# Carbon Dioxide Capture from Flue Gas

## Development and Evaluation of Existing
## and Novel Process Concepts

By

Mohammad R. M. Abu Zahra

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## Development and Evaluation of Existing and Novel Process Concepts

Proefschrift

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*door*

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*To my beloved wife (Manal)*

# SUMMARY

One of the main global challenges in the years to come is to reduce the $CO_2$ emissions in view of the apparent contribution to global warming. Carbon dioxide capture, transport, and storage (CCS) from fossil fuel fired power plants is drawing increased interest as an intermediate solution towards sustainable energy systems in the long term. However, CCS is still facing some challenges, such as large scale implementation requires high energy demands and leads to high cost. Innovation and optimization of the capture process is needed to reduce the energy requirement and to minimize the investment cost in order to make CCS viable for application in the near future.

The $CO_2$ post-combustion capture based on the absorption/desorption process with monoethanolamine (MEA) solutions, is considered as the state-of-art technology. In this thesis, the MEA process has been defined as the reference case for the purposes of comparison and benchmarking. By analysing the MEA reference case, it can be concluded that this is an energy intensive process due to the regeneration energy of the MEA solution (4 GJ/tonne $CO_2$).

For this conventional process, major energy savings can be realized by optimizing the lean solvent loading, the amine solvent concentration, as well as the stripper operating pressure. A minimum thermal energy requirement of 3.0 GJ/tonne $CO_2$ can be obtained using a 40 wt. % MEA solution and a stripper operating pressure of 210 kPa. Significant energy and cost savings can be achieved by increasing the MEA concentration in the absorption solution. It is, however, still to be investigated if high MEA concentrations can be used due to possible corrosion and solvent degradation. Increasing the temperature (operating pressure) in the stripper will lead to a higher efficiency of the regeneration and will reduce thermal energy requirement. Moreover, a high operating pressure will reduce the cost and the energy needed for $CO_2$ compression.

The economic baseline for $CO_2$ post-combustion capture using MEA is defined using 600 MWe coal fired power plant as a reference case and assuming 2005 as the reference year, 8% discount factor and 25 years as a project life. The process modelling results are used for providing the required input to the economic modelling. The economic evaluation for the MEA conventional process has shown that this process will lead to a cost of ~40 €/tonne $CO_2$ avoided. Using the baseline techno-economic evaluation as a starting point, a parameter study for the conventional $CO_2$ post-combustion capture process is performed. The main operating variables considered in this study were the MEA solvent concentration, the $CO_2$ removal percentage, the solvent lean loading, and the stripper operating pressure. The economic results show a minimum $CO_2$ avoided cost of 33 €/tonne $CO_2$ with an optimized process conditions of 0.3 mol $CO_2$/mol MEA lean solvent loading, using a 40 wt. % MEA solution and a stripper operating pressure of 210 kPa. This translates to 53 €/MWh cost of electricity, compared to 31 €/MWh for the power plant without capture. The difference in costs per tonne $CO_2$ avoided is small for $CO_2$ removal in the range between 80% and 95%.

The $CO_2$ post-combustion capture process overall performance is evaluated using pilot plant experimental results. Two different modelling approaches (equilibrium-stage and rate-based) are validated and compared using these large-scale pilot plant data. Equilibrium-stage and rate-based models are implemented using the commercial Aspen plus simulation tool. The study indicates that there are no major differences between the two modelling approaches in predicting the overall capture process behaviour for this pilot plant case (e.g. regeneration energy requirement, $CO_2$ removal % and solvent rich loading). Hence an equilibrium-stage model was preferred as the basis for over-all process modelling and benchmarking different capture solvents in view of its lesser complexity. The rate-based model, however, did yield more accurate predictions of the

temperature profiles and mass transfer inside the columns. As a result, for a detailed process design or understanding of the mass and energy profiles in the absorber and stripper columns, the rate-based approach should be applied.

The Hypogen concept (electricity generation with co-production of hydrogen) is considered one of the future energy options. This option will facilitate the use of a clean source of energy (hydrogen) for purposes like transportation and heating. This concept is based on the use of syngas for power production with $CO_2$ post-combustion capture incorporating the possibility of co-production of hydrogen (5-10% of the total syngas). In this concept, hydrogen is produced and purified in two different methods. The first method is based on increasing hydrogen content using the water gas shift reaction, followed by the separation of hydrogen from $CO_2$ using a high-pressure absorber. This absorber column is integrated with the ambient post-combustion capture process. The second method is based on the separation of hydrogen from syngas using polymeric membranes. In both options, the hydrogen will be further purified using a pressure swing adsorption system. Both options are feasible with an overall $CO_2$ capture cost comparable to the conventional post-combustion capture process. However, there are some limitations in the hydrogen purity using polymeric membranes. The advantage of the high-pressure absorber is more obvious if an advanced solvent, like the sterically hindered 2-amino-2-methyl-1-propanol (AMP), is used instead of a conventional solvent like MEA.

Increasing the $CO_2$ content in the flue gas is investigated by recycling the flue gas over the gas turbine. The flue gas recycle is beneficial for the overall capture process behaviour. The total flue gas flow rate is reduced with increasing flue gas recycle ratio. This reduction in the flue gas flow rate results in a smaller absorber column. The capital investment, the cost of electricity and cost of $CO_2$ avoided are reduced with increasing the flue gas recycle ratio. There is a marginal effect of the flue gas recycle on the solvent regeneration energy using the conventional MEA solvent. This is due to the limitation in MEA solvent capacity. Moreover, the effect of the flue gas recycle on the energy requirement and the overall cost is more significant using a different solvent with higher loading capacity (e.g. AMP).

As has been observed out of the MEA conventional process analysis, the desorption energy requirement is a significant burden for large-scale applications. To overcome the high-energy demand and to increase the operational flexibility, a new process concept is investigated. This process concept is based on dividing the $CO_2$ capture process into a bulk removal step and a deep removal step using two different solvent/systems. This two-step concept is evaluated for two different cases. Both cases are based on the use of MEA in the first step. In the second step, either AMP solution or coal/activated carbon is used for the removal of the remaining $CO_2$. The results show that the removal of $CO_2$ using coal or activated carbon is not advantageous due to the large quantity of coal/activated carbon needed. On the hand, the use of the two-chemical solvent has shown potential for possible process improvement. The overall energy requirements for the two-solvent concept can be reduced by 16 % as compared to the MEA reference case. Due to the higher capital costs, the overall cost of carbon dioxide avoided in the 2-step concept increases by 13 %. Still, increasing the capture process flexibility can be an advantage of the 2-step concept. This flexibility allows the application of different operating conditions and/or process systems in the different absorption-desorption units. One of the benefits can be the use of waste heat for regeneration, by operating one of the desorbers at lower temperature.

From the analysis of the post-combustion capture process that has been done in this thesis, it is evident that to achieve significant reduction of the capture process cost, multiple process parameters need to be improved. For future development of the $CO_2$ post-combustion capture process, it would be beneficial to direct the solvent development research towards solvents systems, which have lower reaction enthalpy and higher capacity. A significant improvement can be obtained by the development of solvent systems where the solvent is regenerated at higher pressure. In addition, smart process improvement and integration are required to achieve a reasonable cost reduction. Flue gas recycle over the gas turbine can contribute by reducing the overall capital investment. Splitting the capture process and/or combining it with co-production of hydrogen can be an extra economic parameter in the overall process optimization. It can be expected that by improving the process design and the solvent, implementation of post combustion capture on larger scale will be possible in the near future.

# SAMENVATTING

Een van de belangrijkste wereldwijde uitdagingen is het reduceren van $CO_2$ emissies. Koolstof dioxide-afvangst, -transport en -opslag (Carbon Capture Storage, CCS) van met fossiele brandstoffen gestookte energiecentrales trekt steeds meer aandacht als een tussentijdse bijdrage tot het komen tot een duurzame energiesysteem. Voor CCS zijn er echter uitdagingen zoals het feit dat grootschalige implementatie hiervan grote hoeveelheden energie vraagt en daardoor leidt tot hoge kosten. Innovatie en continue verbetering van het afvang proces is nodig om de energiebehoefte en de investeringskosten terug te dringen. Hierdoor kan het mogelijk worden om op korte termijn tot implementatie van CCS te komen.

De zogenaamde $CO_2$ post combustion afvangst gebaseerd op het absorptie/desorptie proces met monoethanolamine (MEA) als absorptievloeistof, wordt beschouwd als state-of-the-art technologie. In dit proefschrift wordt het MEA-proces verder gedefinieerd en gebruikt als referentiesysteem zodat andere systemen hiermee vergeleken kunnen worden. Uit analyse van het MEA-proces kan geconcludeerd worden dat dit een energie-intensief proces is door de hoge regeneratie energie (4 GJ/ton $CO_2$).

Voor het conventionele MEA gebaseerde proces kunnen significante energiebesparingen bekomen worden door optimalisatie van zowel de belading van de geregenereerde oplossing, als de MEA concentratie en de druk in de stripper. Een minimale regeneratie-energie van 3.0 GJ/ton $CO_2$ kan verkregen worden met behulp van een 40% MEA-oplossing en een werkdruk in de stripper van 210 kPa. Het is duidelijk dat er significante energie- en kostenbesparingen mogelijk zijn door het verhogen van de MEA-concentratie in de absorptievloeistof. Een kanttekening daarbij is wel dat bij hoge concentraties mogelijk problemen kunnen ontstaan met betrekking tot corrosie van apparatuur en stabiliteit van de absorptievloeistof. Een hogere temperatuur gekoppeld aan een hogere werkdruk in de stripper zal leiden tot hogere efficiëntie van de regeneratiestap en zal leiden tot een lagere energiebehoefte. Bovendien zal een hogere druk in de stripper de kosten en de energie die nodig is voor het comprimeren van $CO_2$ terugdringen.

Het economisch ijkpunt voor $CO_2$ post-combustion afvangst met MEA is gedefinieerd op basis van een 600 MWe kool gestookte energiecentrale met 2005 als referentie jaar, 8% rente en een afschrijving van 25 jaar. Om de nodige input te verkrijgen voor de economische modellen werden procesmodellen gebruikt. De economische evaluatie van het conventionele MEA-proces laat zien dat de kost voor het reduceren van 1 ton $CO_2$ 40 euro is. Gebruikmakend van deze technische-economische analyse is een studie uitgevoerd naar het effect van wijzigingen in de hoofd-proces-parameters op financieel vlak. De onderzochte parameters zijn de MEA-concentratie, het verwijderingpercentage $CO_2$, de belading van de geregenereerde absorptievloeistof en de werkdruk in de stripper. De resultaten van deze economische studie laten zien dat de minimale kost voor het terugdringen van $CO_2$ 33 euro per ton is, dit bij een belading van de geregenereerde absorptievloeistof van 0,3 mol $CO_2$ per mol MEA, gebruik makend van 40 wt% MEA oplossing en druk in de stripper van 210 kPa. Dit betekent dat de kosten voor elektriciteit met afvangst stijgt tot 53€/MWh in vergelijking met 31 €/MWh zonder afvangst. Het verschil in kosten voor $CO_2$-afvangst per ton verminderde $CO_2$ -uitstoot is voor een verwijdering tussen de 80 en 95% ervan, gering.

Twee verschillende benaderingen, evenwicht-gebaseerd versus kinetiek-gebaseerd, voor het modeleren van het $CO_2$ post combustion afvangst proces werden, geëvalueerd op basis van pilot-plant gegevens. De twee modellen worden met behulp van het Aspen plus simulatiepakket geëvalueerd. Het onderzoek wijst uit dat er geen grote verschillen zijn tussen de twee benaderingen op het gebied van het voorspellen van het macroscopische procesgedrag van de gebruikte pilootplant-casus (ondermeer op het vlak van regeneratie-energie, $CO_2$ -

verwijderingspercentage en absorptievloeistof-belading). Het evenwicht-gebaseerde model geniet, wegens de lagere complexiteit ervan, de voorkeur als basis voor de macroscopische procesmodelering en de vergelijking van verschillende absorptievloeistoffen. Het kinetiek-gebaseerde model resulteerde echter in een betere voorspelling van de temperatuurprofielen en van het massatransport binnen de absorptie- en de desorptiekolom. Dit is de reden dat, voor een gedetailleerd proces ontwerp, of voor het beter begrijpen van de massa- en temperatuursprofielen, de kinetiek-gebaseerde aanpak gebruikt dient te worden.

Het 'Hypogen'-concept (elektriciteitopwekking met gelijktijdige productie van waterstof) kan beschouwd worden als een van de toekomstige energie-opties. Deze optie zal het gebruik van waterstof als een schone vorm van energie, voor toepassingen als transport en verwarming, mogelijk maken. Dit concept is gebaseerd op het gebruik van syngas voor het opwekken van elektriciteit met $CO_2$ post combustion afvangst, waarbij het mogelijk wordt gelijktijdig waterstof te produceren (5-10% van het totale syngas). Hierbij kan waterstof geproduceerd en opgezuiverd worden volgens twee verschillende methoden. De eerste methode is gebaseerd op het verhogen van de waterstof-concentratie met behulp van de water–gas-shiftreactie, gevolgd door de scheiding van waterstof en $CO_2$ door middel van een hoge druk absorber. Deze absorptie kolom is geïntegreerd met het lage druk post-combustion afvangst proces. De tweede methode is gebaseerd op de verwijdering van waterstof uit syngas met behulp van polymeer-gebaseerde membranen. Voor beide opties geldt dat waterstof verder opgezuiverd wordt met behulp van pressure swing adsorptie. De economische studie laat zien dat beide opties vergelijkbaar zijn met het conventionele post combustion afvangst proces. Er zijn echter grenzen aan de zuiverheid van de waterstof na de afscheiding ervan met behulp van membranen. De voordelen van de hoge druk absorber wordt meer uitgesproken als een meer geavanceerde absorptievloeistof wordt gebruikt, zoals bijvoorbeeld 2-amino-2-methyl-1-propanol (AMP), in plaats van de conventionele absorptievloeistof MEA.

Het effect van het verhogen van het $CO_2$ -gehalte in rookgas door het gedeeltelijk terugvoeren van het rookgas naar de gasturbine werd onderzocht. De terugvoer van rookgas heeft een positief effect op het afvangst-proces in het geheel. De totale hoeveelheid rookgas wordt gereduceerd door het verhogen van de rookgas-terugvoer-verhouding. Het terugdringen van het rookgasdebiet leidt tot een absorptiekolom met een kleinere diameter. De kapitaalsinvestering, de kost voor het produceren van elektriciteit en de kost per ton $CO_2$ vermindering dalen door het verhogen van de rookgas-terugvoer-ratio. Er is een klein effect van de terugvoer van het rookgas op de energiebehoefte voor de regeneratie van de conventionele MEA-absorptievloeistof. Dit komt door de limiet aan de capaciteit ervan. Vandaar dat het effect van het terugvoeren van rookgas op de energieconsumptie meer uitgesproken wordt met een absorptievloeistof met een hogere capaciteit (bijvoorbeeld AMP).

Zoals duidelijk wordt uit de procesanalyse van het conventionele MEA-gebaseerde proces, is de regeneratie-energie een obstakel voor grootschalige toepassing. Om de hoge energieconsumptie te verminderen en om meer operationele flexibiliteit te verkrijgen, werd een nieuw procesconcept onderzocht. Dit nieuwe procesconcept is gebaseerd op het splitsen van het $CO_2$ -afvangst-proces in een bulk- verwijderingstap en een finale verwijderingstap waarbij het laatste gedeelte van de gewenste $CO_2$ -verwijdering wordt. Dit twee-stappen-concept werd geëvalueerd aan de hand van twee verschillende casussen. Beide zijn gebaseerd op het gebruik van MEA in de eerste stap. In de tweede stap wordt ofwel AMP gebruikt als absorptievloeistof, ofwel (actieve) kool gebruikt als adsorbens voor de verwijdering van de resterende $CO_2$. De resultaten tonen aan dat de verwijdering van $CO_2$ met behulp van adsorptie niet voordelig is door de grote hoeveelheid (geactiveerde) kool welke nodig is. Hiertegenover biedt het gebruik van een tweede absorptievloeistof de mogelijkheid tot procesverbetering. De totale energie behoefte voor het twee –absorptievloeistoffen-concept kan verminderd worden met 16% ten opzichte van de MEA-referentie-casus. Door de hogere investeringskosten nemen de totale kosten voor de vermindering van $CO_2$ volgens dit concept met 13% toe. Echter, het verkrijgen van een grotere flexibiliteit kan op zichzelf een voordeel zijn voor dit procesconcept. Deze flexibiliteit wordt verkregen doordat onder verschillende condities in twee absorptie- desorptie cycli gewerkt kan worden. Een van de voordelen kan het gebruik zijn van afvalwarmte voor regeneratie van één van de absorptievloeistoffen.

Het blijkt duidelijk uit de analyse van het post-combustion capture proces zoals beschreven in dit proefschrift dat het, om een significante vermindering in kosten te krijgen, noodzakelijk is om meerdere procesparameters te verbeteren. Voor de ontwikkeling van verbeterde $CO_2$ post-combustion capture processen kan het voordelig zijn om te werken naar absorptievloeistof-systemen met een lagere reactie-enthalpie en een hogere capaciteit. Een significante verbetering kan verkregen worden door de ontwikkeling van absorptievloeistof-systemen waarbij de absorptievloeistof wordt geregenereerd bij hogere druk. Bovendien zijn slimme procesverbeteringen en -integratie nodig om een redelijke kostenverbetering te komen. Rook gas terugvoer naar de gasturbine kan leiden tot een verlaging van de investering. Het splitsen van het afvangstproces en/of het combineren ervan met gelijktijdige productie van waterstof kan een bijkomende economische parameter zijn in de totale procesoptimalisatie. Het kan verwacht worden dat door het verbeteren van het procesontwerp en de absorptievloeistof de implementatie van post combustion capture op grote schaal in de nabije toekomst mogelijk wordt.

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“The content of a man’s character is not where he stands in times of comfort and convenience, but where he stands at times of challenge and controversy” Martin Luther King

# 1

# INTRODUCTION

## 1.1 General introduction

The atmospheric concentration of greenhouse gases GHGs (e.g. carbon dioxide, methane, nitrous oxide and chlorofluorocarbons) has increased gradually in the last century. The Intergovernmental Panel on Climate Changes (IPCC) has evaluated the size and impact of this increase. One of the conclusions is that the reasons behind the increased concentration of the greenhouse gases in the atmosphere are the human activities [1]. As a result, the global atmospheric concentration of $CO_2$ increased from a pre-industrial value of about 280 parts per million by volume (ppmv) to 384 ppmv in 2007(see Figure 1-1) [2]. Moreover, the GHGs concentration is expected to increase to about 600 ppmv by 2050 if no mitigation and emissions reduction options are applied [3] . The emissions of the different greenhouse gases have been monitored and measured all around the globe. It is evident that carbon dioxide is the most important anthropogenic GHG. Its annual emissions have grown between 1970 and 2004 by about 80%, from 21 to 38 gigatonnes, and represented 77% of total GHGs emissions in 2004 (Figure 1-2) [3].

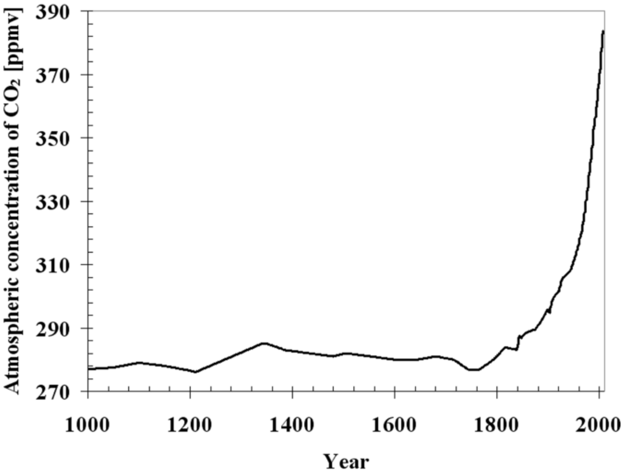

**Figure 1-1: $CO_2$ global concentration [2]**

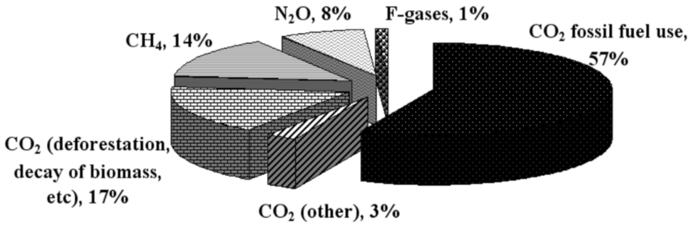

**Figure 1-2: Share of different Greenhouse gases in total global emissions in 2004 [3]**

There is a growing consensus that temperature increase due to climate change should be limited to around 2-3 degree celsius. There are many scenarios presented and discussed to evaluate the required level of $CO_2$ emissions reduction to achieve this target [1,3,6,8]. The International Energy Agency (IEA) has considered two climate policy scenarios corresponding to long term stabilisation of greenhouse gas in the year of 2030 at 550 (an increase in global temperature of approximately 3 °C) and 450 (a rise of around 2 °C) ppm of $CO_2$ [8]. This can be achieved by combining different solutions (renewable, energy efficiency, CCS, nuclear) to cut down the $CO_2$ emissions by 50-65% in 2030 comparing to the reference case level in 2006 [8]. The European Union (EU) emphasis the necessity to reduce $CO_2$ emissions by developed countries by 30% in 2020 compared to 1990 levels [3,4]. In addition, the EU is committed to achieve a 20% reduction of its greenhouse gas emissions by 2020 compared to 1990 [5]. To reach this ambitious goal, the focus is mainly on the $CO_2$ emissions from the consumption of fossil fuel, which is responsible of around 57% of the global GHGs emissions (see Figure 1-2). The global intention is directed toward the fossil fuels that are used for electricity generation, which are responsible for 41% of the global $CO_2$ emission in 2004 [6] (see Figure 1-3). The transportation sector is the second largest $CO_2$ emitter and can contribute in reducing $CO_2$ emissions (e.g. by the development of more efficient engines and by switching to more environmental friendly fuel like hydrogen, which is connected to an earlier $CO_2$ separation step).

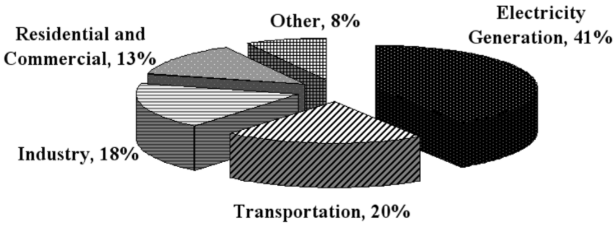

**Figure 1-3: Wold fossil fuel-energy related $CO_2$ emissions by sector 2004 [6]**

Currently, fossil fuels provide around 80% of the world's total energy demand. Coal is playing a major role as the main source of electrical power (38% of the total electricity generation) [7]. The large dependency on fossil fuels makes it difficult to switch completely to other energy sources. Moreover, the international energy agency scenarios have expected the world energy demand to expand by 45% between now and 2030. The prognoses indicate that fossil fuel will still be the main source of energy (see Figure 1-4) [8].

