Available online at www.sciencedirect.com

SciVerse ScienceDirect

Energy Procedia 37 (2013) 1844 – 1854

Energy Procedia

GHGT-11

# Overall Process Analysis and Optimisation for $CO_2$ Capture from Coal Fired Power Plants based on Phase Change Solvents Forming Two Liquid Phases

Ulrich Liebenthal[a,]*, Diego Di D. Pinto[b], Juliana G. M.-S. Monteiro[b], Hallvard F. Svendsen[b], Alfons Kather[a]

[a]*Hamburg University of Technology, Institute of Energy Systems, Denickestraße 15, D-21073 Hamburg, Germany*
[b]*Norwegian University of Science and Technology, Department of Chemical Engineering, N-7491 Trondheim, Norway*

## Abstract

In this work the potential of a novel post-combustion $CO_2$ capture process is analysed with respect to the integrated overall process. As solvent a blend of two amines (DEEA/MAPA) which forms two liquid phases under $CO_2$ loading is used. The two phases have distinct physical characteristics. Only the heavy phase, rich in $CO_2$ loading, is led to the desorber. The novel solvent combination promises very low energy consumption compared to a 30 wt.-% MEA solution. The efficiency penalty, taking into account the integrated overall process, is very low too. Furthermore, different integration configurations in the overall process are investigated to show the effect in greenfield and retrofit power plant cases.

*Keywords*: Post-cobustion; $CO_2$ capture; Integration, phase change solvents

## 1. Introduction

There are many concepts for post-combustion $CO_2$ capture from coal-fired power plants, but it is generally agreed that the implementation of an absorption-desorption process using a chemical solvent is the most developed and mature process for deployment in the near- to middle-term [1]. A major challenge

---

* Corresponding author. Tel.: +49-40-42878-2771; fax: +49-40-42878-2841.
*E-mail address:* ulrich.liebenthal@tuhh.de.

doi:10.1016/j.egypro.2013.06.064

remains in reducing the thermal heat duty for desorption. Besides the heat duty for solvent regeneration, the power duty for $CO_2$ compression is the second largest contributor to the net efficiency loss of the power plant [2]. Within the iCap project (7th framework programme of the EU) a novel absorbent system, consisting of a blend of two amines, a tertiary amine, DEEA (Diethylaminoethanol), and a diamine, MAPA (N-Methyl-1,3-Propanediamine), is developed. This particular system, at certain concentrations, forms two liquid phases which split according to loading. The two phases can be separated by taking advantage of their different density. The heavy phase contains $CO_2$ at a very high concentration resulting in a low circulation rate, reduced thermal energy requirements for $CO_2$ desorption, and a possibility for a desorption process at elevated pressure which decreases the energy requirement for $CO_2$ compression. The light phase is lean in $CO_2$ and is recycled to the absorber after mixing with the regenerated heavy phase.

Screening tests were performed to evaluate the new solvent performance as regards $CO_2$ absorption. $CO_2$ partial pressures from 1 to 20 kPa were used and the absorption rate was measured at three different temperatures: 40 ºC, 60 ºC and 80 ºC. The absorption was stopped after reaching 95% of equilibrium. The new solvent showed high initial absorption rate and loading.

After separating the two phases, vapour liquid equilibrium tests were performed on the heavy phase where the total pressure was measured as function of temperature. The new system has a much higher total pressure than the benchmark MEA 30 wt.-%, which was calculated using the refined electrolyte non-random two-liquid (NRTL) model with the parameters given in [3]. This behaviour allows the regeneration section to operate not only at lower temperatures, but also at elevated pressures. Hence, it is a suitable solvent for reducing energy requirements (and costs) for both regeneration and compression.

Besides equilibrium data, the physicochemical properties of the two-phase system were measured to ensure validated data for process simulation. The data were modelled using empirical and semi-empirical correlations and then implemented into the NTNU/SINTEF in-house simulation tool CO2SIM [4].

