of a coupling of the four energy parts and the mentioned properties, the solvent comparison has to be carried out carefully.

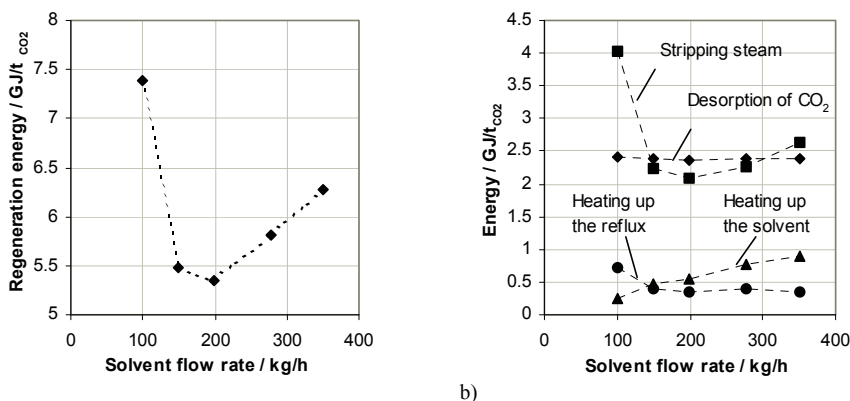


Figure 5: Influence of the solvent flow rate on a) regeneration energy, and b) four different contributions to the regeneration energy. All other process parameters are kept constant see Table 1.

#### 4. Model

The experimental results were compared to simulations that are based on a rigorous rate-based model, which was developed by BASF [6] and was implemented in the process simulator CHEMASIM. In this model the column is divided vertically into segments and in each of these nonequilibrium segments, the gas and liquid are exchanging heat and mass. The two-film model is used to describe this process and it is assumed that the bulk phases are ideally mixed with uniform concentrations and temperatures. The mass-transfer resistance is assumed to lie in two film layers that are separated by the gas/liquid interface. At the interface, the vapor and the liquid are in equilibrium. The films are further divided into film segments. With this film discretization, it is possible to calculate more reliable concentration profiles in the film, which is essential for reactive systems, where as a consequence of the reaction the mass transfer can be enhanced. The simulation model allows the calculation of chemical reactions in the bulk phases, and also within the film. The diffusion of the different components in the film layers is described by the Stefan-Maxwell equations. The simulation results are discussed in the section 5.2.

#### 5. New solvents

The research for new solvents for CO<sub>2</sub> capture in CASTOR was focused on amine solvents. Both pure amine and amine blends were studied. The present report covers two such blends, CASTOR1 and CASTOR2, which are compared to MEA as a reference. For solvent selection several criteria like equilibrium data for the CO<sub>2</sub> solubility, overall mass transfer kinetics, solvent degradation and corrosion behavior were analyzed. Among these criteria the equilibrium data are most important for determination of the regeneration energy of the process.

##### 5.1. Methodology for solvent comparison in the pilot plant

For solvent comparison in the pilot plant, a consistent methodology has to be defined and applied to all solvents, here to MEA, CASTOR1 and CASTOR2. In the present work for that purpose experiments were carried out at constant CO<sub>2</sub> removal rate  $\Psi_{CO_2}$  but with varying solvent flow rates. This was achieved by adjusting the regeneration energy. The results of each of these sets of experiments are analyzed in plots of the regeneration energy versus the solvent flow rate, like the one shown in Figure 5a. This allows finding an optimum solvent flow rate. The optima for the different solvents are then compared. They basically only depend on the specified removal rate that has to be chosen suitably considering the design of the given pilot plant.