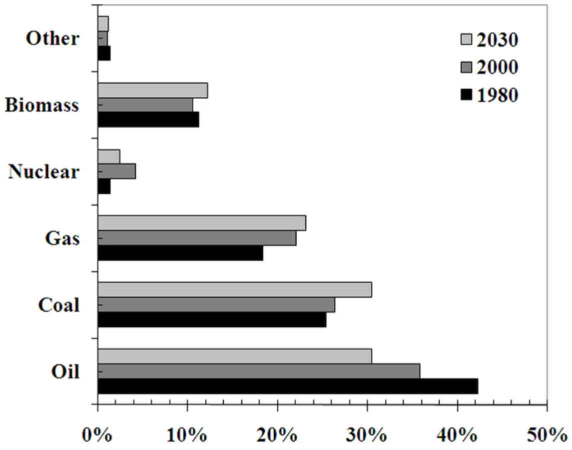

**Figure 1-4: Fuel shares in global primary energy demand.** ***Other includes amongst others hydro energy*** **[8]**

## 1.2 Options to reduce $CO_2$ emissions from the power generation sector

To achieve a major reduction on $CO_2$ emissions to the atmosphere, a deep cut of $CO_2$ emission from the power generation sector is needed. This deep emission reduction would require a combination of several solutions (see Figure 1-5) [1,3]:

- Reduction of energy consumption
- Improve power supply and distribution efficiency
- Massive switching from coal to natural gas
- Widespread use of renewable or nuclear energy
- $CO_2$ capture and storage (CCS)

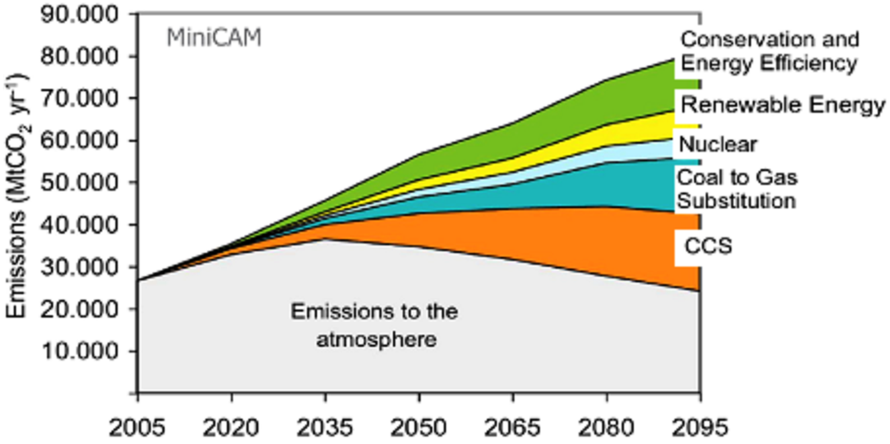

**Figure 1-5: Option to reduce $CO_2$ emissions [1],** ***this figure illustrates the need for multiple solutions to achieve $CO_2$ emissions reduction and not to evaluate the degree of emissions reduction***

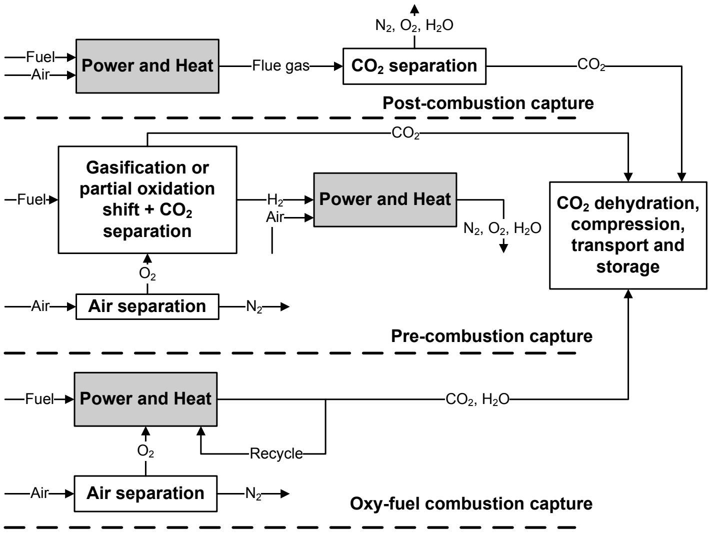

**Figure 1-6: Overview of $CO_2$ capture systems for the power sector [1]**

CCS is a promising method considering the ever-increasing worldwide energy demand and the possibility of retrofitting existing plants with capture, transport, and storage of $CO_2$. The captured $CO_2$ can be used for example for enhanced oil recovery, in the chemical and food industries, or can be stored underground instead of being emitted to the atmosphere. There are three basic systems for capturing the emitted $CO_2$ from the power sector, which are shown in simplified form in Figure 1-6 [1].

### 1.2.1 Post-combustion capture

Capture of $CO_2$ from flue gases produced by combustion of fossil fuels is referred to as post-combustion capture. Post-combustion capture typically uses a solvent to chemically absorb the $CO_2$ from the flue gases after the combustion process. The main line of research is on the development of reactive solvents for the capture of $CO_2$. Reactive absorbents are the preferred choice due to the low partial pressure of $CO_2$ (between 3-15 kPa) in the flue gas with nitrogen to be considered as the main component (see Table 1-1) [10]. Nevertheless, other techniques, such as membranes and adsorption are not as mature and efficient as the absorption process and require further development [9,11].

### 1.2.2 Pre-combustion capture

In this concept, a fuel is reacted with air or oxygen and/or steam to give a syngas (mixture of carbon monoxide and hydrogen). This process is known as the gasification step. In the second step, the carbon monoxide is reacted with steam in a catalytic reactor (water-gas shift reactor) to produce $CO_2$ and more hydrogen. A physical or chemical absorption process then separates the highly concentrated $CO_2$ from the hydrogen (see Table 1-1). The hydrogen rich stream can be used as a fuel in a gas turbine combined cycle plant. Another option is to distribute the hydrogen after extra treatment (e.g. PSA) for use in fuel cells or in the future to provide vehicle fuel [1,10].

### 1.2.3 Oxy-fuel combustion

In oxy-fuel combustion, nearly pure oxygen mixed with recycled flue gas is used for combustion instead of air. This will result in a flue gas that is mainly $CO_2$ saturated with water vapour [12,13]. Having water vapour as the main component in the $CO_2$ stream makes it possible to purify and store $CO_2$ with less downstream processing (see Table 1-1). If fuel is burnt in pure oxygen, the flame temperature is excessively high. However, by recycling the $CO_2$ rich flue gas the flame temperature will be similar to that of a normal air-blown combustor. Oxygen is usually produced by cryogenic air separation. Novel techniques with lower energy consumption and cost are being developed [1,10].

### 1.2.4 Capture routes and technologies evaluation

Significant effort is directed towards the comparison of the three different technological routes for the $CO_2$ capture from fossil fuel power plants [14-17]. Many studies came out with the conclusion that the net efficiency of the power plant, the overall cost of electricity, and cost of $CO_2$ avoided for the different technologies are almost comparable. Figure 1-7 shows an example of the efficiencies of the power plant reference cases without capture are compared with the overall power plant net efficiency after implementing the capture process. It is clear that the overall efficiency of the three $CO_2$ capture routes (post, pre and oxy-fuel combustions) is very similar. This supports the conclusion that the selection of one of the capture routes based on the overall efficiency is not sufficient.

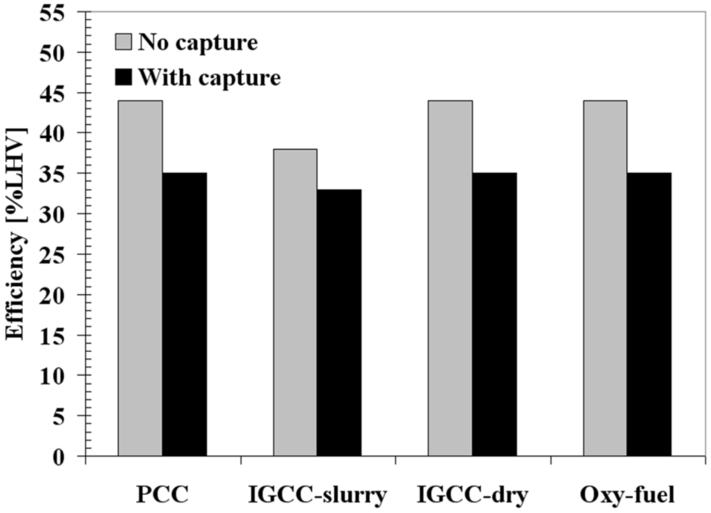

**Figure 1-7: Example of the efficiency for different power plant technologies before and after adding the capture process [14].** ***PCC: Pulverised coal power plant (with and without post-combustion capture), IGCC: integrated gasification combined cycle (pre-combustion capture), Oxy-fuel: oxy-fuel combustion power plant and LHV: low heating value.***

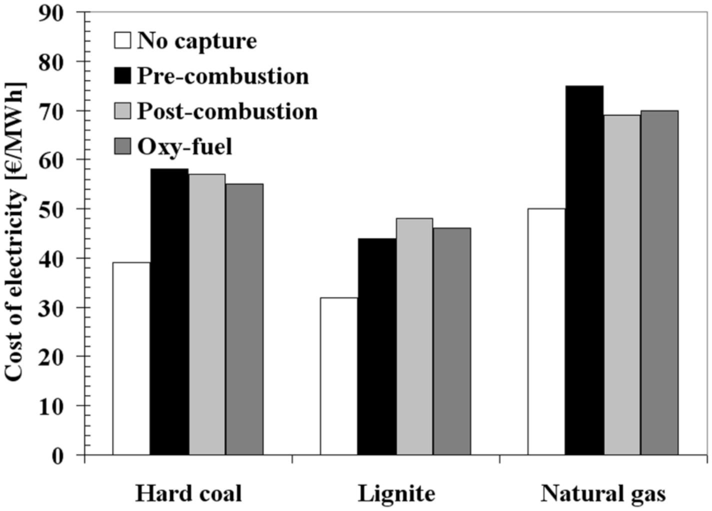

**Figure 1-8: Estimated cost of electricity in 2020 after applying different $CO_2$ capture routes** ***(excluding $CO_2$ transport and storage costs)*** **[18]**

By evaluating the effect of the different $CO_2$ capture routes on the overall estimated cost of electricity, it was found that the difference between these different routes using the same type of fuel is very limited and could not be used to select a preferred capture route, see Figure 1-8. However, the advantage of one technology route over the others could be related to the technology availability, the level of maturity of the technology, the possibility of capture process retrofitting to the existing power plants, the experience and repetition in commercial and large-scale applications and the most important factor is the period needed for the technology implementation.

Currently, it is difficult to make a choice between the main capture technologies, because each one has its own strengths and applications. However, in this thesis, the focus is on the $CO_2$ post-combustion capture route. Post combustion capture has been selected because it has the following potential advantages [19]:

- The possibility of add-on to existing power plants (retrofit possibility).
- Capture technologies are considered available and the solvent technologies are proven on a smaller scale.
- Capture readiness makes the post-combustion capture relatively easy to incorporate into power plants.
- It has more operational flexibility in switching between capture – no capture operation mode.
- Learning by doing will lead to cost reductions similar to experience with $SO_2$ capture process development.

Currently, a wide range of technologies for separation and capture of $CO_2$ from gas streams exist. They are based on different physical and chemical processes including absorption, adsorption, membranes and cryogenics (see Figure 1-9) [9,11].

The choice of a suitable technology depends on the characteristics of the $CO_2$ gas streams, which depend mainly on the power plant. As it can be seen from Table 1-1, for the different $CO_2$ capture routes different types of gases need to be separated. In addition, the pressure and the $CO_2$ content in the gas streams, which are important parameters in selecting the most suited technology for $CO_2$ removal, are different from one route to another.

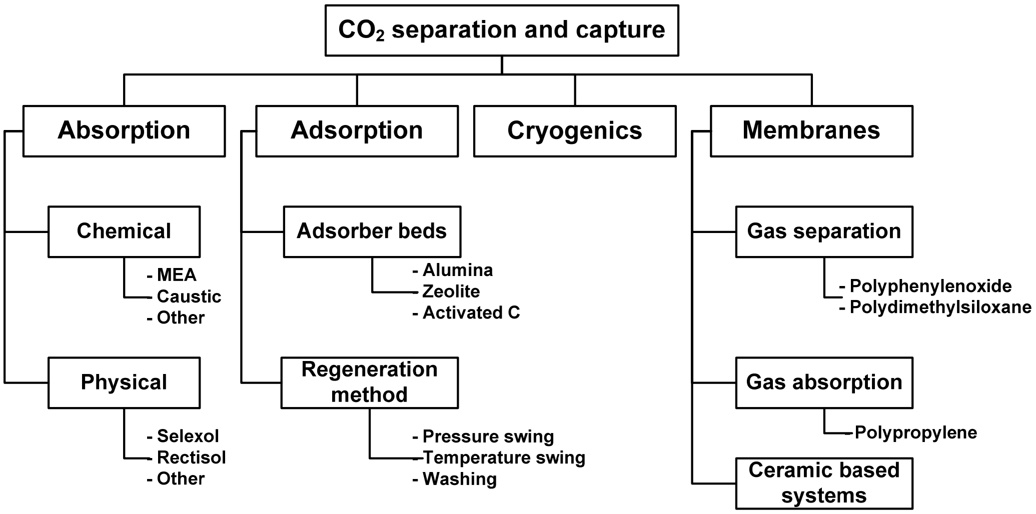

**Figure 1-9: Different technological routes for $CO_2$ capture [11]**

In case of post-combustion, the $CO_2$ is diluted and available at low pressure that makes chemical absorption one of the most efficient options for $CO_2$ removal. However, in the pre-combustion route, the $CO_2$ has higher partial pressure that makes physical absorption or adsorption a good technology candidate for $CO_2$ removal. The relevance and potential of these separation technologies to $CO_2$ capture is subject of research and development efforts worldwide.

**Table 1-1: $CO_2$ capture routes classifications**

| | **Post-combustion (flue gas)** | **Pre-combustion (shifted syngas)** | **Oxy-fuel combustion (exhaust)** |
|---|---|---|---|
| Gases to separate | $CO_2/N_2$ | $CO_2/H_2$ | $O_2/N_2$ |
| p (kPa) | ~100 | 1000-8000 | ~100 |
| $[CO_2]$ (%) | 3-15 | 20-40 | 75-95 |

## 1.3 $CO_2$ capture activities and development lines

The importance of carbon dioxide capture, transport, and storage (CCS) for the reduction of the overall $CO_2$ emission can be considered as a fact. In addition, the understanding of the challenges facing the large-scale CCS application, encourage different governments, nongovernmental organizations, research institutes, universities and many other commercial companies to invest in the CCS chain to make it ready for application in the near future. The CCS research and development takes a significant funding and attention from all related parties. Different projects and activities, which cover most of the aspects in the CCS chain, have been started since the early 1990's.

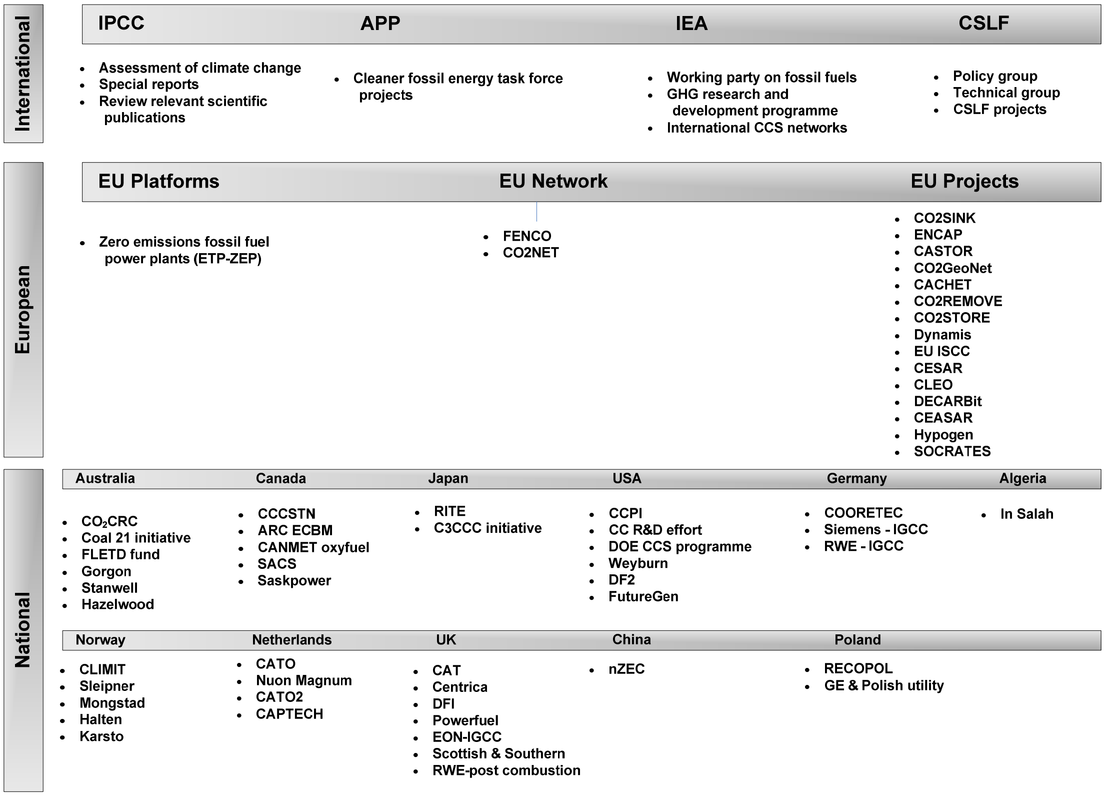

**Figure 1-10: Selection of CCS projects and activities [42-45]**

The global and national efforts in relation to CCS cover a wide range of activities: CCS chain definition, evaluation of different scientific publications and research, legislation, international cooperation, and networking activities organization. In addition to many technical oriented projects those have been carried out or planned for the future with international, EU or national funds. Figure 1-10 shows a selection of different CCS projects. The focus in these projects is varied from one project to another. Part of these projects focus on the development of one capture route like the European CESAR project, which focuses on $CO_2$ post-combustion capture. On the other hand, other projects evaluate the complete carbon capture, transport, and storage chain like in the Dutch $CO_2$ capture and storage programme (CATO project).

The objectives and the main tasks in this thesis have been defined and developed within four CCS projects: the European CASTOR, CESAR, Dynamis and the Dutch CATO project.

## 1.4 $CO_2$ post-combustion capture

Carbon dioxide post-combustion capture is considered one of the most mature capture technologies, since there is a good experience and reputation of this technology within many industrial applications [11].

### 1.4.1 State-of-art technology

Rao and Rubin 2002 [11] shows that for many reasons amine based $CO_2$ absorption systems are the most suitable for combustion based power plants: for example, they can be used for dilute systems and low $CO_2$ concentrations, the technology is commercially available, it is easy to use and can be retrofitted to existing power plants. Typically, absorption processes are based on a thermally regenerable solvent, which have a strong affinity for $CO_2$. The process thus requires thermal energy for the solvent regeneration. The benchmark absorption process is based on an aqueous solution with 30% by weight Monoethanolamine (MEA) as the active ingredient. This amine-based process is considered the state-of-the-art technology [20].

Fluor Daniel markets the 30% aqueous MEA solution based process under the name Econamine FG$^{SM}$ [20,24]. The solution also contains proprietary additives to prevent corrosion and solvent degradation. The presence of these additives is expected to have a negligible effect on the major performance parameters. Fluor Daniel has improved its process performance by various means, including a modification of the solvents and process under the name Econamine FG Plus$^{SM}$. However, none of these novel improvements have been validated on a large-scale process. Some of the proposed improvements are based on modelling studies and lab-scale development. It is acknowledged that the solvent developments for post-combustion $CO_2$ capture are accelerating with the expectation of future $CO_2$ emissions constraints. Apart from Mitsubishi Heavy Industries marketing their KS-1 solvent [25-27], also the CBI-Lummus [21], Cansolv and Praxair are amongst the new suppliers.

#### *1.4.1.1 Process short description*

The general process flow diagram for amine absorption is shown in Figure 1-11. This is the typical conventional MEA-$CO_2$ capture flow sheet, which has been described and discussed in a large number of commercial, industrial and research activities [9,11,19-24,28]. The underlying fundamental principle is the exothermic, reversible reaction between a weak acid (e.g. $CO_2$) and a weak base (e.g. MEA) to form a soluble salt.

The inlet gas is contacted counter-currently with lean solvent in the absorber. The acid gases are preferentially absorbed by the solution. The solution, enriched with $CO_2$, is pre-heated before entering the stripper where, through the addition of heat, the reaction is reversed. The lean solvent leaves the stripper and is lowered in temperature by exchanging heat with the rich solvent. The lean solvent is recycled back to the absorber. From the top of the stripper, a high-purity (dry-basis) $CO_2$ is produced. For the regeneration of the rich solvent large quantities of heat is required. An important aspect is the source of the heat and electricity. One approach is to produce the required heat and electrical power using auxiliary equipment. The other alternative is to extract the required heat from the existing power plant. This option has been considered in this work.

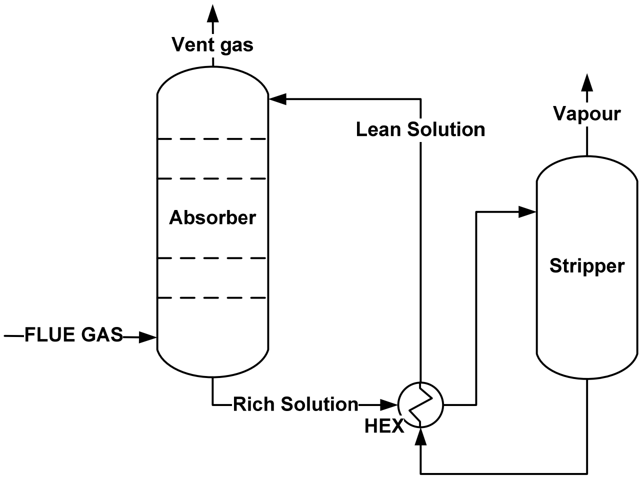

**Figure 1-11: General chemical absorption $CO_2$ capture process flow sheet**

### *1.4.1.2 $CO_2$-Monoethanolamine chemical reactions and thermodynamics*

Since the first applications of this system were in early in 1960's, a large number of studies on the reaction mechanism of $CO_2$-$H_2O$-MEA system have been reported [29-36]. As a general conclusion of these studies, the absorption of $CO_2$ by aqueous MEA solution is based on a complex system of parallel and consecutive reactions in liquid phase. With the overall forward reaction between $CO_2$ and MEA has usually been represented as [34]:

$$CO_2 + HO(CH_2)_2NH_2 \rightleftarrows HO(CH_2)_2NHCOOH$$

$$HO(CH_2)_2NHCOOH + HO(CH_2)_2NH_2 \rightleftarrows HO(CH_2)_2NHCOO^- + HO(CH_2)_2NH_3^+$$

The first step is second-order and rate determining. The second step is considered an instantaneous reaction. However, this scheme is a substantial simplification for the reaction mechanism that actually occurs.

The $CO_2$-$H_2O$-MEA system is considered non-ideal, which could be described in the gas phase using the Soave-Redlish-Kwong equation of state [36]. For the liquid phase, electrolyte-NRTL model is considered as a good representation of this system. The required data and parameters for this system have been developed and presented by Austgen 1989 [37]. In addition, of the main physical properties of this system (density, viscosity, thermal conductivity, and specific heat) have been measured as a function of MEA concentration and operating temperature by Cheng 1996 [38]. Moreover, the solubility and the diffusivity of $CO_2$ into the aqueous MEA solution have been measured and estimated by different studies, which are reviewed and summarized by Versteeg 1996 [31].

### 1.4.2 Post-combustion capture process challenges

Several researchers have studied and evaluated the MEA absorption process [11,14,20-24,28,39]. Most of their conclusions focused on reducing the thermal energy requirement to reduce the overall process expenses. The literature results show different estimations for the regeneration energy requirement for the MEA process. Chapel et al. 1999 estimated the Econamine FG$^{SM}$ energy requirement of 4.2 GJ/tonne $CO_2$, which is around 36% of the overall operating cost [20]. Singh et al. 2003 [23] found by modelling the MEA process for 400 MWe coal fired power plant a specific thermal energy requirement equal to 3.8 GJ/tonne $CO_2$. Alie et al. 2005 [22] found that an energy requirement of 176 kJ/mol $CO_2$ (4 GJ/tonne $CO_2$). Recently, Fluor claims a process development based on the MEA technology leading to a significant reduction of the energy requirement down to around 2.9 GJ/tonne $CO_2$. The improvements are based on process integration and solvent improvements [40].

In conclusion, the high-energy requirement makes the capture process energy-intensive and costly. Therefore, it is important to study the conventional MEA process to have a better understanding of the process to work on reducing the energy requirement.

Moreover, the general conclusion of all the studies is, applying the current state-of-art capture process reduces the overall power plant net efficiency by 8 to 12 percentage points [1,41]. This means, for the conventional hard coal power plant that the overall electricity output will be decreased by almost 20 %. Furthermore, the $CO_2$ capture overall economic evaluation shows that implementing the $CO_2$ capture in the power sector will increase the overall cost of energy production by 50-70%. This implies that for realising the potential of CCS there is a strong need for breakthrough technology.

As a result of the different CCS projects, evaluation and studies, a general conclusion can be made that the current $CO_2$ capture technologies have the following disadvantages:

- Significant efficiency reduction
- Increase of the power generation costs
- Large capture plant equipment dimensions and footprint, which requires further development and modification
- Lack of experience in $CO_2$ capture process at a full power plant scale
- No global political decision to apply the technology and to subsidise it
- Very limited public awareness of the importance of CCS technology as one of the solutions to reduce the global warming problem

## 1.5 Research questions for $CO_2$ post-combustion capture

As has been discussed in the previous sections, $CO_2$ post-combustion capture is becoming an important option for $CO_2$ emission reduction. However, applying this technology on large-scale will not be a reality before tackling different legal, economic, social, political and technical challenges related to the current technologies. There are many questions, which need to be answered before applying large-scale $CO_2$ post-combustion capture:

1. How to reduce the additional power consumption, which results from applying the capture process?
2. How to reduce the overall footprint of the capture process and to make the equipment more compact?
3. What are the main parameters and factors that contribute in the overall cost of the capture process and how to reduce this cost?
4. What are the main technological areas of focus for the future development to achieve the $CO_2$ emission reduction with an acceptable cost?
5. Is there still a room for improvement on the current state-of-art $CO_2$ post-combustion capture process?
6. How reliable are the capture process techno-economic evaluation tools that have been used for process evaluation?
7. How can the $CO_2$ capture processes be made reliable in a power generation environment?
8. How to encourage the decision makers to adopt the CCS development politically and economically?
9. What are the methods and routes that should been followed to increase public awareness?

Most of these questions and many more are needed to be solved in order to apply the capture technology for large-scale applications and achieve the targeted $CO_2$ emission reduction.

## 1.6 Thesis objectives and outline

This thesis focuses on the analysis and evaluation of different post-combustion capture routes, to be able to answer couple of the above mentioned technical research questions. The goals of this work are:

- To develop a better understanding of $CO_2$ post-combustion capture process and the implications for large-scale $CO_2$ emitters application.
- To evaluate and validate the techno-economic evaluation modelling tools those have been used to assess the different capture processes and concepts.
- To assess the possibility of capture process improvement by introducing new process concepts.