Optimisation of the overall process, however, requires consideration of the impact of process characteristics not only on the $CO_2$ capture system itself but also on the overall process in a holistic approach. Towards this, the simulation results from the capture system are implemented in an accurate model of a state-of-the-art coal fired steam power plant and $CO_2$ compressor model. The efficiency penalty is caused by steam extraction for solvent regeneration, electrical power for the $CO_2$ compression, auxiliary demand for the pumps and blowers within the capture plant and the cooling water pumps for the additional cooling duty. Results for both a new power plant model especially designed for $CO_2$ capture (greenfield) and retrofitted power plants (retrofit) were obtained. It is shown that not only the amount of extracted heat (steam mass flow) but also the quality of extracted steam (pressure) strongly influences the overall net efficiency. To enable a direct comparison with available technologies a capture plant using 7 molal (~ 30 wt.-%) MEA is taken as reference.

This work will give an overview of the optimisation procedure and an energetic evaluation of the two-phase absorption process combined with a power plant in comparison also with a system using MEA.

## 2. Description of the capture process

Industrial processes for removing acid gases from different gas streams by means of chemical absorption with amine solutions are well established. The 30 wt.-% MEA process is still considered the benchmark technology. The process proposed here requires only minor modifications of the traditional process plant design. As described above, the chosen solvent, a mixture of 5 M DEEA and 2 M MAPA, forms two liquid phases upon $CO_2$ loading. At the bottom of the absorber, the rich solution consists of a $CO_2$ and MAPA rich phase (heavy phase) and a DEEA rich phase (light phase) that is lean in $CO_2$. After separation, only the heavy phase is regenerated in the desorber. After regeneration, this solution is mixed with the light phase and fed back to the top of the absorber. Figure 1 shows a simplified flow sheet of the process described.

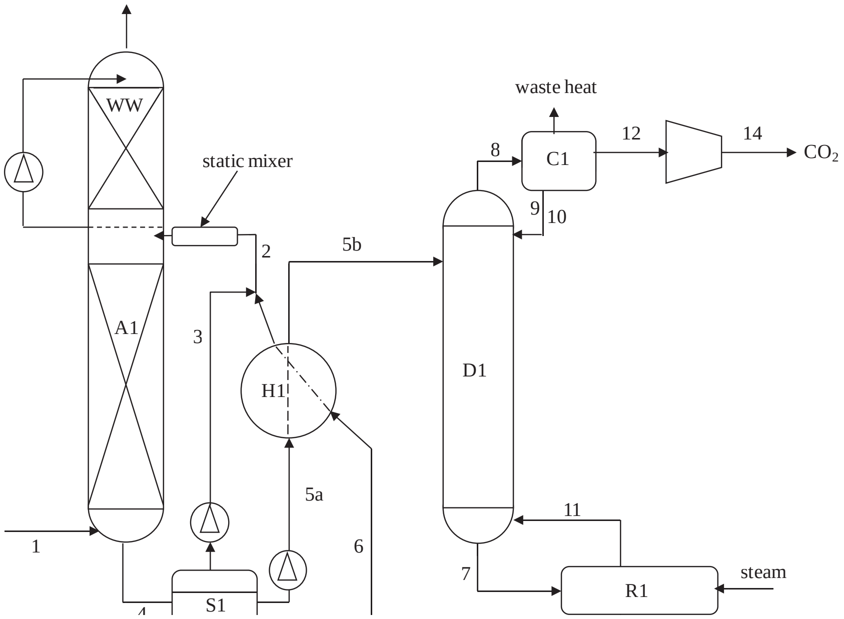


Figure 1: Simplified flow sheet for the capture process

The modifications lead to a lower liquid flow rate in the desorber. Moreover, DEEA, which is a tertiary amine, is preferentially stripped, potentially lowering the energy demand of the reboiler. Given the high $CO_2$ capacity of the heavy phase, it is possible to operate the desorber column at pressures higher than atmospheric, hence saving power for the subsequent $CO_2$ compression. Higher pressures in the desorber can also lead to a reduced size of the column. The operational pressure, however, implies an increased heat duty in the reboiler. This trade-off allows for plant optimisation through process integration.