## 5.2. Comparison of new solvents with MEA

For CO<sub>2</sub> capture from power plant flue gas, the target is a CO<sub>2</sub> removal rate of 90 %. Although the total height of the pilot plant is approx. 8 m, especially the packing height of the absorber (4.2 m) is not sufficient to reach 90 % CO<sub>2</sub> removal with a reasonable energy. As consequence, experiments were carried out with a lower removal rate of ~54 % as already discussed above. Figure 6 shows the comparison of the regeneration energy for MEA, CASTOR1 and CASTOR2 solvents with the variation of the solvent flow rate. MEA experiments show a decrease of the regeneration energy with decreasing solvent flow rates down to the lowest flow rate of 150 kg/h. This was also confirmed by simulations with MEA that show a similar decrease of the regeneration energy with decreasing solvent flow rates down to 150 kg/h, but an increase of the regeneration energy at a lower solvent flow rates and an optimum at about 150 kg/h. The model predictions for MEA are reasonable, even though the model slightly overestimates the regeneration energy requirement especially at low solvent flow rates. One of the reasons for these deviations could be the inaccuracy of the mass transfer correlations.

At a first glance on Figure 6 CASTOR1 and CASTOR2 do not seem to have advantages compared to MEA. A detailed analysis, however, shows that the apparently unfavorable results for CASTOR1 and CASTOR2 are mainly due to kinetical effects. This can be seen from Figure 7, which shows absorber operating lines for CASTOR1, CASTOR2 and MEA compared to their equilibrium curves at 40°C (absorber conditions). The distance between the operating line and the equilibrium curve gives an indication of the driving force for the mass transfer. For CASTOR1 and CASTOR2 very high driving forces are needed, due to the slow reaction kinetics, which are also confirmed by independent kinetic studies carried out by other partners in the CASTOR project. Furthermore, experiments like those shown in Figure 4 (for the case of MEA) were also carried out for CASTOR1 and CASTOR2. They confirm the very strong influence of kinetics on the results for these solvents. For MEA, only low driving force was needed due to the fast reaction kinetics. If higher columns or more effective packings were used, it can be expected that the energy requirement would be considerably lower for CASTOR1 and CASTOR2 but not for MEA. Experiments on this are under the way. Figure 7 also contains equilibrium curves at 120°C (desorber conditions). The comparison of the equilibrium curves at 40°C and 120°C shows that very high cyclic capacities can be expected for CASTOR2. This should result in a minimum energy requirement at lower solvent flow rates that could not be reached in the present study due to limitations of the pumps (see Figure 6), so that further improvements can be expected also from this side.

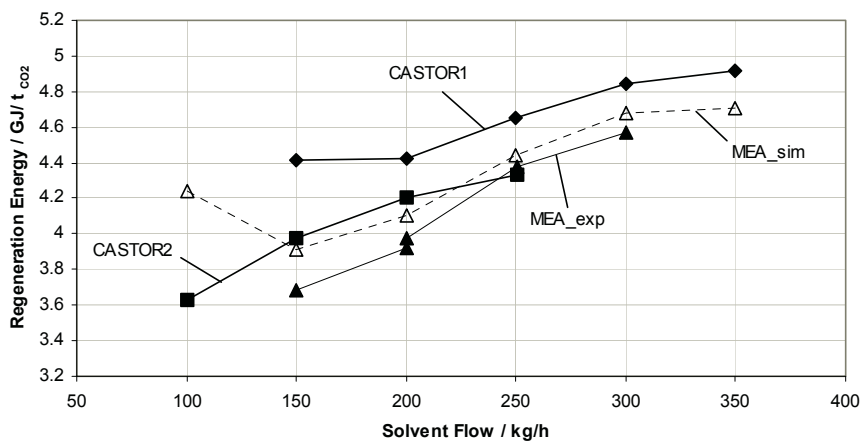


Figure 6: Regeneration energy comparison for MEA, CASTOR1 and CASTOR2 for a constant removal rate of 54 %.