The increased knowledge will help in defining the directions for future research activities for the improvement of the capture process and, thereby, making it more economically attractive to be applied.

**Chapter 2** focuses on the conventional post-combustion capture process definition, design, and technical evaluation. In this chapter, the state-of-art capture technology has been defined as the starting point for further development. In addition, this base case has been optimized by changing the main process parameters (solvent flow rate, solvent concentration and other operational conditions). The effect of each of these parameters has been evaluated. The emphasis of this chapter is on the technical performance of the capture process, which includes evaluating the process energy requirement, cooling water requirement, solvent requirement, and the overall carbon dioxide capture efficiency.

In **Chapter 3**, the economic evaluation of the defined base case process has been done. An economic evaluation tool has been defined and developed in this chapter. The economic evaluation consists of an overall vision of the capture process connected and integrated with the power plant. In this chapter, the effect of the $CO_2$ capture on the power plant energy output, overall efficiency, and cost of electricity are included.

The economic evaluation work is based on large set of different parameters. The key economic parameters (fuel price, interest rate, project life) can be expected to vary from time to time and from one region to another. Therefore, an economic sensitivity analysis is included at the end of this chapter.

In **Chapter 4**, different modelling tools are validated against large-scale pilot plant data. In this chapter, the pilot plant experimental results are analysed and evaluated. Two different modelling approaches, namely the rate-based and the equilibrium-stage models, are compared. The results of this evaluation have been used to evaluate the potential of using these different models in the capture process assessment.

In **Chapter 5**, new process concepts are introduced and evaluated. These new concepts are directed toward the combination of post-combustion capture with co-production of hydrogen. In this chapter, a multi criteria analysis has been applied to evaluate the complete power plant and capture plant-integrated flow sheet. Future technologies and possible improvements are evaluated and discussed.

In **Chapter 6**, two-step separation concept for post-combustion capture is introduced and evaluated. Integrating two chemical absorbent processes or a chemical absorbent in combination with solid adsorbent are assessed. In this chapter, the capture process is divided into two steps: the first step is considered the $CO_2$ bulk removal step, which can be expected to be less energy intensive. In the second step, the remaining $CO_2$ is removed. By splitting the capture process in two steps, the capture process can be optimised further.

In **Chapter 7,** a perspective is given on the cost reduction lines for the $CO_2$ post-combustion capture technology. In this future outlook, relevant guidelines for solvent and process development can be found. In addition, major recommendations to improve the post-combustion capture process are discussed.

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"When your work speaks for itself, don't interrupt" Henry Kaiser

# 2

# BASE CASE $CO_2$ POST-COMBUSTION CAPTURE PROCESS DESIGN AND PARAMETRIC STUDY

*Capture and storage of $CO_2$ from fossil fuel fired power plants is drawing increasing interest as a potential method for the control of greenhouse gas emissions. An optimization and technical parameter study for a $CO_2$ capture process from flue gas of a 600 MWe bituminous coal fired power plant, based on absorption/desorption process with MEA solutions, using ASPEN Plus with the RADFRAC subroutine, was performed. This optimization aims to reduce the energy requirement for solvent regeneration, by investigating the effects of $CO_2$ removal percentage, MEA concentration, lean solvent loading, stripper operating pressure, and lean solvent temperature.*

*Major energy savings can be realized by optimizing the lean solvent loading, the amine solvent concentration, as well as the stripper operating pressure. A minimum thermal energy requirement was found at a lean MEA loading of 0.3, using a 40 wt. % MEA solution and a stripper operating pressure of 210 kPa, resulting in a thermal energy requirement of 3.0 GJ/tonne $CO_2$, which is 23% lower than the base case of 3.9 GJ/tonne $CO_2$. Although the solvent process conditions might not be realisable for MEA due to constraints imposed by corrosion and solvent degradation, the results show that a parametric study will point towards possibilities for process optimisation.*

## 2.1 Introduction

Human activity has caused the atmospheric concentration of greenhouse gases such as carbon dioxide, methane, nitrous oxide, and chlorofluorocarbons to increase gradually over the last century. The Intergovernmental Panel on Climate Changes (IPCC) has evaluated the size and impact of this increase, and found that since the industrial revolution, their concentrations in the atmosphere have increased and carbon dioxide as such is considered responsible for about 50 % of this increase [1].

The main $CO_2$ source is the combustion of fossil fuels such as coal, oil, and gas in power plants, for transportation and in homes, offices, and industry. Fossil fuels provide more than 80% of the world's total energy demands. It is difficult to reduce the dependency on fossil fuels and switch to other energy sources. Moreover, the conversion efficiency of other energy sources for power generation is mostly not as high as that of fossil fuels. A drastic reduction of $CO_2$ emissions resulting from fossil fuels can only be obtained by increasing the efficiency of power plants and production processes, and decreasing the energy demand, combined with $CO_2$ capture and long-term storage (CCS). CCS is a promising method considering the ever-increasing worldwide energy demand and the possibility of retrofitting existing plants with capture, transport, and storage of $CO_2$. The captured $CO_2$ can be used for enhanced oil recovery, in the chemical and food industries, or can be stored underground instead of being emitted to the atmosphere.

Technologies to separate $CO_2$ from flue gases are based on absorption, adsorption, membranes, or other physical and biological separation methods. Rao and Rubin 2002 [2] showed that for many reasons amine based $CO_2$ absorption systems are the most suitable for combustion based power plants: for example, they can be used for dilute systems and low $CO_2$ concentrations, the technology is commercially available, it is easy to use and can be retrofitted to existing power plants. Absorption processes are based on thermally regenerable solvent, which have a strong affinity for $CO_2$. They are generated at elevated temperature. The process thus required thermal energy to the regeneration of the solvent. Aqueous monoethanolamine (MEA) is an available absorption technology for removing $CO_2$ from flue gas streams. It has been used in the Fluor Daniel technology's Econamine FG™ and Econamine FG Plus™ [3,4], and the ABB Lummus Global technology [5]. Many researchers are aiming to develop new solvent technologies to improve the efficiency of the $CO_2$ removal. Process simulation and evaluation are essential items to maximize the absorption process performance.

Several researchers have modelled and studied the MEA absorption process [2-10], most of their conclusions focused on reducing the thermal energy requirement to reduce the overall process expenses. Chapel et al. 1999 gave the Econamine FG™ requirement [4]: regeneration energy of 4.2 GJ/tonne $CO_2$ was used, which was calculated to be responsible of around 36% of the overall operating cost. This high-energy requirement makes the capture process energy-intensive and costly. Therefore, it is important to study the conventional MEA process trying to reduce this energy requirement. Alie et al. 2005 [6] proposed a flow sheet decomposition method, which is a good start to estimate the process tear streams initial guess. However, it is important to use a complete and closed flow sheet to keep the water balance in the system. Alie et al. 2005 [6] found that the lowest energy requirement of 176 kJ/mol $CO_2$ (4 GJ/tonne $CO_2$) can be achieved at lean solvent loading between 0.25 and 0.30 mol $CO_2$/mol MEA. Singh et al. 2003 [7] found that the thermal energy requirement for MEA process is a major part of the process overall operating cost, and by modelling the MEA process for 400 MWe coal fired power plant he found the specific thermal energy requirement equal to 3.8 GJ/tonne $CO_2$.

In this work a parametric study is presented aimed at developing an optimized absorption/desorption process which has a lower thermal energy requirement compared to the available literature data of around 4 GJ/tonne $CO_2$. The base case flow sheet for this parametric study is the conventional flow sheet that is available in commercial application [3]. However, the Fluor improved process Econamine FG Plus™ [4] was not considered as a base case because it has no commercial applications yet. This parametric study uses the ASPEN Plus software package [11] to the process modelling based on aqueous MEA solution. In this work a variation in several parameters has been included, because the combined effect of several parameters is expected to give a larger effect on the overall process performance compared to a variation of single parameter.

After the process simulation, a design model for both the absorber and the stripper was built to investigate the effect of chemical reaction and mass transfer on the absorption process. The following parameters were varied: the $CO_2$ lean solvent loading, the $CO_2$ removal percentage, the MEA weight percentage, the stripper operating pressure and the lean solvent temperature. In particularly the effect on the thermal energy requirement for the solvent regeneration, the amount of cooling water and the solvent flow rate was amended. These are key performance parameters for the absorption/desorption process and the focal part in the optimization.

## 2.2 Process description

The process design was based on a standard regenerative absorption-desorption concept as shown in the simplified flow diagram in Figure 2-1 [2]. The flue gases from the power plant enter a direct contact cooler (C1) at a temperature depending on the type of the power plant, after which they are cooled with circulating water to around 40°C. Subsequently, the gas is transported with a gas blower (P1) to overcome the pressure drop caused by the MEA absorber. The gases flow through the packed bed absorber (C2) counter currently with the absorbent (an aqueous MEA solution), in which the absorbent reacts chemically with the carbon dioxide (packed bed columns are preferred over plate columns because of their higher contact area). The $CO_2$ lean gas enters a water wash scrubber (C3) in which water and MEA vapour and droplets are recovered and recycled back into the absorber to decrease the solvent loss. The treated gas is vented to the atmosphere.

The rich solvent containing chemically bound $CO_2$ is pumped to the top of a stripper *via* a lean/rich cross heat exchanger (H3) in which the rich solvent is heated to a temperature close to the stripper operating temperature (110-120°C) and the $CO_2$ lean solution is cooled. The chemical solvent is regenerated in the stripper (C4) at elevated temperatures (100-140°C) and a pressure not much higher than atmospheric. Heat is supplied to the reboiler (H4) using low-pressure steam to maintain regeneration conditions. This leads to a thermal energy penalty because the solvent has to be heated to provide the required desorption heat for the removal of the chemically bound $CO_2$ and for the production of steam, which acts as stripping gas. Steam is recovered in the condenser (C5) and fed back to the stripper, after which the produced $CO_2$ gas leaves the condenser. Finally, the lean solvent is pumped back to the absorber *via* the lean/rich heat exchanger (H3) and a cooler (H2) to bring its temperature down to the absorber level.

The absorber was simulated at 110 kPa with a pressure drop of 4.8 kPa, using three equilibrium stages of the RADFRAC subroutine. A preliminary study into the determination of the minimum number of stages required to achieve equilibrium revealed that three stages were quite adequate in achieving equilibrium. Increasing the number did not result in a more detailed and better description of the absorption process. To simulate the stripper, with an operating pressure of 150 kPa and a pressure drop of 30 kPa, 8 equilibrium stages were required.

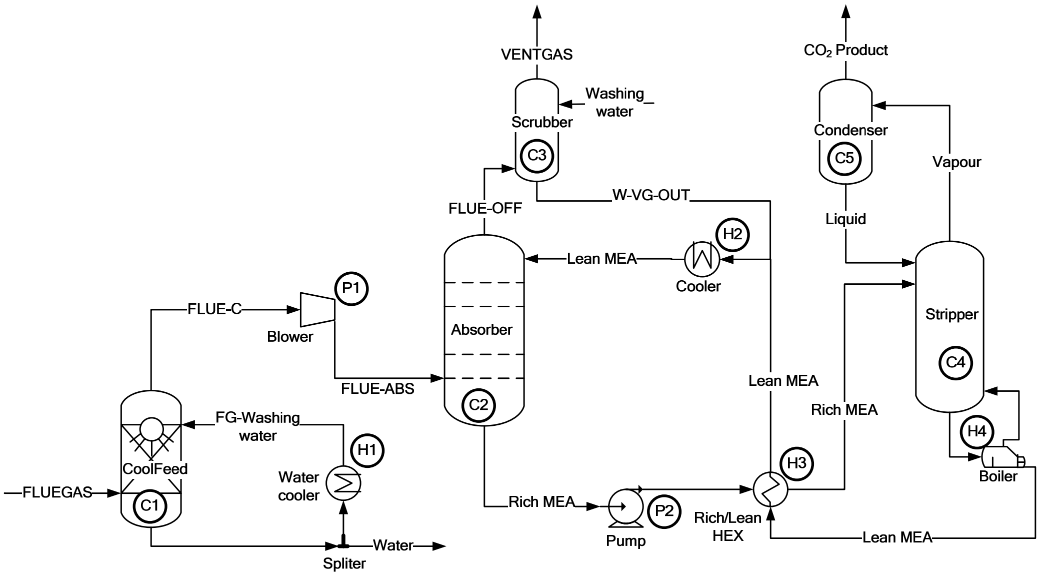

**Figure 2-1 process flow sheet of $CO_2$ removal using chemical absorption amine**

### 2.2.1 Baseline case definition and simulation

The flue gas flow rate and composition for 600 MWe coal-fired power plant, which has been used in the study, are presented in Table 2-1.

**Table 2-1 Flue gas flow rate and composition**

| | |
|---|---|
| Mass Flow (kg/s) | 616.0 |
| Pressure (kPa) | 101.6 |
| Temperature (°C) | 48 |
| Composition | Volume % wet gas |
| $N_2$+Ar | 71.62 |
| $CO_2$ | 13.30 |
| $H_2O$ | 11.25 |
| $O_2$ | 3.81 |
| $SO_2$ | 0.005 |
| $NO_x$ | 0.0097 |

Simulations were performed using the ASPEN plus version 13.1 [11].The thermodynamic and transport properties were modelled using a so-called “MEA Property Insert”, which describes the MEA-$H_2O$-$CO_2$ system thermodynamically with the Electrolyte-NRTL model. The following base case was defined:

- A 90 % $CO_2$ removal;
- A 30 MEA wt. % absorption liquid;
- Using a lean solvent loading of 0.24 mol $CO_2$/mol MEA (i.e. a 50 % degree of regeneration).

### 2.2.2 Design model

The reactive absorption of the $CO_2$-MEA-$H_2O$ system is complex because of multiple equilibrium and kinetic reversible reactions. The equilibrium reactions included in this model are:

Amine protonation $$\mathrm{MEA} + H_3O^+ \rightleftharpoons \mathrm{MEA}^+ + H_2O$$

Bicarbonate formation $$CO_2 + 2\,H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$

Carbonate formation $$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{-2}$$

Carbamate formation $$\mathrm{MEA} + HCO_3^- \rightleftharpoons \mathrm{MEACOO}^- + H_2O$$

Water hydrolysis $$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$$

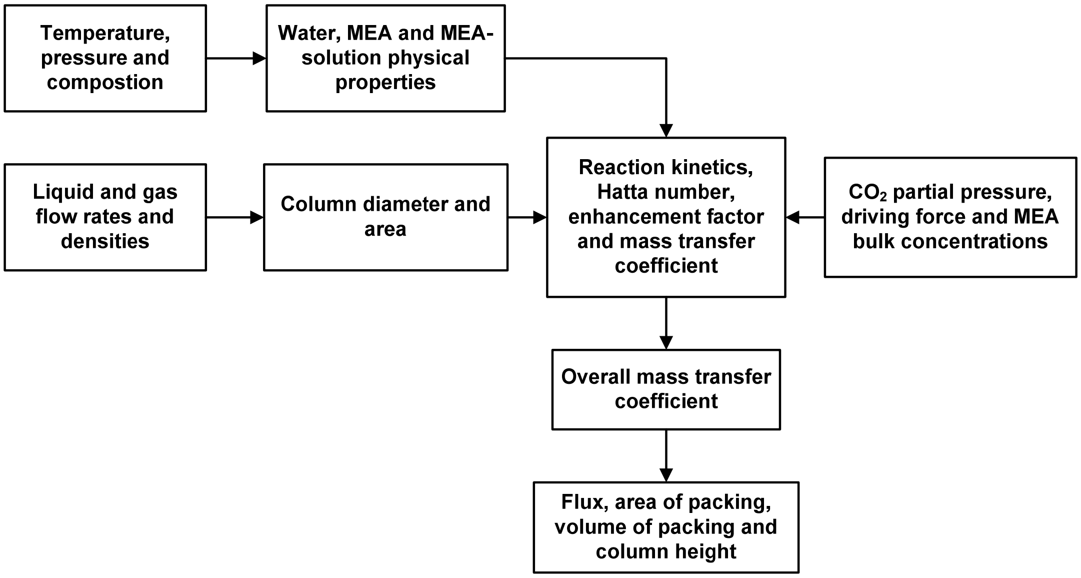

**Figure 2-2 Absorber model block diagram**

The absorber will treat large volumes of flue gases and is therefore the largest equipment in a capture plant. As such it is expected to have a major capital cost, associated with it. Given its importance in investment terms, a design model for the absorber column based on first principles using the equilibrium stage model data, was built. From the overall mass transfer coefficient and the driving force, the mass transfer flux was calculated, which then have been used to estimate the required area of packing. The structure of the absorber model that has been used can be seen in the absorber model block diagram in Figure 2-2 and the methods used can be found in more detail in the appendix. An identical procedure was also followed for the regenerator columns.

### 2.2.3 Parameter study

In this study, some of the main parameters affecting the capture process will be varied as an initial step towards an optimization of the process. Starting from the baseline case the following process parameters will be varied:

- The $CO_2$ lean solvent loading (mol $CO_2$/mol MEA), by varying the degree of regeneration (20, 30, 40, 50 and 60 % degree of regeneration).
- The amount of $CO_2$ removed (80, 90, 95, and 99 % removal).
- The MEA weight percentage in the absorption solvent (20, 30 and 40 wt. %).
- The stripper operating pressure.
- The lean solvent temperature, at the absorber inlet.

The following performance indicators in the absorption/desorption process were used to investigate the effect of the parameters:

- The thermal energy required in the stripper (GJ energy/tonne $CO_2$ removed).
- The amount of cooling water needed in the process ($m^3$ cooling water/tonne $CO_2$ removed).
- The solvent circulation rate needed for the absorption ($m^3$ solvent/tonne $CO_2$ removed).

These indicators were chosen because they present information on both the operating and the capital costs. The thermal energy is expected to be a major contributor to the production cost and a change in the energy required will give a clear effect on the operating costs. Both the amount of cooling water and solvent required affect the size of the equipment, which in turn influences the capital costs.

## 2.3 Results and discussion

### 2.3.1 Baseline case

The capture base case was simulated considering the complete $CO_2$ capture process and using closed flow sheet to keep the overall water balance to zero. This makes the flow sheet more difficult to converge due to the recycle structure in the flow sheet. However, this is important, as only then the results will be realistic. The choice and the initial estimation of the tear streams are important factors in the flow sheet convergence. The results of the baseline case simulations are shown in Table 2-2.

The energy requirement was 3.9 GJ/tonne $CO_2$, which agrees well with the numbers reported in industry today. For example, the Fluor Econamine FG™ process requires 4.2 GJ/tonne $CO_2$ [4], and the Fluor Econamine FG Plus™ technology required a somewhat lower energy requirement of 3.24 GJ/tonne $CO_2$ [15]. However, the latter technology consists of a different and more complex process configurations (split flow configurations and absorber inter-cooling) and improved solvent characteristics. The cooling water and solvent requirement for both the base case processes were in line with the data of Fluor Daniel FG™.

**Table 2-2 Results of the baseline case**

| | |
|---|---|
| Amine lean solvent loading (mol $CO_2$/mol MEA) | 0.242 |
| Amine rich solvent loading (mol $CO_2$/mol MEA) | 0.484 |
| Thermal heat required (GJ/tonne $CO_2$) | 3.89 |
| Solvent flow rate required ($m^3$/tonne $CO_2$) | 20.0 |
| Cooling water required | |
| Feed cooling water ($m^3$/tonne $CO_2$) | 9 |
| Condenser ($m^3$/tonne $CO_2$) | 41.5 |
| Lean cooler ($m^3$/tonne $CO_2$) | 42 |
| Scrubber ($m^3$/tonne $CO_2$) | 0.2 |
| $CO_2$ product compressor inter-cooling ($m^3$/tonne $CO_2$) | 13.16 |
| Total cooling water required ($m^3$/tonne $CO_2$) | 106 |

### 2.3.2 Effect of different lean solvent loading including the effect of the $CO_2$ removal percent

The lean solvent loading of the MEA solution representing the degree of regeneration, was varied to find the optimum solvent loading for a minimal thermal energy requirement. This can be achieved by changing the reboiler energy input. For a given degree of regeneration, to achieve the same $CO_2$ removal capacity, the absorption solvent circulation rate was varied. While studying the effect of the different lean loading on the capture process, the stripper reboiler temperature was varied to change the values of the lean loading. At the same time, the solvent flow rate has been changed to achieve the targeted $CO_2$ removal percentage. On the other hand, the rest of the process conditions were kept constant (e.g. stripper pressure, number of equilibrium stages, MEA concentration, heat exchangers and columns conditions).

At low values of lean solvent loading, the amount of stripping steam required to achieve this low solvent loading is dominant in the thermal energy requirement. At high values of lean solvent loading, the heating up of the solvent at these high solvent circulation flow rates is dominant in the thermal energy requirement. Therefore, a minimum is expected in the thermal energy requirement. From Figure 2-3 it is indeed clear that the thermal energy requirement decreases with increasing lean solvent loading until a minimum is attained. The point at which the energy requirement is lowest will be defined to be the optimum lean solvent loading. The overall regeneration energy consists of three major parts: the energy required to release the bonded $CO_2$, the sensible heat required to heat up the solvent and the energy required for water evaporation. The contributions of each of these parts are varied while changing the lean loading. Figure 2-4 presents an example of the various contributions to the regeneration energy at 90% $CO_2$ removal. It can be seen that the energy required to release $CO_2$ is almost constant because of the constant $CO_2$ removal percentage. Lowe lean loading, means higher reboiler temperature. This results in larger amount of water evaporation and as a consequence a higher energy contribution. At higher lean loading, larger amount of solvent is needed to achieve the same $CO_2$ removal. This higher solvent quantity requires larger sensible heat to heat up the solvent to the striper temperature. This explains the behaviour of forming a minimum value of the regeneration energy while increasing the solvent lean loading. For 90 % removal and a 30 MEA wt. % solution the optimum lean solvent loading was around 0.32-0.33 mol $CO_2$ /mol MEA, with a thermal energy requirement of 3.45 GJ/tonne $CO_2$. This is a reduction of 11.5% compared to the base case. It must be noted, however, that the solvent circulation rate was increased to 33 $m^3$/tonne $CO_2$. Above lean solvent loading of a 0.32 mol $CO_2$ /mol MEA the solvent circulation rate increases more than linearly with the lean solvent loading (see Figure 2-5).