## 3. Integrated overall process

Post-combustion $CO_2$ capture based on wet chemical absorption decreases the net efficiency of the power plant through the interaction between the power plant, the capture plant and the compression train. The main interface quantities affecting the net efficiency are

- the heat duty needed for solvent regeneration in the reboiler of the capture plant;
- the electrical duty of the $CO_2$ compressor;
- the electrical duty of pumps and blowers within the capture plant;
- the electrical duty of the circulation pumps for the large amounts of cooling water needed in the capture and compression processes.

For an overall process evaluation and optimisation the detailed consideration of all these interface quantities is necessary. Even if the heat duty represents the largest contributor to the efficiency penalty of the overall process, the lowest heat duty does not lead generally to the lowest overall efficiency penalty [5].

### *3.1. Integration*

The best extraction point to provide for the large amounts of steam at the required pressure level and at minimal efficiency penalty, low investment costs, high flexibility, and a good part-load capability is the crossover pipe connecting the IP and LP steam turbine (IP/LP crossover).

Two main integration options must be differentiated:

1. The integration of a capture plant and a $CO_2$ compression train in an existing power plant (retrofit).
2. The integration of a capture plant and a $CO_2$ compression train already during the design of a new power plant (greenfield).

*Retrofit integration*

The integration of a $CO_2$ capture process in an existing power plant requires modifications to ensure the supply of steam for solvent regeneration at the right steam quantity but also quality. Typical IP/LP crossover pressures (at operation without $CO_2$ capture) range between 3 and 9 bar, depending on power plant size, turbine configuration and manufacturer. When extracting steam for the reboiler, the crossover pressure decreases according to Stodola’s ellipse law. To provide the reboiler with the required steam quantity and quality, two additional components must be applied in the water-steam cycle of the power plant:

1. A throttle is to be located in the steam branch to the reboiler. With this component, excessive pressure can be reduced to provide the steam at a pressure that ensures condensation at the correct temperature.
2. A pressure maintaining valve (PMV) is to be retrofitted upstream of the LP turbine inlet. With this component the pressure can be held at a certain value as required by the reboiler. Depending on the amount of steam extracted, thus depending on the pressure drop due to Stodola’s ellipse law, the maintaining of the pressure causes a pressure drop over the PMV and an additional energy penalty due to the lower LP turbine inlet pressure.

Because of the steam extraction the pressure in the IP/LP crossover drops below the nominal pressure. Therefore, the volume flow in the last stages of the IP turbine increases since the live steam mass flow remains constant. Due to the increased volumetric steam flow, mechanical stresses become higher compared to the design case and can lead to turbine damage. To provide for a safe operation, a retrofit of the IP turbine (designed for operation with $CO_2$ capture) can be applied. In this work the PMV is activated in case of volume flows higher than 140 % compared to the design case. With this measure the minimal exit pressure is limited to avoid extreme mechanical stresses.

The reboiler condensate is forwarded to the feed water preheaters of the power plant. The exact feed-in position depends on the temperature level of the reboiler condensate (Figure 2).