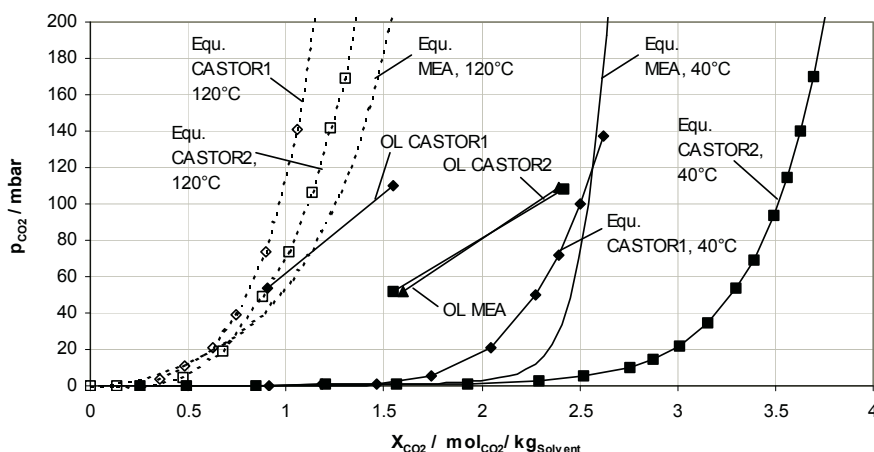


Figure 7: Comparison of absorber operating lines (OL) for MEA, CASTOR1 and CASTOR2 for a solvent flow rate of 150 kg/h and for a constant removal rate of 54 %.

## 6. Conclusions

Systematic parameter studies on CO<sub>2</sub> capture from flue gases were carried out with the standard solvent MEA in a pilot plant, to obtain a baseline for the new solvents. A rate based simulation model, which is implemented in the process simulator CHEMASIM, was able to predict the experimental results for MEA. A new methodology for comparison of new solvents with MEA has been developed and using this new methodology, two new solvents were tested in the pilot plant. Results from the pilot plant show that for lower solvent flows CASTOR2 show an advantage and for higher heights of the absorber column, CASTOR1 and CASTOR2 should allow lower regeneration energy compared to MEA.

## Acknowledgment

This work was carried out within the CASTOR Integrated Project and supported by the European Commission (Contract n° SES6-CT-2004-502586).

## References

- 1 CASTOR: CO<sub>2</sub> from Capture to Storage. Integrated Project partially funded by the European Commission under the 6<sup>th</sup> Framework Program (Contract n° SES6-CT-2004-502586). <https://www.co2castor.com>
- 2 R. Notz, N. Asprion, I. Clausen, H. Hasse: Selection and Pilot Plant Tests of New Absorbents for Post Combustion Carbon Dioxide Capture, *Chemical Engineering Research and Design* 85 (2007) 510-515
- 3 T. Mimura, S. Shimijo, T. Suda, M. Iijima, S. Mitsuoka: Research and Development on Energy Saving Technology for Flue Gas Carbon Dioxide Recovery and Steam System in Power Plant. *Energy Convers. Mgmt* 36 (1995) 397–400
- 4 T. Mimura, H. Simayoshi, T. Suda, M. Iijima, S. Mitsuoka: 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* 38 (1997) S57-S62
- 5 R. Notz: CO<sub>2</sub>-Abtrennung aus Kraftwerksabgasen mittels Reaktivabsorption. PhD Thesis- Universitaet Stuttgart, Germany (2009)
- 6 N. Asprion: Nonequilibrium Rate-Based Simulation of Reactive Systems: Simulation Model, Heat Transfer, and Influence of Film Discretization, *Ind. Eng. Chem. Res.* 45 (2006) 2054-2069
- 7 I. Kim, H.F. Svendsen: Heat of Absorption of Carbon Dioxide (CO<sub>2</sub>) in Monoethanolamine (MEA) and 2-(Aminoethyl)ethanolamine (AEEA) Solutions. *Ind. Eng. Chem. Res.* 46 (2007) 5803-5809
- 8 M.R. Abu-Zahra, L.H.J. Schneiders, J.P.M. Niederer, P.H.M. Feron, G.F. Versteeg: CO<sub>2</sub> capture from power plants: Part I. A parametric study of the technical performance based on monoethanolamine. *International Journal of Greenhouse Gas Control* 1 (2007) 37-46