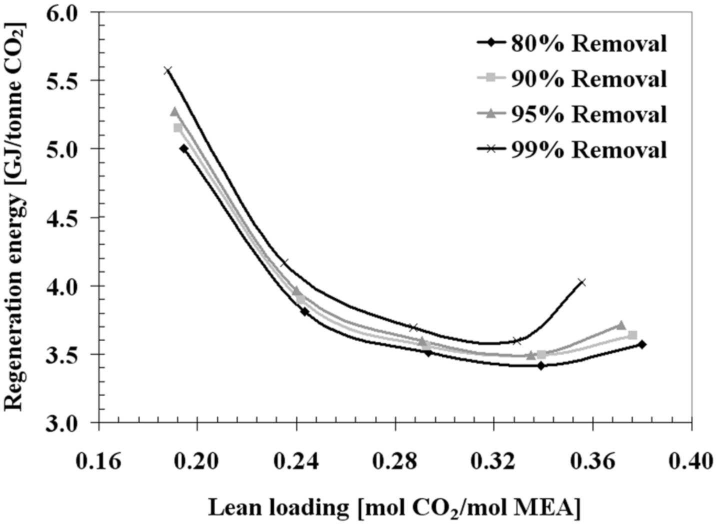

**Figure 2-3 Thermal energy requirement at various lean solvent loadings for different $CO_2$ removal %**

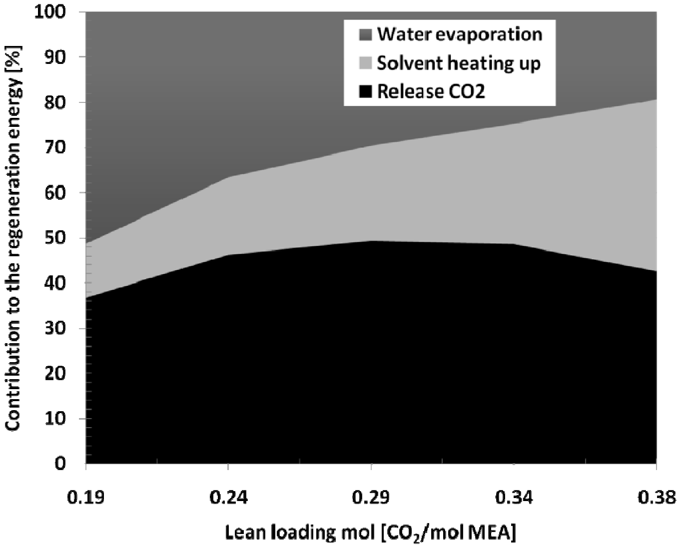

**Figure 2-4: Various contributions to the regeneration energy as function of lean loading (example at 90% $CO_2$ removal and 30 wt-% MEA solution)**

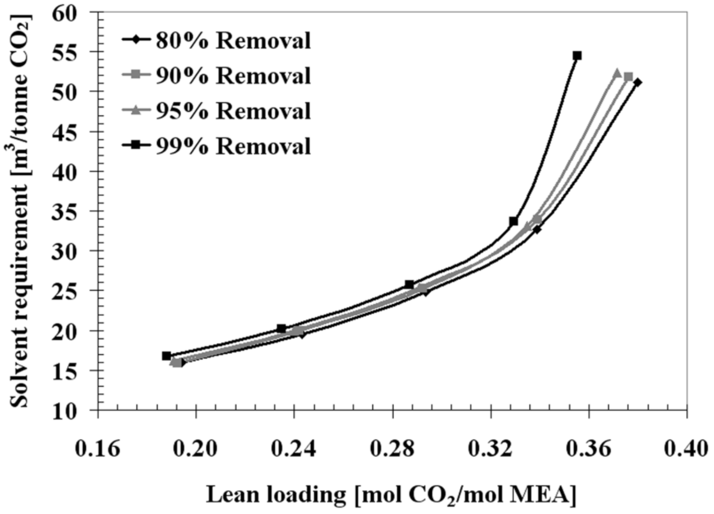

**Figure 2-5 Solvent flow rate requirement at various lean solvent loadings for different CO$_2$ removal %**

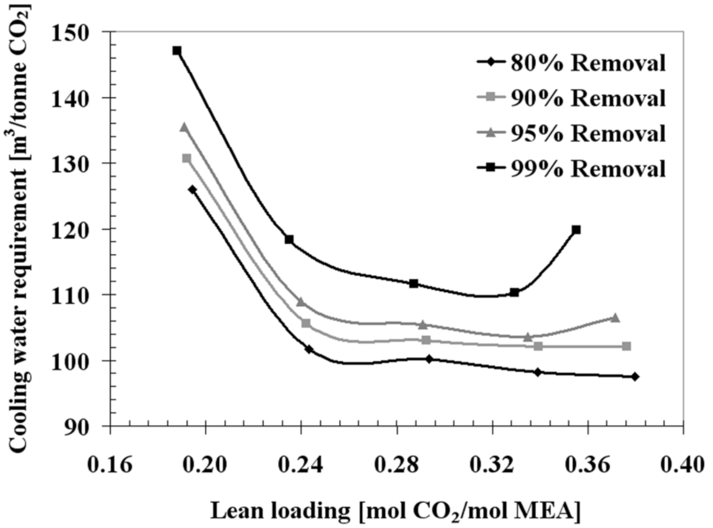

**Figure 2-6 Cooling water consumption at various lean solvent loadings for different CO$_2$ removal %**

For the cooling water required (see Figure 2-6), the occurrence of a local minimum was not strictly encountered: the amount of thermal cooling water decreased with increasing lean solvent loadings, in line with the reduced energy requirement. The amount of cooling water needed remained constant for a lean solvent loading between 0.26 to 0.33 mol CO$_2$/mol MEA. This can be explained by the fact that at high lean solvent loadings the lean solvent was not cooled to 35°C as in the base case. To meet the requirement of a closed water balance, the temperature of the lean solvent entering the absorber was allowed to increase. Consequently, the absorber operates at a higher temperature allowing evaporation of water from the top of the absorber to maintain a closed water balance in the complete process (lean solvent temperatures were varied from 35 $^{o}$C up to 50 $^{o}$C). If the lean solvent temperature was kept constant at high solvent flow rates, this would have led to excessive condensation in the absorber. This water would have to be removed in the stripper.

Increasing the percentage of $CO_2$ removed from 80% to 99% resulted in a small increase in the thermal energy, solvent and cooling water as clearly shown in Figure 2-3 to Figure 2-6. The differences between the different removal percentages were most pronounced at high lean solvent loadings. To obtain the same removal percentage at high lean solvent loadings, which means lowering the driving force in the top of the absorber, more solvent would be needed, which rapidly increases the energy requirement at high lean solvent loadings.

### 2.3.3 Effect of MEA weight %

The thermal energy requirement was found to decrease substantially with increasing MEA concentration (see Figure 2-7). It seems attractive to use higher MEA concentrations. However, increasing the MEA concentration is expected to have pronounced corrosive effects. It is therefore required to use better corrosion inhibitors in order to realise the energy saving potential of higher MEA concentrations.

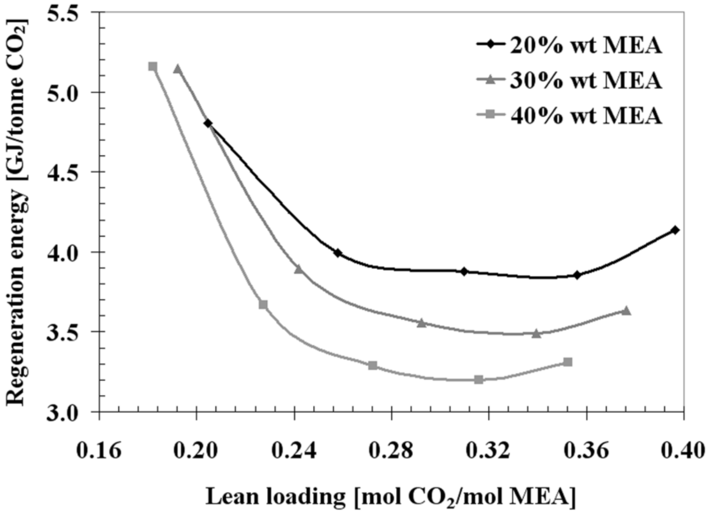

**Figure 2-7 Thermal energy requirement at various lean solvent loadings for different MEA wt. %**

Moreover, at high MEA concentration, it is expected to have a higher MEA content in the vent gas, but a good washing section can overcome this problem and keep the MEA content in the vent gas as low as possible. The wash section used in the process flow sheets always resulted in an MEA-content lower than 1 ppm. Upon an increase of the MEA concentration from 30 to 40 wt. %, the thermal energy requirement decreased with 5-8 %. Furthermore, the cooling water and solvent consumption decreased with increasing MEA concentration (see Figure 2-8 and Figure 2-9). The optimum lean solvent loading was for example around 0.32 and 0.29 mol $CO_2$/mol MEA for 30 MEA wt. % and 40 MEA wt. % solutions, respectively. This lower solvent loading with increasing MEA concentration is due to the lower rich solvent loading obtained when using high MEA concentrations.

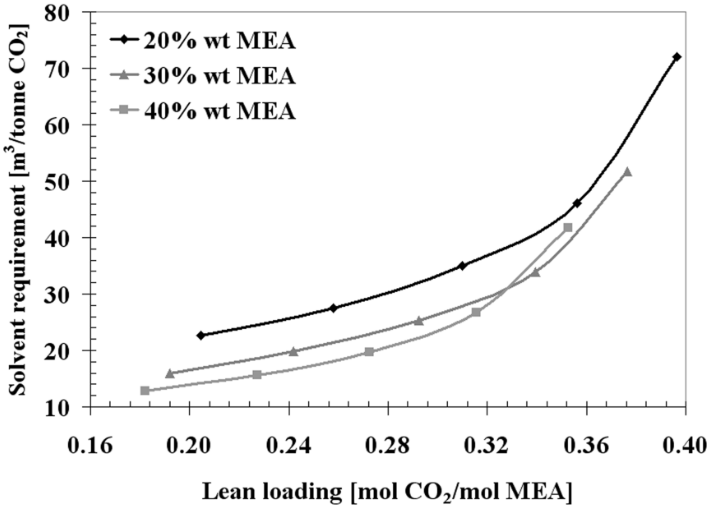

**Figure 2-8 Solvent flow rate requirement at various lean solvent loadings for different MEA wt. %**

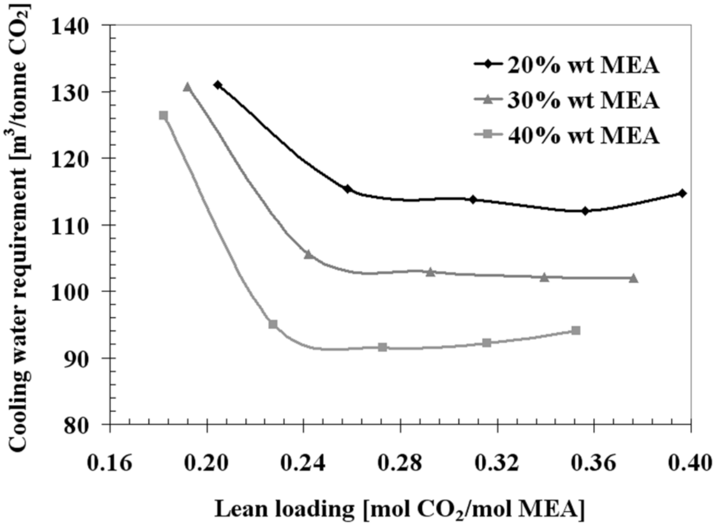

**Figure 2-9 Cooling water consumption at various lean solvent loadings for different MEA wt. %**

### 2.3.4 Effect of the stripper operating conditions

The effect of different conditions (temperature and pressure) of the stripper has also been investigated. In this investigation, the striper conditions (temperature and pressure) where changed while keeping the main process specifications (number of equilibrium stages, solvent flow rate and lean loading) constant. It is expected that at high temperature (and therefore pressure) the $CO_2$ mass transfer rate, throughout the stripper column is positively affected via the increased driving force. Starting from the base case (90 % $CO_2$ removal, 30 wt. % MEA solution and 0.24 mol $CO_2$/mol MEA lean solvent loading) the effect of the stripper operating pressure (90-210 kPa) was investigated, assuming a total pressure drop of 30 kPa over the stripper packing and wash section. Table 2-3 shows the effect of the stripper pressure and temperature on the process requirement.

**Table 2-3 Results of the main process parameters at different stripper pressure**

| Stripper pressure kPa | Stripper temperature °C | Thermal energy GJ/tonne $CO_2$ | Solvent $m^3$/tonne $CO_2$ | Cooling water $m^3$/tonne $CO_2$ |
|---|---|---|---|---|
| 90 | 108 | 4.87 | 19.5 | 128 |
| 120 | 114 | 4.24 | 19.7 | 114 |
| 150 | 120 | 3.89 | 19.8 | 105 |
| 180 | 124 | 3.68 | 19.9 | 101 |
| 210 | 128 | 3.56 | 20 | 98 |

Clearly, with increased operating pressure of the stripper the energy requirement decreased significantly; i.e., from 150 kPa (base case) to 210 kPa led to an 8.5 % reduction in the energy requirement. However, it might be realistic to expect that higher amine degradation rates and corrosion problems will occur at these elevated pressures and temperature. Nevertheless, it demonstrates the possibility of lowering the thermal energy requirement for solvent regeneration by increasing the stripper temperature. The operating pressure of the stripper is more than doubled between 108 °C and 128 °C. The impact of the higher pressure on the design and construction of the stripper has to be taken into account. The amount of solvent required is almost constant with a very small increase (max. 0.5 $m^3$/tonne $CO_2$) at the maximum stripper pressure used in this study. Because the flue gas specifications and the removal % of $CO_2$ are the same in all cases, the amount of solvent required does not depend much on the stripper conditions. The cooling water requirement is decreased; from *ca.* 128 $m^3$/tonne $CO_2$ at 90 kPa to *ca.* 98 $m^3$/tonne $CO_2$ at 210 kPa (see Table 2-3). Increasing the stripper temperature will increase the driving force; this will result in a smaller column and hence a lower capital investment.

### 2.3.5 Effect of the lean solvent temperature

In section 2.3.2, it was mentioned that, at high lean solvent loadings the absorption temperature needs to be increased to ensure a closed water balance in the process. The lean solvent temperature was varied between 25 and 50°C for the base case (90 % removal, 30 MEA wt. % and 50 regeneration %), to investigate the effect of the lean solvent temperature on the process parameters. Increasing the lean solvent temperature had a negative effect on the thermal energy requirement because the rich solvent loading is lower at higher lean solvent temperature. This will result in higher regeneration energy (see Figure 2-10).

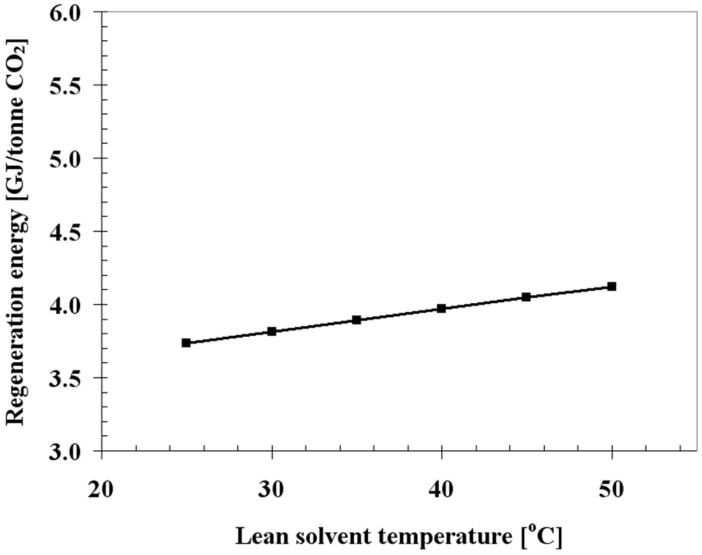

Figure 2-10 Thermal energy requirement for different lean solvent temperatures

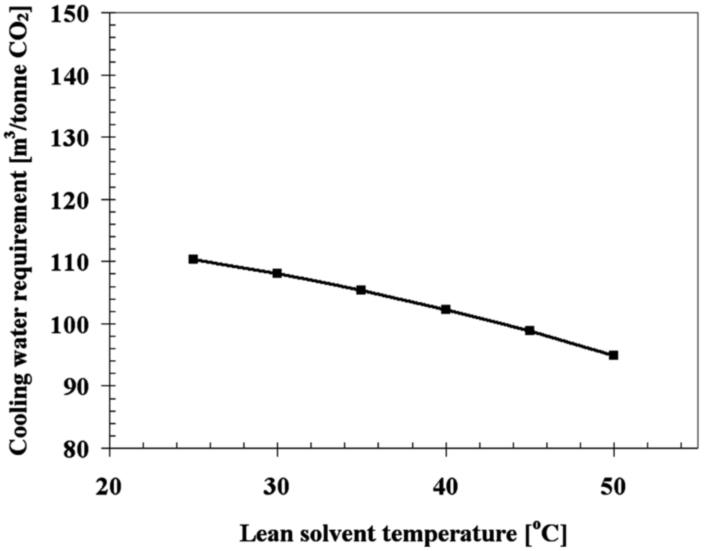

Figure 2-11 Cooling water consumption with different lean solvent temperatures

Decreasing the temperature to 25°C led to a 4 % reduction in the thermal energy requirement compared to the base case. The solvent circulation rate is nearly constant over the temperature range, because the lean solvent loading is almost constant in all cases and the $CO_2$ recovery was kept the same. However, the effect on the cooling water was the opposite because less cooling energy is required in the lean cooler, resulting in lower total cooling water consumption with an increased solvent temperature (see Figure 2-11). At a higher lean solvent temperature, the absorber as a whole will be operated at a higher temperature. This higher operating temperature will increase the evaporation rate of MEA from the top of the absorber. To avoid this high evaporation rate of MEA, the washing section is required to operate at a higher washing water rate.

## 2.4 Process optimisation with respect to thermal energy requirement

### 2.4.1 Definition of the optimum process

The thermal energy requirement in the capture process is the most important factor, because it is responsible of the major reduction of the power plant overall thermal efficiency. The optimum process will be defined as the process which has the lowest thermal energy requirement for the five parameters investigated, i.e. $CO_2$ removal %, MEA solvent concentration, lean solvent loading, stripper operating pressure and lean solvent temperature.

For the optimization 90% $CO_2$ removal was chosen, because the analysis showed that this parameter was not a critical factor. Increasing the MEA wt. % decreased the energy requirement, with a minimum observed for a 40 wt. % solutions. Two optimum processes were defined: the first one with a MEA concentration of 40 MEA wt. % and the second one, chosen close to currently used solvent composition, with a concentration of 30 MEA wt. %. The latter concentration is probably more realistic due to the practical constraints imposed by solvent corrosion and degradation. The optimum lean solvent loading equalled 0.30 and 0.32 mol $CO_2$/mol MEA for 40 wt. % and 30 wt % MEA solutions, respectively.

Higher stripper operating pressures always resulted in a lower thermal energy requirement and an optimum stripper operating pressure of 210 kPa, which was the maximum considered in this study. Decreasing the absorption lean solvent temperature resulted in lower thermal energy requirement. Therefore, a lean solvent temperature of 25°C will be used in the process optimization. However, as discussed earlier, for high lean solvent loadings the lean solvent temperatures had to be increased in order to maintain the water balance over the complete process, therefore it may difficult to realize convergence for all of the process simulations at 25°C. Therefore, the optimum lean solvent temperature will be defined as the lowest temperature that can be achieved; for some cases, this could be higher than 25°C because of computational reasons. The specifications of the two optimum processes are summarised in Table 2-4.

**Table 2-4 Optimum process specifications**

| | **30% MEA** | **40% MEA** |
|---|---|---|
| $CO_2$ removal percentage | 90 | 90 |
| MEA wt. % | 30 | 40 |
| Lean solvent loading (mol $CO_2$/mol MEA) | 0.32 | 0.30 |
| Stripper operating pressure (kPa) | 210 | 210 |
| Absorption solution temperature (°C) | ca. 25 | ca. 25 |

### 2.4.2 The optimum processes

The defined processes in Table 2-4 were simulated with ASPEN Plus; the results are presented in Table 2-5 including the base case results for a clear comparison. Clearly, the optimum processes that were defined had a lower thermal energy requirement than the base case process, with a reduction of 16% and 23 % for 30 and 40 MEA wt. % solutions, respectively. This decrease in the thermal energy requirement would cause the operating costs to decrease significantly, thereby strongly improving the process. However, it should be noted that, because of the changes in the process operating conditions, capital costs could increase as well as the operating costs due to the need of e.g. corrosion additives and more stripper design requirement at high operating pressure.

**Table 2-5 Optimum process results**

| | Base case | 30% MEA | 40% MEA |
|---|---|---|---|
| Amine lean solvent loading (mol $CO_2$/mol MEA) | 0.242 | 0.32 | 0.30 |
| Amine rich solvent loading (mol $CO_2$/mol MEA) | 0.484 | 0.493 | 0.466 |
| Reboiler heat required (GJ/tonne $CO_2$) | 3.89 | 3.29 | 3.01 |
| Solvent flow rate required ($m^3$/tonne $CO_2$) | 20.0 | 27.8 | 22 |
| Lean Solvent Temperature (°C) | 35 | 30 | 25 |
| Cooling water required | | | |
| Feed cooling water ($m^3$/tonne $CO_2$) | 9 | 9 | 9 |
| Condenser ($m^3$/tonne $CO_2$) | 41.5 | 24 | 19.7 |
| Lean cooler ($m^3$/tonne $CO_2$) | 42 | 57 | 54 |
| Scrubber ($m^3$/tonne $CO_2$) | 0.2 | 0.03 | 0.03 |
| $CO_2$ product compressor inter-cooling ($m^3$/tonne $CO_2$) | 13 | 13 | 13 |
| Total cooling water required ($m^3$/tonne $CO_2$) | 106 | 103 | 96 |

For the optimum process, the cooling water required in the capture process decreased by 3-10 % compared to the base case. Furthermore, the solvent required in the optimum processes increased with 10-40 % compared to the base case, and that is because of the higher lean solvent loading used in the optimization.

## 2.5 Conclusions

The modelling work and parametric study has shown that that Aspen Plus with RADFRAC subroutine is a useful tool for the study of $CO_2$ absorption processes. The lean solvent loading was found to have a major effect on the process performance parameters such as the thermal energy requirement. Therefore, it is a main subject in the optimisation of solvent processes.

Significant energy savings can be realized by increasing the MEA concentration in the absorption solution. It is however still to be investigated if high MEA concentrations can be used due to possible corrosion and solvent degradation issues.

Increasing the operating pressure (temperature) in the stripper would lead to a higher efficiency of the regeneration and would reduce requirement of the thermal energy. Moreover, a high operating pressure would reduce the costs and the energy needed for $CO_2$ compression.

Decreasing the lean solvent temperature would save energy in the process, but the amount of cooling water required would counter balance this effect.

From the optimization of the absorption/desorption cycle for $CO_2$ capture process, it can be concluded that a reduction of around 20 % in the thermal energy requirement seems realistic to be expected. For the optimum process, using a 30 MEA wt. % solution the energy requirement was found to be 3.3 GJ/tonne $CO_2$, which looks promising in reducing the costs and increase of the efficiency of the capture process. Moreover, when the absorption solution consisting of a 40 wt. % MEA could be used, the energy requirement is 3.0 GJ/tonne $CO_2$, which is a substantial reduction compared to 3.9 GJ/tonne $CO_2$ as found for the base case.

## 2.6 Appendix: Column design model

The absorber design was based on the data provided from the equilibrium stage Aspen Plus simulation using RADFRAC. This provided the detailed gas and liquid composition (including solvent loading) and temperature data for each equilibrium stage. For each equilibrium stage the logarithmic mean driving force ($\Delta P$) and $CO_2$ absorption flux can then be determined, which is used in the absorber column sizing.

The two most important parameters for the column sizing are the column diameter and the column volume. The column diameter is function of the liquid and gas flow rates and densities. The two main parameters in determining the column diameter are the flooding limitation and the pressure drop of packed height. The columns diameter has been calculated according to [14]. In order to calculate the height of each stage and then the total column height first the mass transfer flux and the amount of $CO_2$ absorbed was calculated. The mass transfer flux can be obtained using

$$J = K_{OV} \Delta C \tag{2-1}$$

Then the area of packing could be determined from:

$$A_P = \frac{\phi_{CO_2}}{J} \tag{2-2}$$

From the required area of packing and in combination with the specific area of packing, the volume of packing was calculated in each stage. The packing volume for each stage was added up resulting in an overall packing volume. The height of packing in addition to extra factors (e.g. column entrance and exit, height needed for liquid distributors) have resulted in the overall column height. For each equilibrium stage, the overall mass transfer coefficient needs to be estimated. The overall mass transfer coefficient can be written as:

$$K_{OV} = \frac{1}{\frac{1}{K_G} + \frac{1}{mEK_L}} \tag{2-3}$$

The enhancement factor $E$, is the ratio between the chemical and the physical absorption flux at the same driving force. It is given as a function of two parameters, the Hatta number (Ha) and the enhancement factor of an infinitely fast reaction ($E_\infty$). The enhancement factor may be considered a correction to the liquid side mass transfer coefficient due to the chemical reaction occurring in the concentration boundary layer. The Hatta number, indicative of the rate of diffusion transport vs. chemical reaction, is given by:

$$Ha = \frac{\sqrt{D_{CO_2,am} k_2 C_{MEA}}}{K_L} \tag{2-4}$$

The enhancement factor for an infinitely fast reaction dependent on the choice of the mass transfer model. In case of the film model, it may be written as:

$$E_\infty = \left[1 + \frac{D_{MEA,am} C_{MEA}}{\gamma D_{CO_2,am} C_{CO_2,i}}\right] \tag{2-5}$$

The concentrations used in this equation are in the mol/m$^3$ units. $C_{MEA}$ is the free MEA in the bulk, which can be calculated from the MEA concentration and the loading as following:

$C_{MEA} = C[1-2\alpha]$, as 1 mol of $CO_2$ used 2 moles of MEA in the reaction

To calculate the value of enhancement factor an iterative solution for the equation below that is described in [17] was used:

$$E = \left[\frac{Ha\sqrt{\dfrac{E_\infty - E}{E_\infty - 1}}}{\tanh\left[Ha\sqrt{\dfrac{E_\infty - E}{E_\infty - 1}}\right]}\right] \tag{2-6}$$

The value of E was determined for each equilibrium stage at the point where the logarithmic mean driving force equal to the local driving force, as suggested in [18]. The analysis assumes that the reaction between $CO_2$ and MEA is simple second order, as shown in [13]. The reaction rate is given by:

$$k_2 = 4.4 * 10^8 \exp\left[\tfrac{-5400}{T}\right] \tag{2-7}$$

Strictly speaking, this relation is valid up to 40 $^oC$, but we assume that this relation is also applicable in the range of absorber temperatures (< 55 $^oC$). The reversible reaction constant in the stripper column was estimated using the correlation below developed by Jamal [16], which is valid to temperatures up to the stripper conditions.

$$K_{-1} = 3.95 * 10^{10} \exp\left[\frac{-6863.8}{T}\right] \tag{2-8}$$

Mellapak structure packing Y125 was used for both absorption and stripping columns. The physical mass transfer coefficient was estimated using the Bravo, Fair's correlation [14].