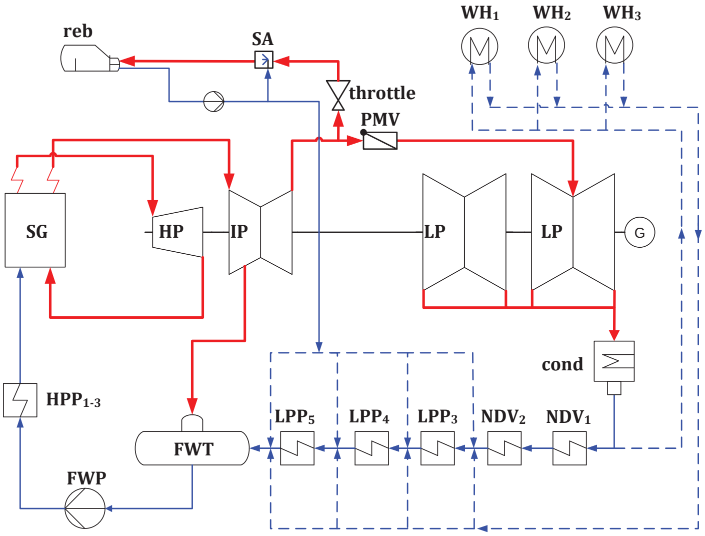
### *Greenfield integration*

In a greenfield power plant, the water-steam cycle can be adapted to optimise the operation with $CO_2$ capture. In this work it is assumed that the power plant is designed and optimised for a capture rate of 90 % at full-load operation. Hence, the IP/LP pressure is chosen to perfectly match the pressure required by the reboiler. This eliminates the losses induced by the throttle or the PMV that occur in the retrofit integration case. Note that a perfect match of IP/LP steam pressure and required steam pressure is only valid for one operational point. As soon as the power plant load or the capture rate of the capture plant differs from the design point, the throttle or the PMV must be activated leading to an additional efficiency penalty. Special measures to improve the part-load efficiency are not considered further in this work.

The reboiler condensate is forwarded to the feed water preheating train of the power plant as described already for the retrofit integration (Figure 2).

### *Additional waste heat integration*

The water steam cycle offers the possibility to integrate parts of the waste heat. Especially waste heat from the overhead condenser of the capture process and the intercoolers of the $CO_2$ compression possess usable temperature levels. Simulations show that the power plant process usually does not contain enough



cond: condenser
FWT: feed water tank
FWP: feed water pump
G: generator
HP: high pressure
HPP: high pressure preheater
IP: intermediate pressure
LP: low pressure
LPP: low pressure preheater
PMV: pressure maintaining vavle
reb: reboiler
SA: spray attemperation
SG: steam generator
WH: waste heat

Figure 2: Integration of the interfaces quantities in the water-steam cycle

heat sinks to integrate the whole amount of waste heat available. Two heat sink categories can be identified: The combustion air preheating and the preheating train of the water-steam cycle. The effort involved in realising the heat integration by preheating of the combustion air is much higher than the measures that involve the condensate preheating train. In [6] it is concluded that the potential of using combustion air as heat sink is very limited. Therefore, only the preheating train of the water-steam cycle is used as waste heat sink in this work.

### *3.2. Power plant model*

The power plant model[†] used in this work is based on a state-of-the-art supercritical power plant. The hard-coal-fired power plant with high live steam parameters (285 bar, 600 °C) has a gross output of 1100 $MW_{el}$ and a net efficiency of 45.3 % (related to LHV) at its design point (full load operation without $CO_2$ capture). The preheating train consists of three high pressure preheaters, the feed water tank and five low pressure preheaters.

The cooling system is based on a natural draft cooling tower. In case of operation with $CO_2$ capture an additional cooling system is assumed, which compensates for the cooling duty of the $CO_2$ capture and compression process. In a retrofit integration the condensate mass flow is strongly decreased due to steam extraction for solvent regeneration. The minimal cooling water mass flow is limited to 80 % related to full-load operation without $CO_2$ capture. Consequently, the cooling water temperature gain and so the condenser pressure is decreased at operation with $CO_2$ capture. This has a positive effect on the efficiency of the water-steam cycle. For a greenfield integration the condenser pressure is not affected, as the design is based on operation with $CO_2$ capture.

The turbine efficiencies are calculated taking into consideration the dry isentropic efficiencies (depending on the size of the turbine), influence of wet steam (Baumann Correlation), and exit losses in the last stages of the LP turbine. All boundary conditions used in this work have been agreed beforehand with manufacturers and electric supply companies so as to reflect current reality. The main characteristics of the power plant model (without $CO_2$ capture) are listed in Table 1.

Table 1: Characteristics of the power plant model without $CO_2$ capture

| Heat input | 2243 $MW_{th}$ | *Flue gas downstream of FGD unit* | |
|---|---|---|---|
| Net output | 1015 $MW_{el}$ | Mass flow | 1063 kg/s |
| Net efficiency | 45.3 % | Pressure | 1.018 bar |
| Spec. $CO_2$ emissions | 769 g/kWh | Temperature | 50 °C |
| Live steam temperature | 600 °C | $CO_2$ | 13.5 vol.-% |
| Live steam pressure | 285 bar | $H_2O$ | 20.0 vol.-% |
| Reheat temperature | 620 °C | $N_2$ | 70.2 vol.-% |
| Reheat pressure | 55 bar | $O_2$ | 3.5 vol.-% |
| Condenser pressure | 40 mbar | Ar, $SO_x$, $NO_x$ | 0.8 vol.-% |

---

[†] The power plant is modelled with the commercial software tool EBSILON®*Professional.*

### 3.3. $CO_2$ Compressor model

In this study an integrally-geared radial compressor is considered. A calculation method for the real gas behaviour is chosen to take into account the non-ideal behaviour of the $CO_2$ during compression and cooling. As the $CO_2$ leaving the overhead condenser (downstream of the desorber) is water saturated, the compressor has to cope with moist $CO_2$. The stage efficiencies range (depending on the size of the blades) from 80 % - 85 %. Detailed information about the assumptions in modelling the $CO_2$ compressor is published in [7]. All assumptions again agree well with information from manufacturers.

The desired $CO_2$ compressor discharge pressure (= pipeline pressure) is assumed to be 110 bar. Varying desorber pressures lead to varying suction pressures. To cover the range of suction pressures different compressor configurations are taken into consideration. The pressure ratio of each stage is between 1.4 and 2.1. The quality and the quantity of the waste heat of the compression process depend on the number of intercoolers, position of the intercoolers and the intercooling temperature [7]. A higher quality of waste heat implies both more effective heat integration potential, but also a higher electrical demand of the compression process. In this work an optimisation algorithm was applied to find the best compressor configuration with respect to the overall process, considering the above described counteracting effects.

The steam extraction for solvent regeneration reduces the water mass flow in the LP preheating train. Hence, the steam extraction strongly reduces the potential of heat integration. The more steam extracted, the less heat can be transferred to the preheating train. If waste heat from the capture process is available, avoidance of additional waste heat from the compression process is likely to be most beneficial.

## 4. Results

### 4.1. Capture process simulations

The process described in Figure 1 was simulated using the CO2SIM software. The L/G ratio was varied for two different reboiler pressures: 4 and 6 bar. As a reference a capture process based on 30 wt.-% MEA is considered, too.

The energetic interface quantities generated with the capture plant models are listed in Table 2 for the optimal operation point of each solvent. These parameters are then implemented into the overall process model to predict the potential of this novel capture process.

Table 2: Interface quantities (between the capture process model and the overall process model) for the optimal operation points

| Type of interface quantity | MEA | DEEA/MAPA | Unit |
|---|---|---|---|
| Reboiler heat duty | 3.5 | 2.4 | $(MJ_{th} / kg\ CO_2)$ |
| Accumulated cooling duty | 4.1 | 2.8 | $(MJ_{th} / kg\ CO_2)$ |
| Electrical power duty (pumps and blowers) | 0.05 | 0.11 | $(MJ_{el} / kg\ CO_2)$ |
| Reboiler temperature (solvent side) | 120 | 88 | (°C) |
| Desorber pressure | 2.0 | 4.0 | (bar) |
| Available waste heat @ overhead condenser* | 1.0 | 0.1 | $(MJ_{th} / kg\ CO_2)$ |
| Temperature level of available waste heat | 104 | 77 | (°C) |