## 2.7 Notation

| | | |
|---|---|---|
| $A_P$ | Area of packing | $m^2$ |
| C | MEA concentration | $mol/m^3$ |
| $C_{CO2,i}$ | Carbon dioxide concentration at the interface | $mol/m^3$ |
| $C_{MEA}$ | MEA concentration | $mol/m^3$ |
| $D_{CO_2,am}$ | $CO_2$ diffusivity in the MEA solution | $m^2/s$ |
| $D_{MEA,am}$ | MEA diffusivity in the MEA solution | $m^2/s$ |
| $E$ | Enhancement factor | |
| $E_\infty$ | Enhancement factor of an infinitely fast reaction | |
| Ha | Hatta modules | |
| J | Mass transfer flux | $mol/m^2.s$ |
| $K_{-1}$ | Regeneration reaction rate constant | $m^3/mol.s$ |
| $k_2$ | Forward second order reaction rate constant | $m^3/mol.s$ |
| $K_G$ | Mass transfer coefficient in the gas phase | m/s |
| $K_L$ | Mass transfer coefficient in the liquid phase | m/s |
| $K_{ov}$ | Overall mass transfer coefficient | m/s |
| MEA | Monoethanolamine | |
| m | Solubility of carbon dioxide at equilibrium | |
| T | Temperature | K |
| $\Delta C$ | Actual driving force | $mol/m^3$ |
| $\alpha$ | $CO_2$ loading | mol $CO_2$/mol MEA |
| $\varphi_{CO2}$ | $CO_2$ flow | mol/s |
| $\gamma$ | Stoichiometric ratio in the reaction | |

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"To succeed in life, you need two things: ignorance and confidence"
Mark Twain

# 3

# BASE CASE $CO_2$ POST-COMBUSTION CAPTURE PROCESS ECONOMIC EVALUATION

*While the demand for reduction in* $CO_2$ *emission is increasing, the cost of the* $CO_2$ *capture processes remains a limiting factor for large-scale application. Reducing the cost of the capture system by improving the process and the solvent used must have a priority in order to apply this technology in the future. In this paper, a definition of the economic baseline for post-combustion* $CO_2$ *capture from 600 MWe bituminous coal-fired power plant is described. The baseline capture process is based on 30% (by weight) aqueous solution of monoethanolamine (MEA). A process model has been developed previously using the Aspen Plus simulation programme where the baseline* $CO_2$ *removal has been chosen to be 90%. The results from the process modelling have provided the required input data to the economic modelling. Depending on the baseline techno-economic results, an economic parameter study for a* $CO_2$ *capture process based on absorption/desorption with MEA solutions was performed.*

*Major capture cost reductions can be realized by optimizing the lean solvent loading, the amine solvent concentration, as well as the stripper operating pressure. A minimum* $CO_2$ *avoided cost of 33 €/tonne* $CO_2$ *was found for a lean solvent loading of 0.3 mol* $CO_2$*/mol MEA, using a 40 wt. % MEA solution and a stripper operating pressure of 210 kPa. At these conditions 3.0 GJ/tonne* $CO_2$ *of thermal energy was used for the solvent regeneration. This translates to 22 €/MWh increase in the cost of electricity, compared to 31.4 €/MWh for the power plant without capture.*

## 3.1 Introduction

The amine based absorption systems are the most suitable for $CO_2$ post-combustion from power plants [1]. The technology is commercially available and it has been used in the Fluor technology's Econamine FG™ and Econamine FG Plus™ [2,3] and the ABB Lummus Global technology [4].

The estimated cost of $CO_2$ capture increases the cost of electricity production by 35-70% for natural gas combined cycle (NGCC), and 40-85% for a supercritical pulverized power plant (PC). Overall, the electricity production cost for fossil fuel plants with capture (excluding $CO_2$ transport and storage costs) ranges from 0.04-0.09 US$/kWh, as compared to 0.03-0.06 US$/kWh for similar plants without capture [5].

New or improved methods of $CO_2$ capture, combined with advanced power systems and industrial process designs, could reduce $CO_2$ capture cost and energy requirements. At present, many research activities underway trying to improve the capture process or applying an improved solvents to reduce the energy requirement and as a result, the $CO_2$ capture cost.

Several studies have been done in the area of techno-economic modelling. The majority of these activities were focused on defining a baseline case for different power plants i.e. coal-fired or natural gas combined cycle [2,3,11] for a single design point, e.g. percent $CO_2$ removal. Depending on the definitions of the capture baseline cases, other work was focused on the comparison of these baseline cases with new processes like $O_2/CO_2$ recycle combustion [13]. None of these studies considered the impact of variation in process design parameters, such as the percentage of $CO_2$ removal or desorption conditions, on the process economics.

The objective of this work was to develop tools for process design and economic analysis to arrive at an optimised MEA based capture process depending on several techno-economic parameters. The parametric study was based on the conventional technology commercially available on a small scale [2], without any novel process changes and improvement like split-flow and inter-cooling [3], because they have not been used yet in commercial applications. This optimization included investigating the effect of $CO_2$ removal percentage, MEA concentration, lean solvent loading, and stripper operating pressure. In addition to the process design parameters, the impact of economic parameters such as fuel prices and interest rate was investigated.

## 3.2 Definition of economic baseline

### 3.2.1 Methodology and baseline description

The general methodology for the economic evaluation was based on a step-wise approach consisting of the following:

1. Capture process simulation; the $CO_2$ absorption/desorption process design was based on MEA as the main component in the solvent system. ASPEN Plus was shown to be very useful as the process simulation tool [6].
2. Modelling and design of the main equipment; the absorber and regenerator column were modelled and designed in detail, using the results from the Aspen Plus simulation. The rest of the equipment was sized to provide information on equipment cost and use of utilities and consumables as required for the economic calculations.

3. Process economics, determination of capital and operating expenses and overall process evaluation with reference to techno-economic performance parameters.

To enable a complete investigation of the capture process, information on both equipment and operating cost was obtained from a number of sources; including vendor input and public sources [1,2,7-10]. The cash flow analysis method over the project life was used to evaluate the total annual cost. The cost of electricity (CoE) was estimated for the reference power plant before and after adding the capture process. This cost of electricity was considered the one, which resulted in a zero net present value at the end of the project life. Cost of electricity in combination with the $CO_2$ emission values, can then translated into cost of $CO_2$ emission avoided. This cost is important for comparative evaluations of $CO_2$ capture and storage with other measures for reductions of $CO_2$ emissions. It can be calculated as follows:

$$Cost\ of\ CO_2\ Avoided\ (Euro/ton) = \frac{Cost\ of\ Electricity_{capture} - Cost\ of\ Electricity_{reference}}{CO_2 Emission_{reference} - CO_2 Emission_{capture}}$$

A 600 MWe gross coal fired power plant was chosen as the reference power plant with a constant fuel input before and after adding the capture system. Capital and operating cost for this European reference power plant were readily available. The baseline capture process was designed to remove 90% of the $CO_2$ present in the flue gas. The solvent used was 30 MEA wt. % and in the baseline process the lean solvent loading was equal to 0.242 mol $CO_2$/mol MEA lean solvent loading representing a degree of regeneration equal to 50 %. The assumptions used in carrying out the economic evaluation are shown in Table 3-1.

**Table 3-1 Economic evaluation assumptions**

| | |
|---|---|
| Project life (years) | 25 |
| Equipment salvage value | zero |
| Construction period (years) | 3 |
| Plant operating (hour/year) | 7500 |
| Maintenance cost (% of fixed capital investment) | 4 |
| Interest rate (%) | 8 |
| MEA price (Euro/tonne) | 1000 |
| Cooling water make up ($m^3$/GJ thermal) | 1.0 |
| Cooling water price (Euro/$m^3$) | 0.2 |
| MEA degradation rate (kg/tonne $CO_2$) [1] | 1.5 |
| $CO_2$ product temperature ($^oC$) | 25 |
| $CO_2$ product pressure (bar) | 110 |

### 3.2.2 Base case specifications and results

Capital and operating cost for the capture process were determined using the methodology described in section 3.2.1.

#### 3.2.2.1 *Capital cost*

The capital cost consists of three main components:

1. Power plant specific cost: These were defined and agreed upon in joint effort by European power plant companies supporting the study.
2. Capture plant cost: The cost of the equipment for the capture process was estimated using several references [7-9].
3. $CO_2$ compression cost: Compressor cost has been taken from [12]. Table 3-2, gives an overview of the equipment cost for solvent process for the base case power plant with 90% $CO_2$ capture. This does not include the $CO_2$ compressor.

**Table 3-2 Overview of equipment cost**

| Type of Equipment | Cost (M€) |
|---|---|
| Reboiler | 0.67 |
| Lean/rich HEX | 0.35 |
| Lean Cooler | 0.12 |
| Reflux Condenser | 0.10 |
| DCC water Cooler | 0.10 |
| Storage Tank | 0.61 |
| Gas Blower | 2.6 |
| Gas Scrubber | 0.21 |
| Absorber Fluid Pump | 0.49 |
| Condenser Fluid Pump | 0.01 |
| Stripper Fluid Pump | 0.50 |
| Cold Water Pump | 1.7 |
| Absorber | 9.2 |
| DCC (Feed Direct Cooler) | 0.45 |
| Stripper | 2.85 |
| Total | 19.96 |

The most expensive equipment is the absorber, which is responsible for about 50% out of 20 million Euros for the total equipment purchased cost. In total, the equipment related to the gas path contributes 75% of the equipment cost. Outside the gas path, the second major equipment cost is for the stripper, which also contributes of about 14% of total equipment purchased cost. It is clear that an improved and cheaper packing material or a simpler absorber could reduce the cost of the overall equipment significantly.

No auxiliary units or equipment were included in this work, because the fuel input kept constant and no extra boiler is needed. The rest of the direct and indirect cost was estimated as a factor of the overall equipment cost using [8] and by using factors from the IECM model documentation [10]. Table 3-3, shows the composition of the total capital investment (CAPEX).

**Table 3-3 MEA scrubbing process total capital investment (CAPEX)**

| **Direct Cost** | **% of purchased Cost** | **used** | **Cost (M€)** |
|---|---|---|---|
| ISBL | | | 44.67 |
| Purchased equipment [7-9] | 100 | 100 | 19.96 |
| Purchased equipment installation [8] | 25–55 | - | 10.54 |
| Instrumentation and Control [8] | 8–50 | 20 | 3.99 |
| Piping [8] | 20–80 | 40 | 7.98 |
| Electrical [8] | 15–30 | 11 | 2.20 |
| OSBL | | | 8.98 |
| Building and building services [8] | 10–80 | 10 | 2.00 |
| Yard improvements [8] | 10–20 | 10 | 2.00 |
| Services facilities [8] | 30–80 | 20 | 3.99 |
| Land [8] | 4–8 | 5 | 1.00 |
| Total Direct Cost | | | 53.66 |
| **Indirect Cost** | **% of purchased Cost** | **used** | **Cost (M€)** |
| Engineering [10] | 10 | 10 | 5.37 |
| Construction Expenses [10] | 10 | 10 | 5.37 |
| Contractor's Fee [10] | 0.5 | 0.5 | 0.27 |
| Contingency [10] | 17 | 17 | 9.12 |
| Total Indirect Cost | | | 20.12 |
| $CO_2$ Compressor Inv Cost [12] | | | 31.73 |
| Fixed Capital Investment | | | 105.51 |
| | **% of FCI** | **used** | **Cost (M€)** |
| Fixed Capital Investment | 100 | 100 | 105.51 |
| Working Investment [8] | 12–28 | 25 | 26.38 |
| Start-up Cost + MEA Cost [8] | 8–10 | 10 | 14.66 |
| **Total Capital Investment (CAPEX)** | | | **146.55** |

The total capital investment (CAPEX) for the amine plant including $CO_2$ compression is 147 million Euro, which compares well to the 179 million dollar (149 million Euro) figure identified in Singh 2003 [13] after removing the cost of the auxiliary units which are not needed in this work. The total specific capital investment for the power plant after adding the capture process is almost, double which is clear in Table 3-5. The increase in the power plant capital investment contribution of the overall capital investment is also due to the reduction in the thermal efficiency of the power plant after addition of the capture process.

#### 3.2.2.2 *Operating cost*

The total operating cost (OPEX) includes two main categories:

1. The production cost, which consists of the O&M, cooling water, chemicals, labours, local taxes, and plant overhead.
2. The general expenses, which contain the R&D, administration, and marketing cost. In Table 3-4, the total operating cost of amine plant is shown.

**Table 3-4 MEA scrubbing process total operating cost (OPEX)**

| | Range | Used value | Cost (M€/yr) |
|---|---|---|---|
| Fixed Charge | | | 3.17 |
| Local Taxes [8] | 1.0-4.0 % FCI | 2 | 2.11 |
| Insurance [8] | 0.5-1 % FCI | 1 | 1.06 |
| **Direct Production Cost** | | | **14.06** |
| Raw material | | | 0.00 |
| Cooling water | | | 2.65 |
| MEA makeup [1] | 1.5 kg/tonne $CO_2$ | | 4.78 |
| Activated Carbon [3] | | | 0.74 |
| Maintenance [13] | 1.0-10% FCI | 4 | 4.22 |
| Operating labour (OL) [1] | 2 job/shift | 45 Euro/hr | 0.68 |
| Supervision & Support labour [10] | 30% of total labour cost | 30 | 0.29 |
| Operating supplies [8] | 15% of Maintenance | 15 | 0.63 |
| Laboratory charges [8] | 10-20% OL | 10 | 0.07 |
| **Plant Overhead Cost** | 50-70% of (M+OL+S) | 60 | **3.11** |
| **General Expenses** | | | **1.29** |
| Administrative cost [8] | 15-20% of OL | 15 | 0.10 |
| Distribution and Marketing [8] | 2-20% of OPEX | 0.5 | 0.11 |
| R&D cost [8] | 2-15% of OPEX | 5 | 1.08 |
| **Total Manufacturing cost (OPEX)** | | | **21.62** |

The total operating cost found to be 22 million Euro per year. 35% of the direct production cost is MEA make up and almost 32% are maintenance cost. This total operating cost is in a good agreement with Singh 2003 [13] who arrived at a value of 28 million dollar excluding the cost of the natural gas needed for the auxiliary boiler, which is not required in our work. However, adding the capture has a major impact on the overall power plant efficiency. The overall efficiency will decrease from 45% for the reference power plant to 31% due to the addition of the capture process. This 14% reduction is mainly because of the heat needed for solvent regeneration, which is responsible of 55% of total electricity output reduction. The rest is 24% for $CO_2$ product compression and 21% for process pumps and the flue gas blower. The large regeneration heat required and process energy consumption brings us to the conclusion that an improved solvent and process innovation are needed to reduce the absorption process energy requirement.

Table 3-5, shows the overall results of the power plant base case before and after adding the capture process. An increase in the cost of electricity of around 26 €/MWh can be seen as a results of introducing the amine capture process in the power plant. One of the objectives of this work is to reach an optimum process, which has a lower effect on the overall plant efficiency, by reducing the capture capital and operating cost. The cost of electricity increases upon addition of the capture process, and 60% of that increase is due to the operating cost in combined with the fuel cost, which was increased due to efficiency reduction.

**Table 3-5 Summary of techno-economic results for the base case**

| **Item** | **Base case** | |
|---|---|---|
| | **Without capture** | **With capture** |
| **Capture Process Performance** | | |
| Capacity (tonne/hr) | - | 408 |
| Energy requirement (GJ/tonne) | - | 3.9 |
| Electricity (kWh/tonne) | - | 193 |
| **Power Plant Performance** | | |
| Fuel input (MW, LHV) | 1279 | 1279 |
| Fuel price (€/GJ) | 1.6 | 1.6 |
| Net power output (MW) | 575 | 399 |
| Thermal efficiency, % (LHV) | 45 | 31 |
| $CO_2$ emission (kg/MWh) | 772 | 112 |
| **Cost** | | |
| Capture Investment (€/(tonne/hr)) | - | 3.6E+05 |
| Total Investment (€/kW) | 980 | 1841 |
| Operating cost (m€/yr) | 75 | 96 |
| Cost of Electricity (€/MWh) | 31.4 | 57.4 |
| Cost of $CO_2$ Avoided (€/tonne) | - | 39.3 |

Comparing these overall results for the base case with the results obtained by the IPCC [1], we can find that the values in this study are considered in the lower bound of the values specified by IPCC. These lower values can be explained by the difference in the currency change rate between 2002 and 2004, also the capacity factor in this study is higher than the one used in the IPCC study. However, comparing the overall results with a European study, which was carried out by VGB power tech [14] we can see that the values from these studies are in line. The power plant specific cost found in the VGB report are 1020 €/kW before adding the capture process and increased to 1860 €/kW after adding the capture process. Moreover the cost of electricity was increased from 37 €/MWh before capture to 64 €/MWh after adding the capture process with an increase of 27 €/MWh which is in good agreement with this work. The overall avoided cost was found by VGB to be 47 €/tonne $CO_2$, which is around 20% higher than the avoided cost in this study and that can be related to the 20% higher power plant capacity in this study.

## 3.3 Effect of process design on cost of electricity and avoided costs

### 3.3.1 Variation in process design parameters

It has become clear from our previous study [6] that the process design can be subjected to optimisation. For instance, by varying the degree of solvent regeneration it is possible to obtain a minimum in the thermal energy required for solvent regeneration. In this section, the effect of variation of the process design parameters on the cost of electricity and costs per tonne $CO_2$ avoided will be assessed using the economic tools described in section 3.2 and the results of the process design from our previous publication [6].

### 3.3.2 Effect of different lean solvent loading including the effect of $CO_2$ removal percentage

The cost of electricity (CoE) was determined as a function of lean solvent loading, which represents the degree of solvent regeneration the results are shown in Figure 3-1 as a function of different value of $CO_2$ removal. The results in Figure 3-1 show that the CoE has a shallow minimum for the lean solvent loading values between 0.25 and 0.33 mol $CO_2$/mol MEA. This is the range in which, the thermal energy requirement is at its minimum, indicating a link between the thermal energy requirement, and increased electricity cost. The CoE is obviously influenced by the level of $CO_2$ removal, with the lowest cost for the lowest value of $CO_2$ removal.

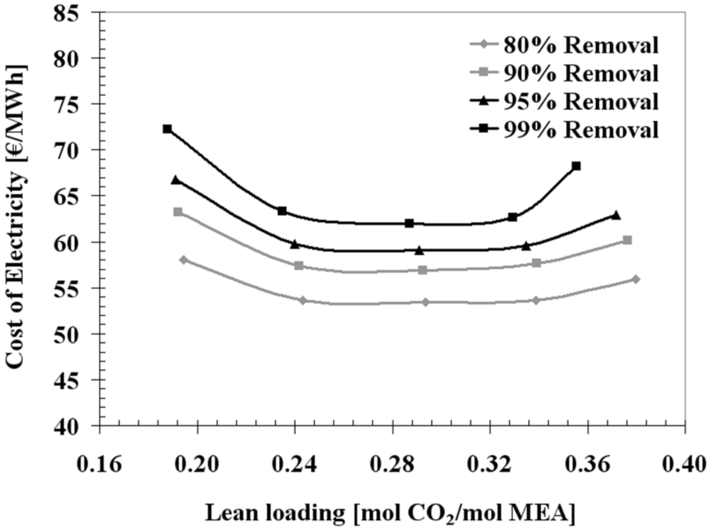

**Figure 3-1 Cost of electricity as a function of lean solvent loading for different $CO_2$ removal**

In Figure 3-2, the costs per tonne $CO_2$ avoided are shown for different values of the $CO_2$ removal as a function of the lean solvent loading. The results show a near constant cost per tonne $CO_2$ avoided for lean solvent loading values between 0.25 and 0.33 mole $CO_2$/mole MEA of around 40 Euro/tonne $CO_2$. This value does not vary for a $CO_2$ removal between 80 % and 95 %. This means that marginal cost for $CO_2$ capture is constant in this range but increase at higher $CO_2$ removal values.

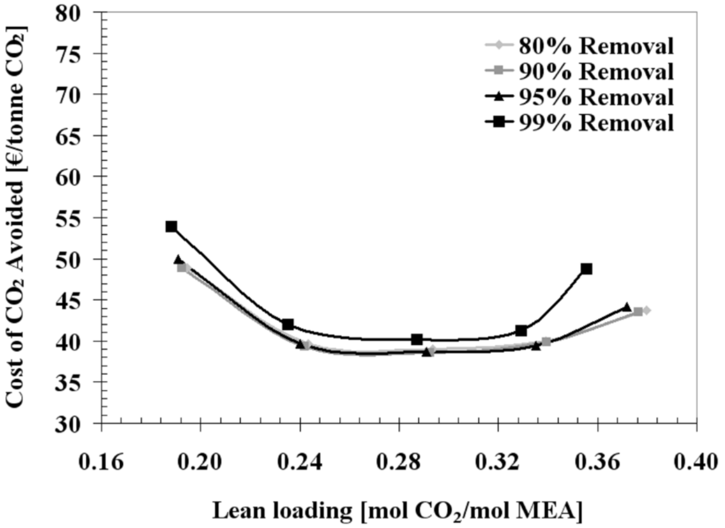

**Figure 3-2 Cost per tonne $CO_2$ avoided as a function of lean solvent loading for different $CO_2$ removal**

The CoE and cost of $CO_2$ avoided were studied at low $CO_2$ removal as well (see Figure 3-3). The results show that the CoE increased with increasing $CO_2$ removal. From these results, it can be concluded that partial removal of $CO_2$ from the flue gas, i.e. $CO_2$ removal below 80%, leads to increased costs per tonne $CO_2$ avoided. It is therefore not economically attractive to aim for partial $CO_2$ removal.

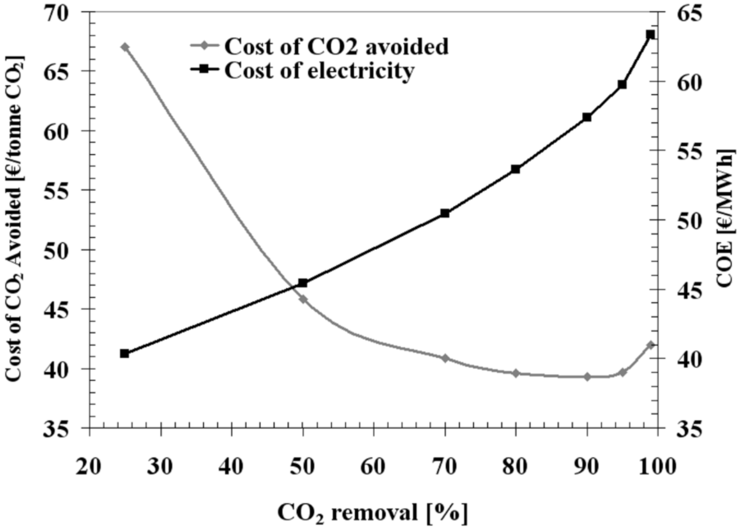

**Figure 3-3 Cost per tonne $CO_2$ avoided and cost of electricity as a function of $CO_2$ removal**

### 3.3.3 Effect of MEA weight %

In Figure 3-4, the cost of electricity is shown as a function of the lean solvent leading for different MEA concentrations. A removal of $CO_2$ equal to 90% was used in the analysis. The results in Figure 3-4 illustrate that there are clear benefits in increasing the MEA concentration in the solvent. Upon an increase of the MEA concentration from 30 to 40 wt. %, the CoE decreases up to 6%. The minimum CoE occurs for lean solvent loading in the range of 0.26 – 0.30 mole $CO_2$/mol MEA, and at 40 MEA wt. %.

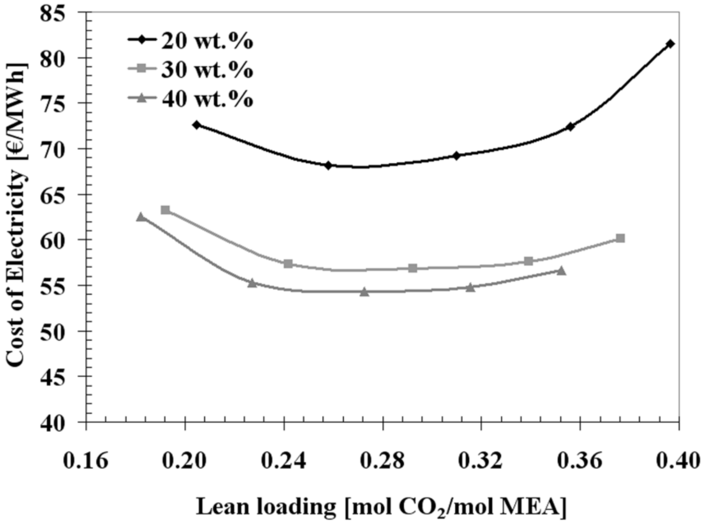

**Figure 3-4 Cost of electricity as a function of lean solvent loading for different MEA concentrations**

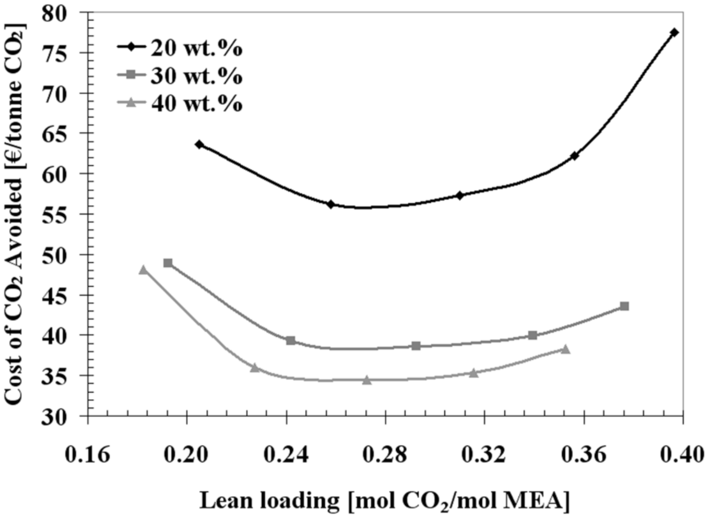

**Figure 3-5 Cost per tonne $CO_2$ avoided as a function of lean solvent loading for different MEA concentrations**

The costs per tonne $CO_2$ avoided for different MEA concentrations as a function of the lean solvent loading are shown in Figure 3-5. Figure 3-5 shows that higher MEA concentrations will result in lower avoided cost. The cost can be reduced to 35 €/tonne $CO_2$ using a 40 % MEA concentration. The lower cost is the result of a reduction in the energy requirement for regeneration and lower investment cost for the capture plant as the liquid flow rates are reduced. Furthermore, using a 20% MEA concentration leads to substantially higher cost of $CO_2$ avoided of at least 56 €/tonne $CO_2$.