*Note that the available waste heat is not equal to the actual useable waste heat

Figure 3a shows the heat duties for both solvents. The capture rate is kept constant at 90 %. For MEA (no absorber intercooling or lean vapour compression) the lowest heat duty is calculated to be 3.5 MJ/kg $CO_2$ at a desorber pressure of 2 bar. DEEA/MAPA shows the lowest heat duty at low desorber pressures reaching 2.2 MJ/kg $CO_2$ at low L/G ratios. The magnitude of L/G in Figure 3 is scaled to allow a direct comparison between both solvents.

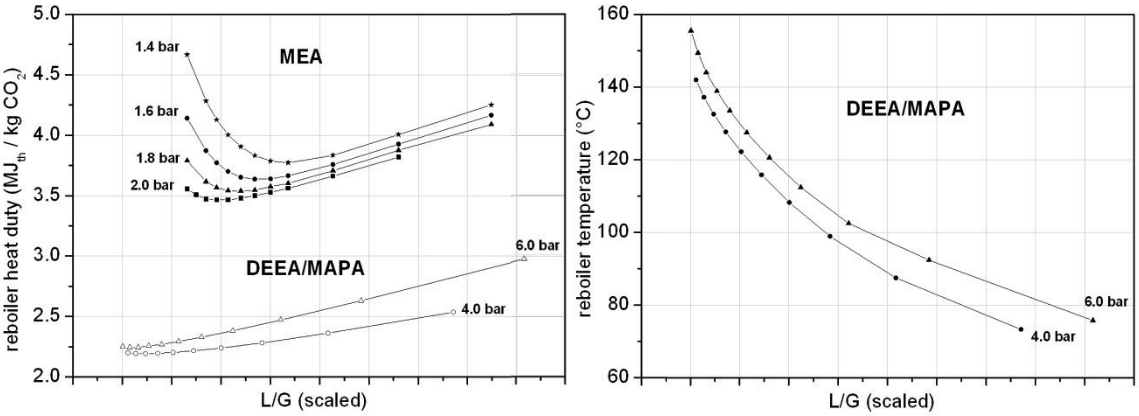


Figure 3a (left): Reboiler heat duty for MEA and DEEA/MAPA for varying L/G and different desorber pressures
3b (right): Reboiler temperature for DEEA/MAPA for varying L/G and different desorber pressures

### *4.2. Overall process simulations*

For both integration options (retrofit and greenfield) the potential of waste heat integration is considered. Waste heat sources are the overhead condenser of the capture process and the intercoolers of the $CO_2$ compression.

*Greenfield integration*

The results of the greenfield analyses are shown in Figure 4a. For MEA the overall efficiency penalty follows the trend of the heat duties (Figure 3a). The optimal operation pressure of the desorber is 2 bar for the entire range of the L/G variation. The lowest efficiency penalty was predicted to be 9.5 %-points.

The DEEA/MAPA solvent shows the lowest overall net efficiency penalty (6.3 %-points) at a desorber pressure of 4 bar. For each desorber pressure it is conspicuous that the optima of the overall process differ from the lowest heat duties (Figure 3a). This is caused by the influence of the reboiler temperature which increases with decreasing L/G (Figure 3b). A higher reboiler temperature leads to a higher required exergy level of the extracted steam (i.e., a higher steam pressure). In contrast to MEA the influence of the reboiler temperature overcompensates for the benefits of the lowest heat duty. This clearly illustrates that both the extracted steam quantity and quality matter in terms of an overall process evaluation.