### 3.3.4 Effect of the stripper operating pressure and temperature

The effect of a higher operating pressure and temperature of the stripper was also investigated. It is expected that the $CO_2$ mass transfer rate throughout the stripper column is positively affected via the driving force. Starting from the base case, the effect of the stripper operating pressure (90-210 kPa) was investigated, assuming a total pressure drop of 30 kPa over the stripper packing and wash section. Increasing the stripper operating pressure (temperature) has a noticeable effect on the capture process by reducing the thermal energy requirement, as was shown in the process study [6].

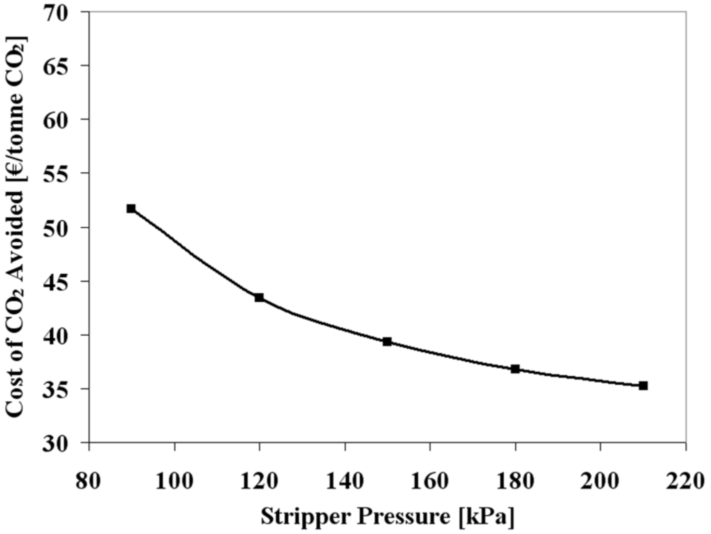

**Figure 3-6 Cost per tonne $CO_2$ avoided as a function of stripper pressure**

The effect of different stripper operating conditions on the costs per tonne $CO_2$ avoided is shown in Figure 3-6. Increasing the pressure from the base case 150 kPa to 210 kPa, will reduce the cost of $CO_2$ avoided with around 10% (see Figure 3-6). This is a significant improvement upon the base line capture process. There does not appear to be a benefit in lowering the stripper pressure and temperature.

## 3.4 Sensitivity analysis

Variations in the values of the economic input parameters will also have a significant impact on the cost of electricity and costs per tonne $CO_2$ avoided. The effect of the fuel price and interest rate on the CoE and the costs per tonne avoided were determined and shown in Table 3-6. For coal prices in the range 1.2 - 3.2 Euro/GJ the CoE for power plants with $CO_2$ capture is in the range 53 - 76 Euro/MWh up from the range 28 - 44 Euro/MWh for the power plant without capture. The increase in CoE is thus 25 - 32 Euro/MWh, which on average represents a 70 – 90% increase in the cost of electricity. Obviously, the fact that the capture of $CO_2$ requires additional energy leads to a strong dependence of the CoE on the cost of fuel.

**Table 3-6 Effect of interest rate and fuel price variation on the cost of electricity and the costs per tonne avoided $CO_2$**

| Fuel price (€/GJ) | Interest rate | CoE no capture €/MWh | CoE with capture €/MWh | Cost of $CO_2$ avoided €/tonne $CO_2$ |
|---|---|---|---|---|
| 1.2 | 0.08 | 28 | 53 | 37 |
| 1.6 | 0.08 | 31 | 57 | 39 |
| 3.2 | 0.08 | 44 | 76 | 48 |
| 1.6 | 0.04 | 27 | 48 | 33 |
| 1.6 | 0.08 | 31 | 57 | 39 |
| 1.6 | 0.12 | 37 | 68 | 47 |

The costs per tonne avoided show a steady increase with increase in fuel price, rising from 37 to 48 Euro/tonne avoided $CO_2$ at an interest rate of 0.08. Typically, a doubling of the fuel cost will lead to a 23% increase in the cost per tonne $CO_2$ avoided. For interest rates in the range 0.04 – 0.08 the CoE for power plants with $CO_2$ capture is in the range 48 - 68 Euro/MWh up from the range 27 - 37 Euro/MWh for the power plant without capture. Costs per tonne $CO_2$ avoided are in the range 33 - 47 Euro/tonne $CO_2$ for the interest rate range 0.04 - 0.08.

### 3.5 Process optimization at minimum thermal energy requirement

By the variation of the four operating parameters, i.e. $CO_2$ removal %, MEA solvent concentration, lean solvent loading, and stripper operating pressure an optimum process was aimed for. It was shown from the comparison between this work and our previous work [6] that the link between minimum thermal energy requirement and minimal cost of electricity or cost per tonne avoided is close. Therefore, the optimum process was defined as the process, which has the lowest thermal energy requirement for all parameters involved. The minimum was determined using ASPEN Plus as the process-modelling tool.

An optimum process would have the following characteristics: 90% $CO_2$ removal, 40 MEA wt. %, and 240 kPa stripper bottom pressure equivalent to a temperature of 128 $^{o}$C. Regarding the optimum lean solvent loading, the results show a shallow minimum at a range of lean solvent loading (0.25-0.33). The optimum value was chosen to be the one that gives the lowest energy requirement depending on the results of Abu-Zahra et al. [6]. For the case of 40 MEA wt. %, 0.30 mol $CO_2$/ mol MEA lean solvent loading was chosen. For currently used solvent compositions (30 MEA wt. %) the optimum lean solvent loading would equal to 0.32 mol $CO_2$/mol MEA.

The process optimization resulted in a major reduction in the process capital and operating expenses and the cost of $CO_2$ avoided as shown in Table 3-7. The optimum process with 40 MEA wt. % has a 23% reduction in the energy requirement compared to the baseline given in Table 3-5. Moreover, the cost of $CO_2$ avoided decreases with 16% comparing to the base case.

**Table 3-7 Optimum process specifications and results**

| Item | 30 % MEA | 40 % MEA |
|---|---|---|
| **Capture Process Performance** | | |
| Capacity (tonne/hr) | 405 | 406 |
| Energy requirement (GJ/tonne) | 3.3 | 3.01 |
| Electricity (kWh/tonne) | 192 | 182 |
| **Power Plant Performance** | | |
| Fuel input (MW, LHV) | 1279 | 1279 |
| Fuel price (€/GJ) | 1.6 | 1.6 |
| Net power output (MW) | 426 | 426 |
| Thermal efficiency, % (LHV) | 33 | 33 |
| $CO_2$ emission (kg/MWh) | 108 | 103 |
| **Cost** | | |
| Capture Investment (€/(tonne/hr)) | 4.00E+05 | 3.50E+05 |
| Total Investment (€/kW) | 1865 | 1712 |
| Operating cost (m€/yr) | 97 | 96 |
| Cost of Electricity (€/MWh) | 56 | 53 |
| Cost of $CO_2$ Avoided (€/tonne) | 37 | 33 |

## 3.6 Conclusions

The impact of the degree of regeneration, $CO_2$ removal, solvent concentration and stripper operating pressure on the economic performance of $CO_2$ capture from a coal-fired power station has been elaborated. The following conclusions can be drawn from this:

- The costs of $CO_2$ avoided and cost of electricity were found to show a shallow minimum for lean solvent loading between 0.25 and 0.33 mol $CO_2$/mol MEA. The costs per tonne avoided are quite similar for $CO_2$ removal in the range between 80% and 95%.
- Increasing the MEA concentration leads to a significant reduction in the costs per tonne $CO_2$ avoided. Hence, it is advantageous to go the highest concentration, if allowable from the corrosion point of view.
- A high stripper operating pressure will reduce the overall capture process costs and expenses in addition to the cost and the energy required for $CO_2$ compression.
- The impact of the fuel price on the costs per tonne $CO_2$ avoided is such that a doubling of the fuel cost will lead to a 23% increase in the cost per tonne $CO_2$ avoided.

The overall process economic analysis shows that process optimization will reduce the overall cost of a $CO_2$ capture process. The avoided cost is equal to 33 €/tonne $CO_2$ compared to the base case of 39 €/tonne $CO_2$. Furthermore, the cost of electricity would be 53 €/MWh, whereas for the base case the electricity cost would be 57 €/MWh.

## 3.7 References

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"Experience is a good school, but the fees are high" Heinrich Heine

# 4

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# EXPERIMENTAL VERIFICATION OF EQUILIBRIUM-STAGE AND RATE-BASED SIMULATIONS

*In this chapter, pilot plant data for $CO_2$ post-combustion capture are discussed and compared with modelling results. The objectives of this paper are to evaluate the overall performance of the pilot plant and to use the experimental results to compare two different modelling approaches (equilibrium-stage and rate-based). Furthermore, a parametric study for the proposed experiments and simulation is presented.*

*Equilibrium-stage and rate-based models are implemented using the commercial Aspen plus simulation tool. This study indicates that there are no major differences between the two modelling approaches in predicting the overall capture process behaviour (macro scale) for this pilot plant case. However, the simulation of the absorber and stripper columns demonstrate that the rate-based model gives a better prediction of the columns temperature profiles and mass transfer inside the columns compared to the equilibrium-stage approach (micro scale). As a result, for a detailed process design or understanding of the mass and energy profiles in the absorber and stripper columns, the rate-based approach should be applied.*

*Out of this work, it can be seen that both modelling approaches can be used for predicting the capture process overall behaviour and requirement for pilot plant scale as well as for industrial scale application.*

## 4.1 Introduction

Chemical absorption is considered the best suited technological option for post-combustion capture of $CO_2$ in the near term [1,2]. Chemical absorption processes for $CO_2$ capture are widely used in industrial applications, although not on the scale required for power stations [3]. In addition to these industrial applications, there are number of smaller lab-scale and pilot plants facilities aiming to develop and evaluate the different $CO_2$ capture processes [4-10].

Beside the experimental work, different modelling and simulation activities have been carried out to evaluate and understand the chemical absorption capture process [11-20]. The objectives of these modelling activities are varied from one research group to another. Carey et al 1991 [11] and Al-Baghli et al. 2001 [14] have developed rate-based models to study the behaviour of the absorption/stripping system with different solvents. Escobillana et al. 1991 [12] have validated their in-house developed model with experimental results. On the other hand, Chang et al. 2005 [19] have used a commercial simulation tool (Aspen plus) to study and optimize the performance of the $CO_2$ capture unit for industrial scale coal power plant. Another conventional tool (gPROMS) has been used by Lawal et al. 2008 [16] to compare the equilibrium-based approach versus the rate-based approach. In their work, they have found that the rate-based approach gives better predictions of the temperature profiles comparing to the equilibrium-based approach. Luo X. et al. 2008 [20] have evaluated different data sets from four different pilot plant studies based on 30 wt% MEA solution using four different commercial simulators and with two in-house codes. They have found that all the simulators are capable of giving reasonable predictions on overall performance, i.e. $CO_2$ absorption rate. But the reboiler duties, as well as concentration and temperature profiles are less well predicted. Most of the above mentioned activities have not included experimental results of large-scale capture process. Or it has included limited experimental data sets. In addition, the focus of these activities has been divided either on the columns behaviour or on the process overall behaviour.

As a part of the European project on the $CO_2$ capture and geological storage (CASTOR), a 1 tonne $CO_2$/hour $CO_2$ post-combustion capture pilot plant has been realised at Dong power plant in Denmark [21]. This pilot plant runs on a split stream of real flue gas from coal power plant. The general target of the pilot plant is to demonstrate long-term steady operation of $CO_2$ capture processes based on real flue gas conditions. In addition, it can be considered as a test facility for standard and novel solvents. The collected data and experimental results from this facility will be used for process benchmarking and models validating [22]. In this pilot plant, different tests have been done, which will enable a better understanding of the steady state operation of the chemical absorption capture process. In this chapter two relevant test series based on the use of monoethanolamine (MEA) as an absorbent are presented. In these tests the solvent flow rate and the stripper pressure have been varied to optimize the capture process.

In this work the focus is on the evaluation of the conventional Aspen plus modelling tools using CASTOR pilot plant data. In addition, the overall capture process (macro scale) and the absorber/stripper columns profiles are analyzed and evaluated (micro scale). The goals of this work are:

1. Large-scale pilot plant experimental data analysis and evaluation,
2. The comparison of two different modelling approaches (equilibrium-stage and rate-based models), and
3. The capture process overall evaluation on macro and micro scale.

## 4.2 Simulation approaches background

In this section the basis of the models, which are used in describing the absorption process is discussed. For the absorption process, two approaches are used in modelling vapour-liquid mass-transfer in a section of packing: the equilibrium-stage approach and the non-equilibrium stage (rate-based) approach (see Figure 4-1). In the equilibrium-stage approach, the vapour-liquid mass transfer is modelled by creating section where it is assumed that the vapour and liquid phases are perfectly mixed and in equilibrium. This means that the liquid phase and the vapour phase leave this packing section at the same temperature. This model is based on the theory of theoretical number stages combined with the concept of efficiency to determine the actual number of stages. These actual number of stages together with the right mass and heat transfer rate can be used for the separation column design [24,25]. However, in the rate-based approach, the actual mass and heat transfer rates are described in a direct way using mass and heat transfer rates [25].

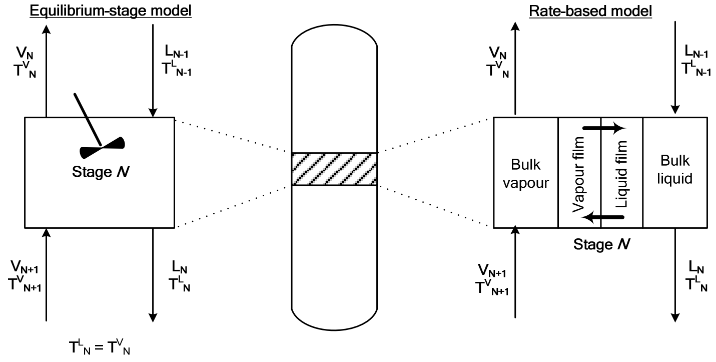

**Figure 4-1: Equilibrium-stage and rate-based models**

### 4.2.1 Equilibrium-stage simulation approach

The equilibrium-stage approach, which is used in this article, is built in the RADFRAC column model in Aspen Plus. To describe the absorber column, three equilibrium stages with no condenser or reboiler have been used. The number of equilibrium stages is based on the operating line in connection with the equilibrium line. For the absorption section three equilibrium stages are sufficient to describe the $CO_2$ separation process using MEA. However, for the regeneration column six equilibrium stages including the reboiler are needed. The specifications of the equilibrium-stage model for the absorber, the washing column (section) and the stripper are shown in Table 4-1. The solvent which used for this discussion is monoethanolamine (MEA). MEA is a primary ethanolamine, which can associate with $H_3O^+$ to form an ion $MEAH^+$, and can also react with $CO_2$ to from a carbamate ion $MEACOO^-$. Chemical equilibrium is assumed with all the ionic reaction in the MEA chemistry. The following set of equilibrium reactions describing the $MEA\text{-}CO_2\text{-}H_2O$ chemistry are used in the equilibrium-stage approach [30]:

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad (4\text{-}1)$$

$$CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^- \qquad (4\text{-}2)$$

$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-} \tag{4-3}$$

$$MEAH^+ + H_2O \rightleftharpoons MEA + H_3O^+ \tag{4-4}$$

$$MEACOO^- + H_2O \rightleftharpoons MEA + HCO_3^- \tag{4-5}$$

**Table 4-1: Specifications for the equilibrium-stage approach**

| **Description** | **Absorber** | **Absorber washing section** | **Stripper** |
|---|---|---|---|
| Calculation type | Equilibrium | Equilibrium | Equilibrium |
| Number of theoretical stages | 3 | 2 | 6 |
| Condenser | None | None | None[*] |
| Reboiler | None | None | Kettle |
| Pressure | ~ 100 kPa | ~ 100 kPa | ~ 180 kPa[†] |
| Pressure drop[‡] | 3-8 kPa | Negligible | ~ 10 kPa |
| Column's design specification | None | Solvent losses is fixed by varying the washing water feed flow rate | Reboiler (stage 6) temperature is fixed by varying the boil up ratio |

The equilibrium constants for these different equilibrium reactions are build in the Aspen properties set of $CO_2$-MEA-$H_2O$ system, which is originally provided from the work of Austgen et al. [29]. The $CO_2$ capture process using the MEA-$H_2O$-$CO_2$ system is thermodynamically described using the Electrolyte-NRTL model [29].

### 4.2.2 Rate-based simulation approach

In the rate-based model, actual rates of mass and heat transfer as well as chemical reactions are considered. The mass transfer is described using the two-film theory using the rigorous Maxwell-Stefan theory [31]. This model has been implemented in the Aspen plus RADFRAC column model using the rate-based calculation method. This model approach is based on the same properties data set ($CO_2$-MEA-$H_2O$) which is provided within Aspen plus. However, some properties modifications have been made based on the Aspen tech work [30] to make it fit with the rate-based calculations. In addition to the previously mentioned equilibrium reactions, the following four kinetic reactions have been implemented in the rate based calculation method:

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \tag{4-6}$$

---

[*] The condenser is modeled as a separate unit

[†] The stripper pressure has been included in the process parametric study. This value is used for the base case.

[‡] The columns pressure drop has been provided based on the experimental results, so it has been changed from one simulation to another.

$$HCO_3^- \rightleftharpoons CO_2 + OH^- \tag{4-7}$$

$$MEA + CO_2 + H_2O \rightleftharpoons MEACOO^- + H_3O^+ \tag{4-8}$$

$$MEACOO^- + H_3O^+ \rightleftharpoons MEA + CO_2 + H_2O \tag{4-9}$$

Power law expressions are used in calculating the rate of the above mentioned reactions (reactions 6-9):

$$r = AT^n \exp\left(-\frac{E}{RT}\right)\prod_{i=1}^{N} C_i^{a_i} \tag{4-10}$$

Where:

$r$ = rate of reaction;

$A$ = Pre-exponential factor [unit depends on the order of the reaction];

$T$ = Absolute temperature [K];

$n$ = Temperature exponent [=0];

$E$ = Activation energy [cal/mol];

$R$ = Gas law constant [cal/mol.K];

$N$ = Number of component in the reaction;

$C_i$ = Concentration of component $i$ [mol/l];

$a_i$ = The Stoichiometric number of the component $i$ in the reaction equation.

The kinetic parameters ($A$ and $E$) for the reactions (6-9) are given in Table 4-2 [30]:

**Table 4-2: Parameters *k* and *E* in equation (4-10) [30]**

| Reaction number | *k* | *E*, cal/mol |
|---|---|---|
| 6 | 4.32e+13 | 13249 |
| 7 | 2.38e+17 | 29451 |
| 8 | 9.77e+10 | 9855.8 |
| 9 | 2.18e+18 | 14138.4 |

The mathematical model behind the rate-based calculations in Aspen rate-based model consists of material balances, energy balances, mass transfer, energy transfer, phase equilibrium, and summation equations [27]. To achieve these complicated calculations a large number of input parameters and specifications need to be provided for the different unit operation blocks. These input and specifications that have been used for the absorber, the stripper and the absorber washing columns are shown in Table 4-3, Table 4-4 and Table 4-5, respectively. Most of these specifications are recommended to be used for the rate-based model of the $CO_2$ capture process by Aspen Tech [30] with some modifications to fit the model with the pilot plant specifications and results [23].

**Table 4-3: Absorber column specifications used in the rate-based MEA model**

Number of stage: 17
Pressure: ~ 100 kPa
Pressure drop: Experimental value used as input
Reboiler: None
Condenser: None
Packing type: IMTP, NORTON, Metal, 50 mm
Packing height: 17 m and section diameter: 1.1 m
Mass transfer coefficient method: Onda et al 1968
Interfacial area method: Onda et al 1968
Interfacial area factor: 1.5
Heat transfer coefficient method: Chilton and Colburn
Holdup correlation: Stichlmair et al 1989
Film resistance : Discrxn for liquid film and Film for vapour film
Flow model: mixed
Design specifications: None

**Table 4-4: Stripper column specifications used in the rate-based MEA model**

Number of stage: 13 includes reboiler
Pressure: ~ 180 kPa bar
Pressure drop: Experimental value used as input
Reboiler: Kettle
Condenser: None
Packing type: IMTP, NORTON, Metal, 50 mm
Packing height: 13 m and section diameter: 1.1 m
Mass transfer coefficient method: Bravo et al 1992
Interfacial area method: Bravo et al 1992
Interfacial area factor: 2
Heat transfer coefficient method: Chilton and Colburn
Holdup correlation: Stichlmair et al 1989
Film resistance : Discrxn for liquid film and Film for vapour film
Flow model: mixed
Design specification: Stage 13 (reboiler) temperature is fixed by varying boil up ratio.

**Table 4-5: Absorber washing section specifications used in the rate-based MEA model**

Number of stage: 3
Pressure: ~ 100 kPa
Pressure drop: Zero
Reboiler: None
Condenser: None
Packing type: Mellapak PL, Sulzer, Standard, 252Y
Packing height: 3 m and section diameter: 1.1 m
Mass transfer coefficient method: Bravo et al 1985
Interfacial area method: Bravo et al 1985
Interfacial area factor: 1.5
Heat transfer coefficient method: Chilton and Colburn
Film resistance : Film for both liquid film and vapour film
Flow model: mixed
Design specification: None

The rate-based modelling approach is expected to have many advantages over the equilibrium-stage approach. It is expected to provide more realistic results [31]. The rate-based model explicitly accounts for the actual column configuration, which affects the column performance. As a result, it is expected to predict the experimental results more accurate.

### 4.2.3 Simulation criteria and limitations

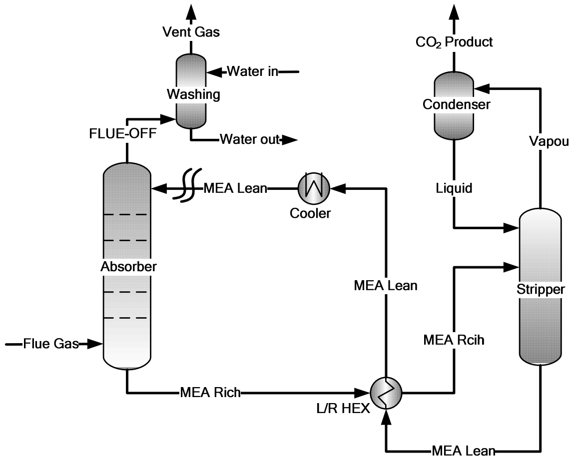

**Figure 4-2: $CO_2$ capture with MEA absorption process: Aspen Plus simulation flow sheet**

The pilot plant results from the MEA test campaign within the European $CO_2$ capture and storage (CASTOR) project have been analysed and used in validating both the equilibrium-stage approach and the rate-based approach [21]. Dong Energy provided the measured parameters from the experiments in the pilot plant at steady state [33]. The simulations were performed using Aspen Plus, version 7 [27] with the process flow sheet shown in Figure 4-2.

The main simulation operating specifications are provided from the experimental results. The input variables are shown in Table 4-6. After running the process simulation using the different models and experimental data sets, the simulation results are compared with the experimental results.

**Table 4-6: Process simulation input using the experimental data**

| Parameter | Specifications |
|---|---|
| Flue gas | Total flow rate, composition, temperature, pressure |
| Lean solvent | Flow rate, composition, temperature, pressure |
| Lean solvent cooler | Pressure, outlet temperature |
| Lean/rich solution heat exchanger | Pressure drop, temperature difference approach |
| Absorption column | Operating pressure and pressure drop |
| Stripper column | Reboiler temperature, operating pressure and pressure drop |

The two modelling approaches have been validated in two different levels: the macro analysis and the micro analysis. In the process macro analysis, different process output parameters have been used to evaluate the experimental results and to validate the different models. These parameters have been chosen depending on its importance for the overall process behaviour; like the regeneration energy requirement, the $CO_2$ removal percentage (process efficiency), the solvent rich loading. In the micro analysis, the experimental results inside the columns are evaluated. The temperature profiles in the absorber/desorber give a good indication on the effectiveness of the $CO_2$ absorption and desorption in the different sections of the columns. Table 4-7 provides the output parameters from the process simulations, which has been used in the process evaluation and models validation.