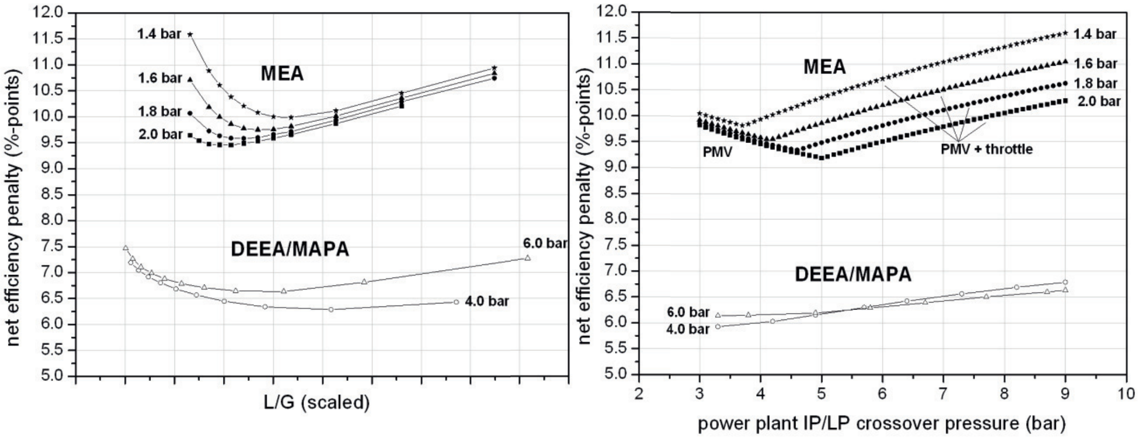


Figure 4a (left): Greenfield integration - net efficiency penalty (LHV) for varying L/G at different desorber pressures
4b (right): Retrofit integration - net efficiency penalty (LHV) for varying IP/LP crossover design pressures at different desorber pressures (optimised L/G)

*Retrofit integration*

In a retrofit integration the main influencing boundary condition is the design pressure in the IP/LP crossover (without $CO_2$ capture). This basically depends on the turbine manufacturer. When integrating a steam extraction for $CO_2$ capture this value plays an important role. Besides the quality and quantity of extracted steam it decides whether a throttle or a pressure maintaining valve is required. A variation of the IP/LP crossover pressure (without $CO_2$ capture) and the referring efficiency penalty is shown in Figure 4b. For each IP/LP crossover pressure the L/G is optimised in this case.

For MEA the net efficiency decreases with increasing design IP/LP crossover pressure. An optimum is reached when the actual pressure in the IP/LP crossover matches the pressure which is required for $CO_2$ capture. A further increase of the design IP/LP crossover pressure leads to an increased efficiency penalty as the pressure loss over the PMV or the throttle increases. The steam extraction for MEA causes a pressure drop in the IP/LP crossover that would lead to a critical increased volume flow at the exit of the IP turbine (cf. Section 3.1). Hence the PMV is activated for the entire range of IP/LP crossover pressure variation. For higher design IP/LP crossover pressures compared to the optimum the throttle needs to be activated as well to yield the steam conditions required for $CO_2$ capture.

For DEEA/MAPA the capture process can be adapted for each desired IP/LP crossover pressure. As the desorber pressure and so the reboiler temperature is very flexible it is possible to find a close match between the required steam pressure and the actual IP/LP crossover pressure. The steam extraction quantity does not lead to a critical increase of volume flow downstream of the IP turbine. Hence, in contrast to MEA, the PMV does not need to be activated. That means that for a wide range neither a PMV nor a throttle is activated. This operation point is referred to as “open valve operation – OVO”. Only at very high design IP/LP crossover pressures a throttle is required, especially for low desorber pressures. Further information about the retrofit integration is described in [2].

The effects described above lead to the net efficiency penalty curves shown in Figure 4b. For high IP/LP crossover pressures the desorber pressure has only a small effect as the reboiler temperature at high desorber pressures compensates for the lower heat duty at low desorber pressures. In general, the DEEA/MAPA process benefits from low design IP/LP crossover pressures.

This analysis shows that the power plant configuration influences strongly the overall efficiency penalty caused by $CO_2$ capture. Even if the desorber pressures of the capture plants show optima at different design IP/LP crossover pressures the optimal operating pressure does only change for IP/LP crossover pressures above 5.4 bar for DEEA/MAPA. For MEA 2 bar is the best desorber pressure for the entire range of the analysis.

An interesting observation is that the lowest efficiency penalty of the optimised retrofit case (9.2 %-points for MEA, 6.3 %-points for DEEA/MAPA) is lower than the greenfield case (9.5 %-points for MEA, 5.9 %-points for DEEA/MAPA). This can be explained by the following effects. In case of retrofit integration the steam mass flow which is now led to the condenser is strongly reduced. This leads to a lower condenser pressure caused by the component overdesign at the new operating point. Hence, the available enthalpy difference for the turbine increases and thus the net output increases. For greenfield integration the condenser is matched to the reduced steam mass flow and corresponds to a pressure of 40 mbar at operation with $CO_2$ capture. Only if a back-up LP turbine were to be considered to enable operation without $CO_2$ capture, a larger condenser would be a realistic assumption for the greenfield case.

## 5. Summary and outlook

In this work the potential of a novel post-combustion $CO_2$ capture process is analysed with respect to the integrated overall process. It turns out that the proposed solvent combination, DEEA/MAPA, promises a very low energy consumption compared to 30 wt.-% MEA. The overall efficiency penalty is very low, too. A greenfield-case analysis shows that the optimal operation point of the novel capture process does not match with the operation point with the lowest energy consumption. The benefits of an elevated desorber pressure to reduce the energy consumption for $CO_2$ compression is overcompensated by the lower heat duty at lower desorber pressures.

An energetic evaluation is carried out not only for new build power plants, which are designed for operation with $CO_2$ capture, but also for several retrofit cases. In contrast to MEA, it is shown for DEEA/MAPA that the overall process for retrofit integration benefits from low IP/LP crossover pressures.

The results presented regarding the novel capture process are still partially based on assumptions that need to be proven within the future research activities of iCap. At NTNU both the capture plant model and a pilot plant are under construction to improve the accuracy of the process predictions. That means that the results presented in this work should serve as a first indication only of the potential offered by the new capture technology. After the proof of principle the technical feasibility of the novel concept must still be investigated further.

## References

[1] Rochelle, G.T. (2009), Amine scrubbing for $CO_2$ capture, *Science*, 325, 1652 - 1654.

[2] Liebenthal et al. (2011), Derivation of correlations to evaluate the impact of retrofitted post-combustion $CO_2$ capture processes on steam power plant performance, *International Journal of Greenhouse Gas Control*, Issue 5, 1232-1239.

[3] Hessen, E. T.; Haug-Warberg, T.; Svendsen, H. F. (2010), The refined e-NRTL model applied to $CO_2$–$H_2O$–alkanolamine systems, *Chem. Eng. Sci.*, 65, 3638 – 3648.

[4] Hillestad, M.; Kvamsdal, H. M.; Chikukwa, A. (2011), A general column model in CO2SIM for transient modelling of $CO_2$ absorption processes, *Proceedings of the Trondheim CCS Conference (TCCS-6)*.

[5] Oexmann, J. (2011), Post-Combustion $CO_2$ Capture: Energetic Evaluation of Chemical Absorption Processes in Coal-Fired Steam Power Plants, Dissertation, TU Hamburg-Harburg.

[6] Pfaff, I.; Oexmann, J.; Kather, A. (2010), Optimised integration of post-combustion $CO_2$ capture process in greenfield power plants, *Energy*, 35 (10):4030-4041.

[7] Liebenthal, U.; Kather, A. (2011), Design and Off-Design Behaviour of a $CO_2$ Compressor for Post-Combustion $CO_2$ Capture Process, *Proceedings of the 5th Int. Conference on Clean Coal Technologies*, Saragoza, Spain.