**Table 4-7: Simulations output parameters**

| Parameter | Unit |
|---|---|
| $CO_2$ recovery | [%] |
| Rich $CO_2$ loading | [mol $CO_2$/mol MEA] |
| Regeneration energy requirement | [kWth] |
| $CO_2$ captured flow rate | [kg/hr] |
| Flue gas outlet temperature | [$^oC$] |
| Absorber temperature profile | [$^oC$] |
| Rich solvent temperature | [$^oC$] |
| Stripper temperature profile | [$^oC$] |

However, a general limitation has been found within ASPEN Plus tool. The vapour liquid equilibrium (VLE) data provided in the data sets does not describe the experimental results in great accuracy. Comparing the VLE data for the MEA-$H_2O$-$CO_2$ system, which has been calculated using the ASPEN model, with experimental data from Lee et al 1976 [32], has shown that the calculated loading at a given partial pressure at the stripper condition is in general higher than the experimental data (see Figure 4-3). However, the calculated loading at a given partial pressure at the absorber condition is in good agreement with the experimental data.

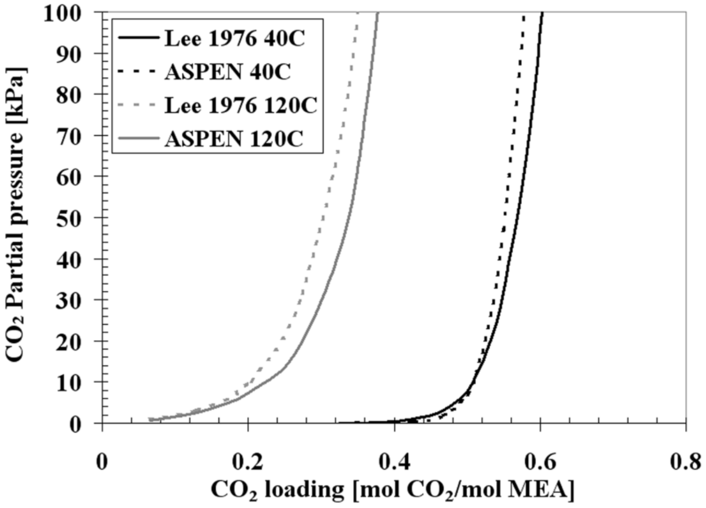

**Figure 4-3: Experimental and calculated VLE data at 40 and 120 $^{o}$C [26,31]**

The disagreement between the simulation and the experimental loading has been found mainly in the high temperature conditions (stripper conditions), which will result in higher values of the lean loading comparing to the values that have been measured in the experiment. These higher values of lean loading are expected to influence the overall $CO_2$ recovery in the absorber. To avoid a major effect of the VLE data on the overall process behaviour and validation of the models, the process is simulated with an open tear stream (MEA-Lean). This allows the use of the experimental lean loading values as input to the absorber and on the same time operating the solvent reboiler at the temperatures based on the experimental results.

## 4.3 Reference case definitions

### 4.3.1 Pilot plant description

The $CO_2$ absorption pilot plant is located at the Esbjerg power plant, Esbjergværket (ESV). ESV is owned and operated by Dong Energy. ESV is a 400 MW pulverised coal-fired power plant equipped with $deNO_x$ and FGD units. In 2005, the $CO_2$ absorption pilot plant was erected and commissioned. This plant operates on a slipstream of the flue gas, taken after the $deNO_x$ and FGD units. The design of the pilot plant is based on the standard $CO_2$ production plant with minor modifications. The pilot plant key design figures and process flow diagram are shown in Table 4-8 and Figure 4-4, respectively.

**Table 4-8: Pilot plant design figures [23]**

| Parameter | Design value |
|---|---|
| Flue gas capacity | 5000 $Nm^3$/hr |
| $CO_2$ captured (at 12 vol. % $CO_2$) | 1000 kg/hr |
| $CO_2$ removal percentage | 90 % |
| Maximum solvent flow rate | 40 $m^3$/hr |
| Maximum reboiler steam flow | 2500 kg/hr (350 kPa) |
| Maximum stripper pressure | 300 kPa |

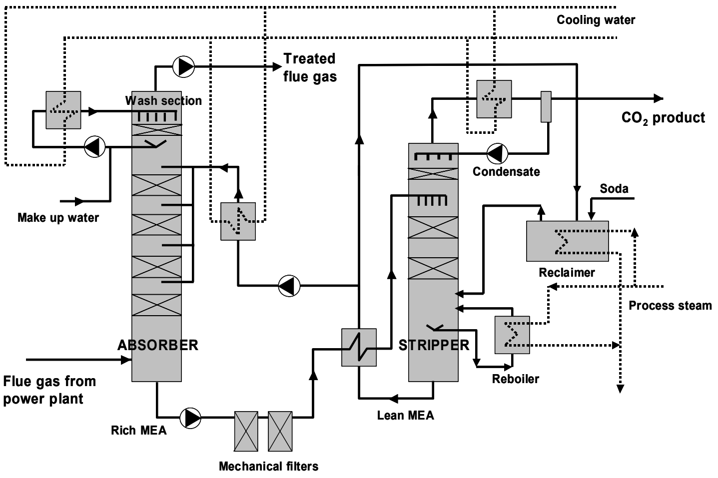

**Figure 4-4: Flow diagram of the CASTOR pilot plant at the coal-fired Esbjerg power plant [23]**

The flue gas enters the absorber tower at the bottom in a counter-current flow with the solvent. The flue gas does not require cooling due to the relatively low inlet temperature (~ 46 $^{o}$C). The gas fan is placed downstream the absorber, which implies that the absorber is operated at a pressure slightly below atmospheric pressure. $CO_2$ analysers continuously monitor the $CO_2$ content of the absorber inlet and outlet.

The pilot plant is equipped with full height absorber and stripper columns to achieve 90% $CO_2$ removal and deep rich solvent regeneration. This full height makes it a real demonstration of the large scale capture process with the need only to scale up the diameter to cope with the larger gas/liquid flow rates. The absorber tower consists of four consecutive packed-beds for $CO_2$ absorption and an additional bed for water wash at the top. The absorber has an internal diameter of 1.1 meter. Each bed for $CO_2$ absorption is 4.25 meters in height and filled with IMTP 50 random packing. The water wash bed is 3.0 meters in height and filled with Mellapak 252Y structured packing.

The rich solvent from the absorber is pumped through two mechanical filters in series (25 and 350 μm) and a plate heat exchanger (heat exchanged with lean solvent from the stripper) before being fed to the stripper. The stripper has an internal diameter of 1.1 meter and consists of two 5.0 meter beds filled with random packing IMTP 50 and an additional bed for water wash at the top (3.0 meters of IMTP 50). A steam driven reboiler supplies the heat input to the stripper. The steam (350 kPa saturated) is supplied by ESV and the reboiler temperature controls the steam flow. The $CO_2$ gas and vapours from the stripper pass through a water-cooled condenser and a gas/liquid separator. The condensate from the separator is returned to the stripper wash section and the resultant gas, which is essentially pure $CO_2$ saturated with water, is returned to the ESV flue gas duct. The $CO_2$ product quality is monitored online by an analyser. The regenerated solvent from the stripper is cooled to its final set point temperature by a water-cooler after it has been heat exchanged with the rich solvent. A slipstream of approximately 10% of the solvent flow is passed through a carbon filter.

In order to monitor energy and cooling water consumptions as well as the general plant performance, the pilot plant is fitted with temperature sensors, pressure gauges and flow meters throughout. All of the measurements are continuously logged on a PC. Among others, the logged data includes: gas and liquid flow rates, $CO_2$ inlet and outlet concentrations and flow rates, pressures and temperatures both in the gas and the liquid phase of the main unit components (absorber, stripper, reboiler, lean cooler, lean/rich heat exchanger, and $CO_2$/water condenser), and temperature profiles in the packed columns.

### 4.3.2 Experimental procedure and results

The purposes of the experimental campaign are to study the effect of real flue gas conditions on the operation of the $CO_2$ capture process and to collect data on the different operating conditions of the process. The obtained data is used for the validation of the different models. To achieve these targets a parametric study has been done using the previous modelling activities as a guide line [28]. Depending on the previous modelling results; the variable parameters for the model validation were chosen. It is important to note that some of the variables, which have been investigated before, were not included in this work. These variables are considered as design specifications for the pilot plant, for example the MEA solvent concentration and lean solvent temperature. In this paper, the parametric study will be evaluated on two different levels: the macro analysis and the micro analysis. For this evaluation, two experimental tests have been carried out by changing two input variables:

- Test 1: The lean solvent flow rate (13-23 $m^3/h$).
- Test 2: The stripper pressure (110-200 kPa).

To validate the different process models the following overall results are examined:

- Process regeneration energy requirement;
- $CO_2$ removal efficiency;
- Solvent rich loading; and
- Packed columns temperature profiles (the temperature measurement points for both the absorber and the stripper are shown in Figure 4-5).

Moreover, in addition to the temperature measurement points within the columns, the columns outlet temperatures and the solvent reboiler temperature have been registered and used for the evaluation of the calculated column temperature profile. This will be discussed in the micro-analysis section.

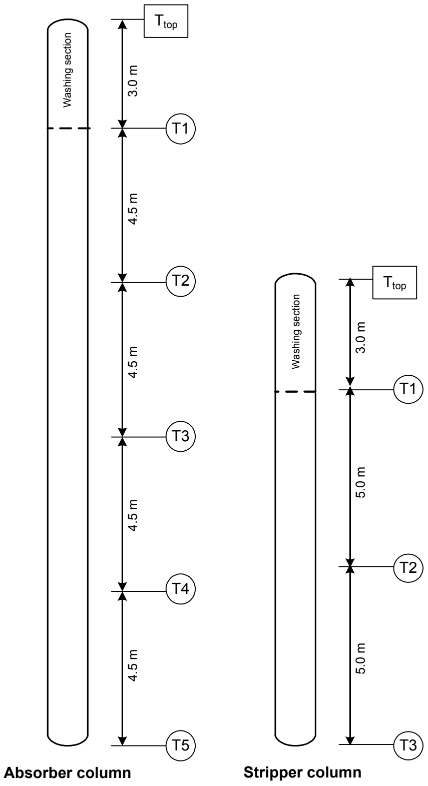

**Figure 4-5: Temperature measurement position in the absorber and the stripper**

#### *4.3.2.1 Test 1 results: varying the lean solvent flow rate*

Table 4-9 summarizes the experimental main input parameters and results of the capture process. The first tests have been done by changing the lean solvent flow rate, while keeping the carbon dioxide removal percentage constant (90 %). This has been achieved by decreasing the solvent lean loading at lower solvent flow rate. The values of the solvent lean and rich loading have been measured by analysing the liquid samples at the inlet and outlet of the absorber. The loading of the lean solvent is controlled by changing reboiler temperature.

**Table 4-9: Summary of pilot plant test 1 main input and results [33]**

| | **Parameter** | | | | | |
|---|---|---|---|---|---|---|
| Input | Solvent flow rate (m3/h) | **23.00** | **19.00** | **16.70** | **14.80** | **12.50** |
| | Flue gas (Nm3/h) | 4915 | 5011 | 4939 | 4926 | 4990 |
| | $CO_2$ at inlet (mol %wet) | 11.86 | 11.94 | 11.76 | 12.12 | 11.77 |
| | Flue gas inlet temp ($^oC$) | 47.3 | 48.0 | 46.8 | 46.9 | 47.2 |
| | Stripper pressure (kPa) | 181 | 181 | 181 | 181 | 181 |
| Results | $CO_2$ at outlet (mol %wet) | 1.54 | 1.53 | 1.53 | 1.39 | 1.56 |
| | $CO_2$ captured (kg/hr) | 1040 | 1075 | 1070 | 1090 | 1060 |
| | $CO_2$ recovery (%) | 90 | 90 | 90 | 91 | 90 |
| | MEA Concentration (% w/w) | 30.4 | 31.2 | 30.8 | 31.4 | 31.1 |
| | Lean $CO_2$ loading (mol $CO_2$/mol MEA) | 0.28 | 0.25 | 0.22 | 0.19 | 0.17 |
| | Rich $CO_2$ loading (mol $CO_2$/mol MEA) | 0.46 | 0.48 | 0.48 | 0.48 | 0.48 |
| | Regeneration energy (MJ/tonne $CO_2$) | 3897 | 3722 | 3725 | 3626 | 3745 |
| | Cooling water (MJ/tonne $CO_2$) | 3434 | 3204 | 3059 | 2907 | 1963 |
| | Flue gas outlet temp ($^oC$) | 47.8 | 49.1 | 48.6 | 48.8 | 49.2 |
| | Absorber temperature 1 (top) ($^oC$) | 58.8 | 61.2 | 62.1 | 62.9 | 63.2 |
| | Absorber temperature 2 ($^oC$) | 75.0 | 73.7 | 72.9 | 72.3 | 69.8 |
| | Absorber temperature 3 ($^oC$) | 73.0 | 69.6 | 66.9 | 65.3 | 61.3 |
| | Absorber temperature 4 ($^oC$) | 67.5 | 62.6 | 59.3 | 57.4 | 54.3 |
| | Absorber temperature 5 (bottom) ($^oC$) | 54.0 | 52.9 | 51.1 | 50.7 | 50.4 |
| | Stripper temperature 1 (top) ($^oC$) | 100.0 | 99.6 | 99.6 | 99.9 | 101.2 |
| | Stripper temperature 2 ($^oC$) | 104.0 | 103.5 | 104.2 | 108.3 | 115.2 |
| | Stripper temperature 3 (bottom) ($^oC$) | 116.0 | 117.6 | 119.1 | 120.1 | 120.8 |
| | Reboiler temperature ($^oC$) | 118.5 | 119.5 | 120.6 | 121.4 | 122.0 |

Increasing the solvent flow rates at constant flue gas flow rate leads to increasing liquid-to-gas ratios (L/G) in the absorber. The lowest regeneration energy demand (3.6 GJ/tonne $CO_2$) can be obtained at a 14.8 $m^3$/h solvent flow rate. However, it should be noted that considering the experimental uncertainty of 5%, the regeneration energy demand is nearly constant in the flow range of 12.5 to 19.0 $m^3$/h. At the higher flow rate (23 $m^3$/h), the specific steam demand is clearly higher. Out of the experiments, it can be concluded that the solvent rich loading is nearly constant and close to the expected equilibrium value (0.5 mol $CO_2$/mol MEA). This could be expected based on the height of the absorption column.

### *4.3.2.2 Test 2 results: varying the stripper pressure (temperature)*

In the second test, the stripper pressure has been varied. It can be seen from Table 4-10 that the $CO_2$ capture percentage varies between 88 and 93% among the different operating points. This is due to the fluctuations in the $CO_2$ concentration in the flue gas originating from changing boiler loads. Therefore, it was difficult to achieve a constant 90% removal in all tests.

It can be clearly seen that the regeneration energy increases as the stripper pressure is reduced from 181 kPa to 112-143 kPa. However, increasing the stripper pressure from 181 to 216 kPa does not lead to regeneration energy decrease. The higher regeneration energy at lower stripper pressures may to some extent is over exaggerated, due to not optimised solvent flow rates.

**Table 4-10: Summary of pilot plant test 2 main input and results [33]**

| | **Parameter** | | | | |
|---|---|---|---|---|---|
| Input | Stripper pressure (kPa) | **216** | **181** | **143** | **112** |
| | Solvent flow rate (m3/h) | 15.00 | 15.50 | 17.00 | 19.00 |
| | Flue gas (Nm3/h) | 4917 | 4971 | 4935 | 4874 |
| | $CO_2$ at inlet (mol %wet) | 10.98 | 11.29 | 10.22 | 10.32 |
| | Flue gas inlet temp ($^oC$) | 48.2 | 46.3 | 46.4 | 45.0 |
| Results | $CO_2$ at outlet (mol %wet) | 1.62 | 1.38 | 0.86 | 1.03 |
| | $CO_2$ captured (kg/hr) | 995 | 1037 | 968 | 957 |
| | $CO_2$ recovery (%) | 88 | 90 | 93 | 92 |
| | MEA Concentration (% w/w) | 29.7 | 30.3 | 29.5 | 28.7 |
| | Lean $CO_2$ loading (mol $CO_2$/mol MEA) | 0.21 | 0.21 | 0.23 | 0.24 |
| | Rich $CO_2$ loading (mol $CO_2$/mol MEA) | 0.48 | 0.46 | 0.46 | 0.46 |
| | Regeneration energy (MJ/tonne $CO_2$) | 3738 | 3692 | 4006 | 4185 |
| | Cooling water (MJ/tonne $CO_2$) | 3025 | 3323 | 3197 | 3195 |
| | Flue gas outlet temp ($^oC$) | 49.2 | 48.0 | 47.8 | 47.0 |
| | Absorber temperature 1 (top) ($^oC$) | 61.6 | 61.8 | 59.6 | 58.6 |
| | Absorber temperature 2 ($^oC$) | 70.6 | 71.6 | 72.5 | 72.4 |
| | Absorber temperature 3 ($^oC$) | 63.8 | 65.4 | 69.1 | 69.7 |
| | Absorber temperature 4 ($^oC$) | 56.9 | 57.7 | 62.3 | 63.6 |
| | Absorber temperature 5 (bottom) ($^oC$) | 51.7 | 50.4 | 51.3 | 51.0 |
| | Stripper temperature 1 (top) ($^oC$) | 103.3 | 99.6 | 95.6 | 91.3 |
| | Stripper temperature 2 ($^oC$) | 107.7 | 105.1 | 103.0 | 99.7 |
| | Stripper temperature 3 (bottom) ($^oC$) | 123.2 | 119.0 | 112.7 | 106.5 |
| | Reboiler temperature ($^oC$) | 124.9 | 120.4 | 113.8 | 107.6 |

## 4.4 Process simulation results validation and discussion

The validation of the equilibrium-stage model and rate-based model for the $CO_2$ capture process is done by comparing the simulation results with the presented experimental data. This validation will be done on two different levels. The macro analysis is used for validating the overall capture process behaviour and requirements. The micro level is used for validating and evaluating the columns behaviour by studying the temperature profiles within the absorber and the stripper.

### 4.4.1 Macro analysis

The two input parameters (the solvent flow rate and the stripper pressure) have been varied in the process simulation to evaluate the overall process behaviour. The equilibrium-stage model and the rate-based model have been used for this simulation. The overall process evaluation is done by evaluating the three following output parameters:

1. The regeneration energy;
2. The $CO_2$ removal efficiency; and
3. The solvent capacity (rich loading).

### *4.4.1.1 The regeneration energy requirement*

The regeneration energy requirements from the modelling prediction have been compared with the data from the pilot plant under steady-state operating conditions. Figure 4-6 and Figure 4-7 show the regeneration energy requirement as function of solvent flow rate and stripper pressure, respectively.

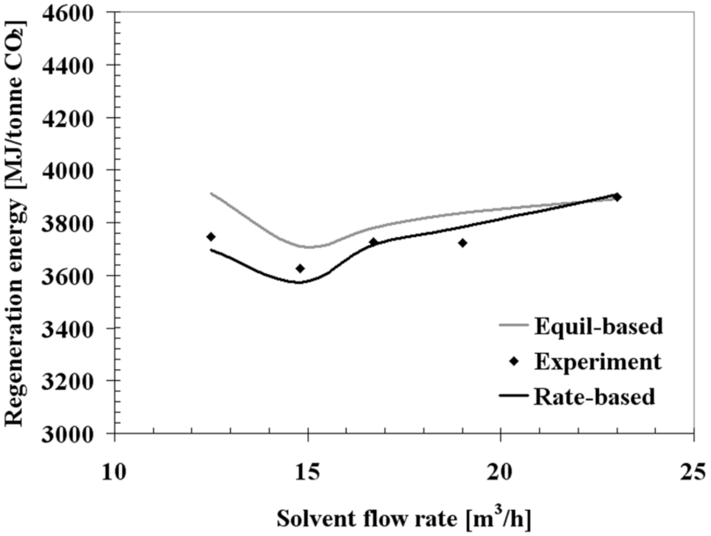

**Figure 4-6: Regeneration energy requirement as a function of solvent flow rate for experimental and simulated results**

Figure 4-6 shows that the regeneration energy requirement has a minimum value of 3.7 GJ/tonne $CO_2$ at a solvent flow rate around 15 $m^3$/hr. This value is somehow lower than the published energy requirement for the conventional MEA process (3.8-4.0 GJ/tonne $CO_2$) [3,27]. This small difference can be related to the different gas liquid ratio, operating conditions and measurement inaccuracy. The theoretical regeneration energy requirement can be divided into three parts: energy required to reverse the chemical reaction and release $CO_2$, energy for water evaporation and the energy required to heat up the solvent from the inlet temperature (around 105 $^oC$) to the operating stripper temperature (around 120 $^oC$). It is important to note that the first part, the amount of energy required to release the $CO_2$, is almost constant in the experiments due to the constant $CO_2$ removal efficiency of 90 %. This means that at lower solvent flow rate, a lower lean loading is required, which results in a higher energy requirement. However, higher solvent flow rate leads to an increase of the energy needed to heat up the solvent to the desired reboiler temperature. These two effects will increase the regeneration energy at high and low solvent flow rate, resulting in a minimum regeneration energy leading to an optimum solvent flow rate.

It can be seen from Figure 4-6 that the predictions of the model are in good agreement with the experimental data and closely flow the pilot plant trends. A difference of less than 5 % between the models prediction and the pilot plant experimental data has been obtained.

Comparing the equilibrium-stage approach and the rate-based approach, it can be seen that at high solvent flow rates the results out of both models are almost identical. However, at lower solvent flow rate the rate-based model gives better fit with the experimental data. This better agreement is expected due to the fact that the rate-based model includes the effect of reaction kinetics and mass transfer.

Next to the investigation of the effect of solvent flow rate, also the effect of the stripper pressure on the regeneration energy has been investigated. The increase in the stripper pressure, which is connected to the stripper temperature, results in a reduction of the regeneration energy requirement at an optimum pressure around 180 kPa (120.4 °C). This can be observed in Figure 4-7, where the simulated and experimental data are depicted (the solvent reboiler temperature is shown between parentheses). Two effects can be noted. The first one is that a higher stripper temperature leads to an improvement in stripper efficiency. However, the second effect is that a higher pressure leads to a lower amount of $CO_2$ released. These two effects lead to the optimum which can be seen in Figure 4-7.

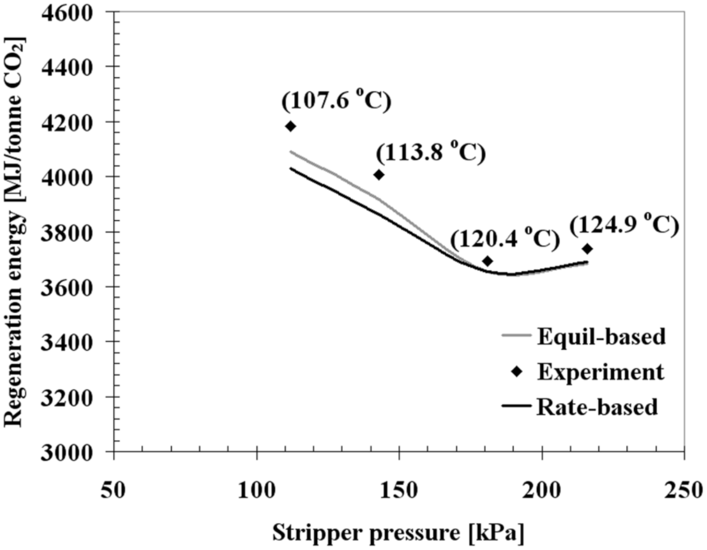

**Figure 4-7: Reboiler duty as function of the stripper pressure and temperature for experimental and simulated results**

Both modelling approaches have shown a slightly lower regeneration energy requirement comparing to the experimental results with an average difference of less than 5 %. Differences can be due to the experimental accuracy, heat losses and modelling accuracy. In general, it can be seen that the rate-based model results in lower regeneration energy comparing to the equilibrium-stage model. It is of importance to note that the regeneration energy is a function of the amount of $CO_2$ removed and the energy needed for heating up the solvent, the amount of steam leaving the stripper and reaction enthalpy. The reason for the difference between rate and equilibrium model can be due to the deviations in the values of the specific heat and heat of formation, which have been used in the rate-based model and the equilibrium-based model. These deviations are expected to influence the overall enthalpy in both of the absorber and the stripper.

#### *4.4.1.2 The carbon dioxide removal efficiency*

In the first experimental test, the $CO_2$ removal percentage has been kept constant while changing the solvent flow rate (see Figure 4-8). The target of 90% removal (gas phase as a reference) has been achieved in the experiments by a slight increase in the reboiler temperature at lower solvent flow rate. In the experimental results, it can be seen that the $CO_2$ mass balances in the gas phase do not match with the $CO_2$ balances calculated from the liquid phase. These differences are related to measurement inaccuracy, especially in the solvent loading analysis. The simulation results of the removal efficiency are lower than the measured removal efficiencies calculated from the gas phase. The lower simulation results are connected to the fact that the simulation has been done using the measured solvent flow rate and lean solvent loading values as input. The modelled results are based on an open tear stream simulation where the lean loading is based on the experimental results. Therefore, it is logical that the simulation results are in good agreement with the $CO_2$ removal from the liquid phase analysis. It is tempting to conclude that the above mentioned deviation is coming from the experimental error of the measured loading and solvent flow rate. However, the measurement of the gas phase is considered more accurate that is why it is used for the evaluation of model results versus experimental $CO_2$ removal values.

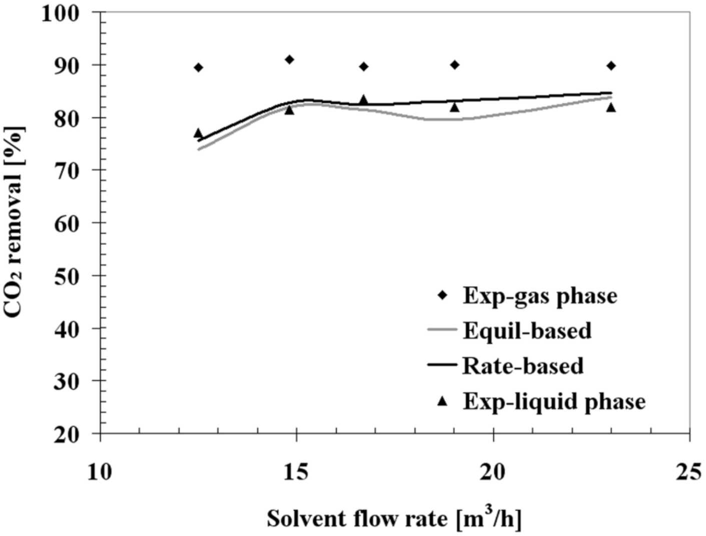

**Figure 4-8: $CO_2$ removal % as function of solvent flow rate for experimental and simulated results**

Regarding the stripper pressure, it can be expected that at constant temperature an increase in stripper pressure should lead to a decrease in removal efficiency. However, the experimental practice is to change both parameters trying to achieve 90% removal. However, in these experiments it was difficult to keep the $CO_2$ removal constant due to the fluctuations in the $CO_2$ concentration in the flue gas originating from changing boiler loads. In addition, at lower stripper pressure, the solvent flow rate has increased with increasing the lean loading. This has an effect on the removal efficiency. At the operating conditions, the modelling results show an agreement with the experimental data trends (see Figure 4-9). As stated before, the estimated removal ratios in the simulations results are lower than the measured data by almost 5 to 8 %. The rate-based approach presents a better agreement with the experimental data comparing to the equilibrium-stage model.

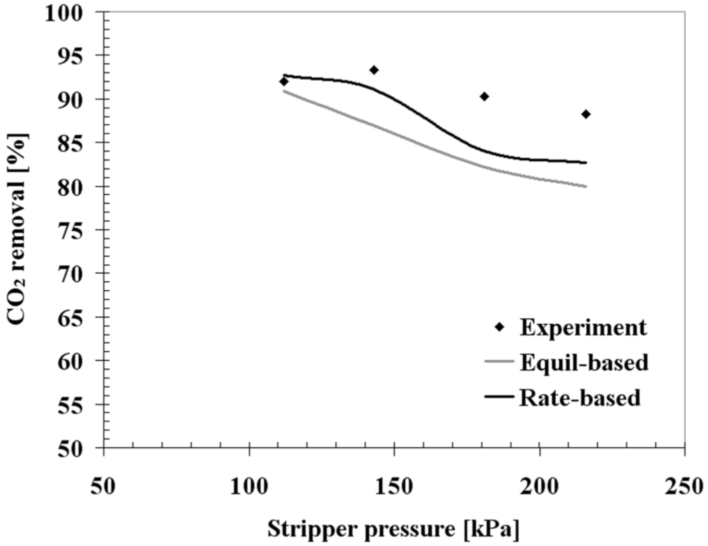

**Figure 4-9: $CO_2$ removal % as function of stripper pressure for experimental and simulated results**

### *4.4.1.3 The solvent capacity (rich loading)*

The rich loading is the solvent loading with $CO_2$ at the absorber outlet. This loading is a good indication to the level of solvent saturation and gives an indication on how efficient the absorption process is. Out of the published and measured loading values [34], it is clear that the rich loading values from the experiments are very close to the maximum rich loading (0.5 mol $CO_2$/mol MEA) that could be achieved at the specified operating absorber temperature (40-55 $^oC$) and $CO_2$ partial pressure. This implies that the experimental process was running very close to equilibrium.

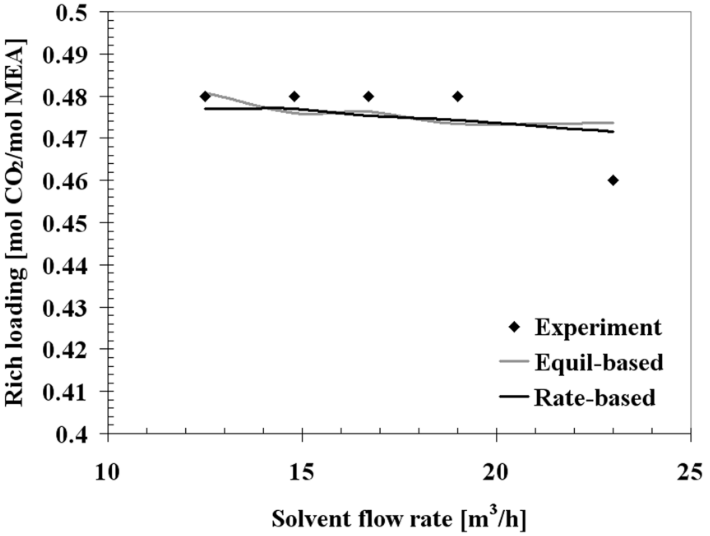

**Figure 4-10: Solvent rich loading as function of solvent flow rate for experimental and simulated results**

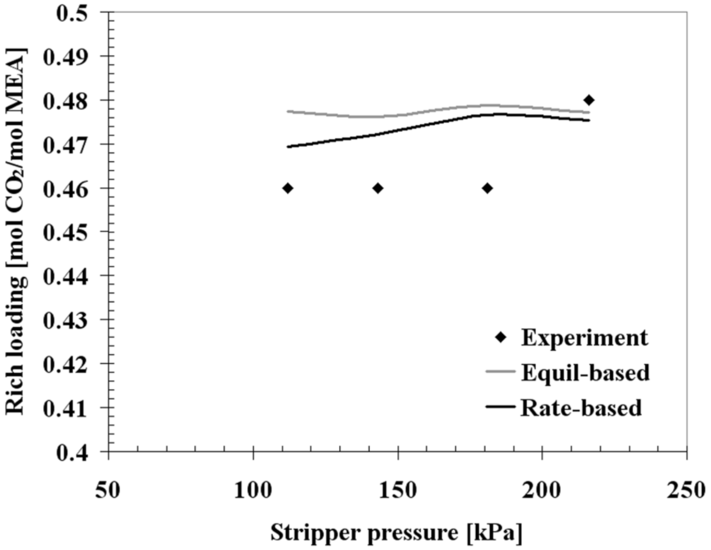

**Figure 4-11: Solvent rich loading as function of stripper pressure for experimental and simulated results**

In Figure 4-10 and Figure 4-11, it can be seen that there is a good agreement between the experimental results and the simulation values, for both modelling approaches. Comparing the two modelling approaches, it can be concluded that there is hardly any difference in the estimated rich loading between the equilibrium-stage and rate-based model. This conclusion is valid for the current situation where the absorber column is designed with a full height packing material. This indicates that for a full height system both approaches can be used for analysing and predicting the capture process requirement on macro scale.

### 4.4.2 Micro analysis

The temperature profile in the absorber shows clearly the effect of the exothermal reaction between $CO_2$ and MEA (see Figure 4-12 and Figure 4-13). The temperature has a maximum (70-75°C) above the 3rd bed (12.8 m of packing) after which it decreases to 58-63°C at the absorber outlet and below 50 °C after the washing section.

In Figure 4-12, the results show that at higher solvent flow rate the absorber outlet (top) temperature decreases. This can be due to the greater cooling capacity of the lean solvent feed at higher flow rates. It can be seen from Figure 4-13 that there is no major influence of stripper pressure on the absorber temperature profile. The slight differences are related to other parameters that have been changed during the experiment (the fluctuation of the $CO_2$ inlet concentration, the lean loading and the solvent flow rate).

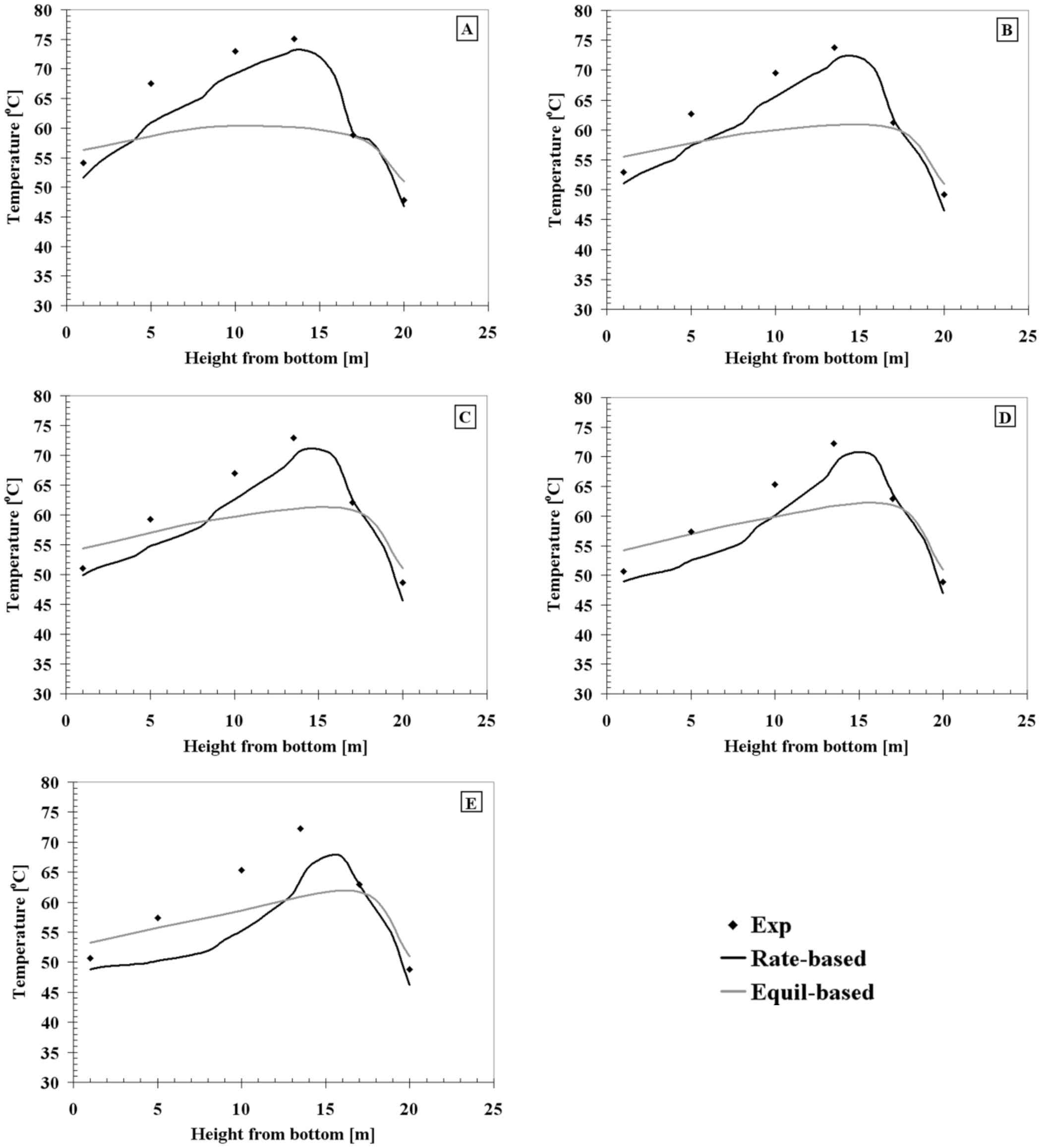

**Figure 4-12: The absorber temperature profile at different solvent flow rates** (A at 23 $m^3$/hr, B at 19 $m^3$/hr, C at 16.5 $m^3$/hr, D at 14.8 $m^3$/hr, E at 12.5 $m^3$/hr)

The rate-based simulation results of the temperature profiles in the absorber have shown a good agreement with the experimental data. It can be observed that the predicted temperature profiles are lower than the measured values. This is related to the predicted lower $CO_2$ removal percentage, which leads to a lower overall heat of reaction. However, in the case of the equilibrium-stage approach, the predicted temperature profiles do not fit with the experimental data. The only points where the equilibrium-stage model shows agreement with the experimental data are at the absorber top and the bottom. This could be explained by the fact that the same gas and liquid inlet temperatures from the experimental data have been used in the simulation, also the absorber is running a near equilibrium conditions.

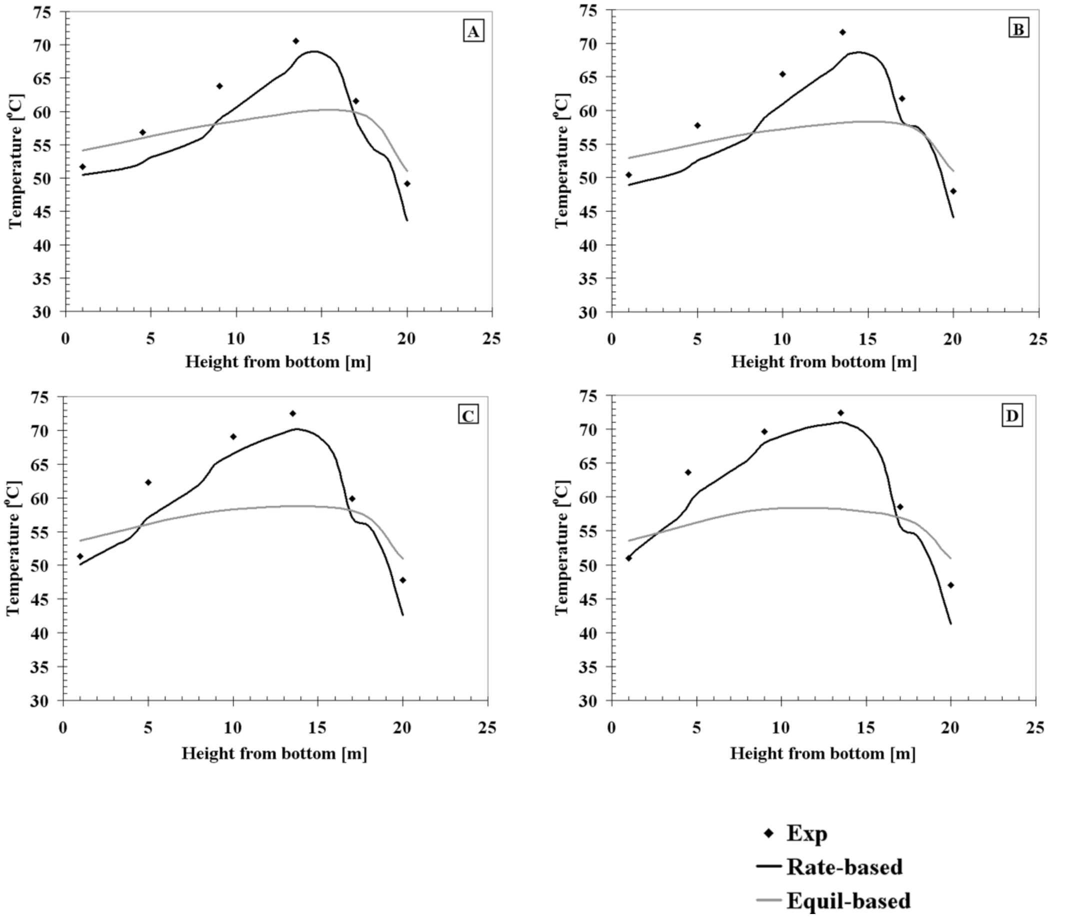

**Figure 4-13: The absorber temperature profile at different stripper pressure** (A at 220 kPa, B at 180 kPa, C at 140 kPa, D at 110 kPa)

In the stripper, the temperature decreases significantly between the bottom and the middle section of the stripper for the tests with high flow rates (16.7 to 23.0 $m^3/h$); whereas only a minor temperature decrease is seen between the middle and top section (see Figure 4-14). This could indicate that most of the $CO_2$ is released in the bottom section. For the other two tests with low solvent flow rates (14.8 and 12.5 $m^3/h$) the temperature decrease in the top section is more significant indicating that $CO_2$ also is released in the top section. Moreover, also more energy per amount of solvent is brought into the system at lower solvent flow rates to obtain a lower lean loading.

In Figure 4-14 and Figure 4-15, it can be observed that the temperature profile of the equilibrium based model is less steeper compared to the rate based model. This is due to the more evenly spread of the $CO_2$ release over the column. Nevertheless, the internal temperature is better predicted with a rate based model than for an equilibrium based model.

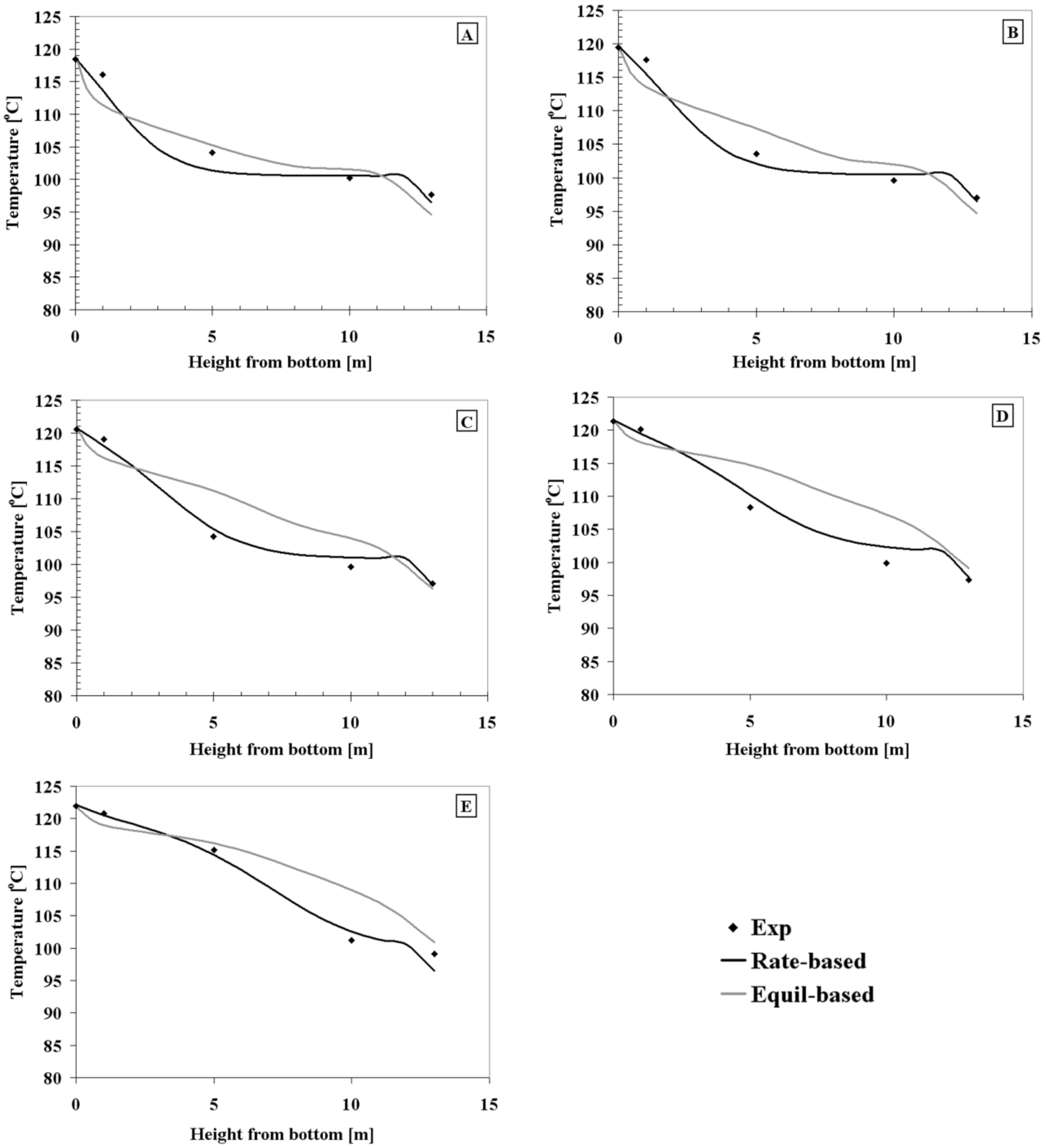

**Figure 4-14: The stripper temperature profile at different solvent flow rates** (A at 23 m$^3$/hr, B at 19 m$^3$/hr, C at 16.5 m$^3$/hr, D at 14.8 m3/hr, E at 12.5 m$^3$/hr)

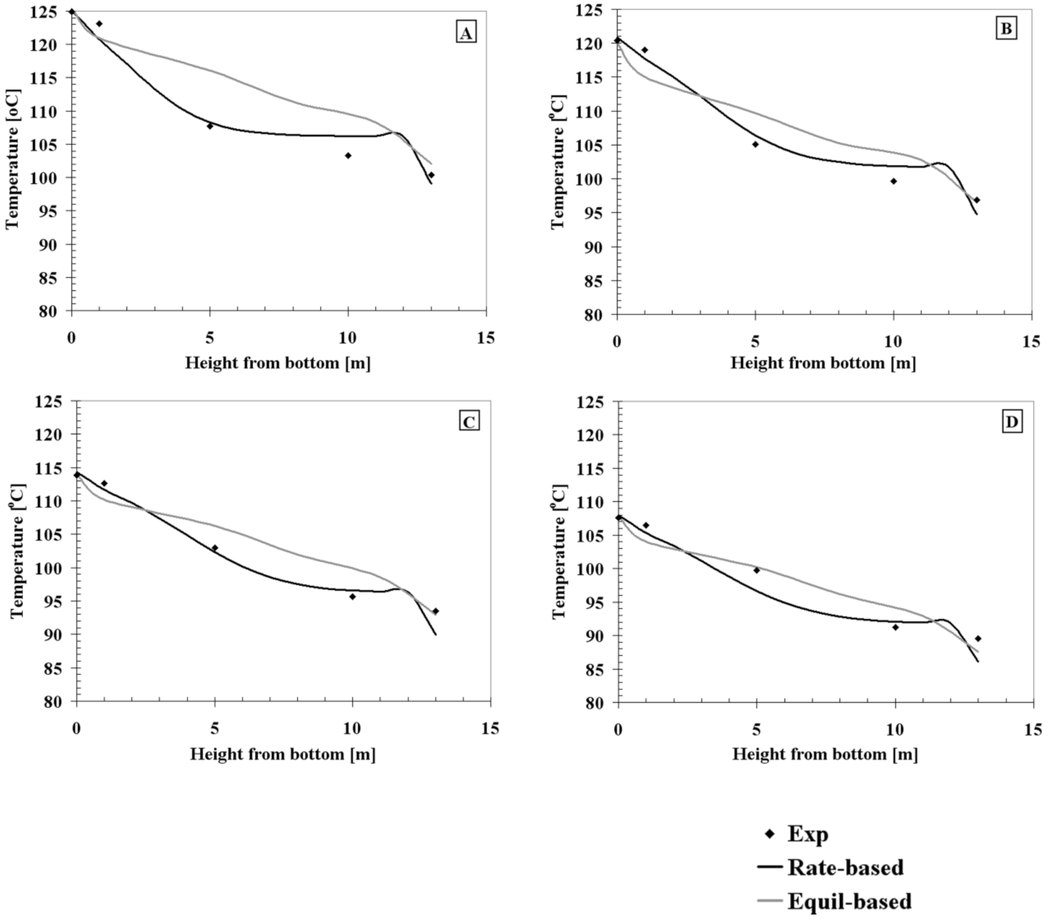

**Figure 4-15: The stripper temperature profile at different stripper pressure** (A at 220 kPa, B at 180 kPa, C at 140 kPa, D at 110 kPa)

Comparing the prediction of the temperature profile of the equilibrium based model for the absorber and the stripper, it can be stated that the equilibrium based model predicts the temperature profile of the stripper more accurate than for the absorber. This can be related to the fact that kinetic resistance is less dominant. Mass transfer rate and reaction kinetics are improved with the increase of temperature. Moreover, in the absorber the mass transfer of $CO_2$ is completely controlled in the liquid film. This is in contrast with the stripper, where in the lower section of the column, the mass transfer is controlled by 50 % in the gas phase and by 50 % in the liquid phase.

## 4.5 Conclusions

In this chapter, the pilot plant experimental results were evaluated and compared to the simulation results. Equilibrium-based and rate-based models are used for describing the reactive absorption process of carbon dioxide based on MEA. These models are implemented within the Aspen plus flow sheet simulation tool.

The process parameter variation tests indicate that the lowest regeneration energy requirement of 3.7 GJ/ton $CO_2$ is obtained at solvent flow rates of 12.5 to 19 $m^3$/h. The tests also show that the specific regeneration energy requirement increases as the stripper pressure is reduced from 185 to 123-150 kPa. On the contrary, increasing the pressure from 185 to 220 kPa has no effect on the regeneration energy requirement. The results of the minimum regeneration energy requirement are in good agreement between the experimental and the simulation results.

The process validation on macro scale shows a good agreement between the experiment and simulation results from both modelling approaches. These results indicate that both the equilibrium-stage and rate –based models can predict the overall capture process in an appropriate way for a full height system. However, the equilibrium approach is advantageous due to the simple calculation approach and the simulation time saving.

The micro analysis shows that the rate-based model gives a better prediction of the columns temperature profiles and internal behaviour comparing to the equilibrium-stage approach. Out of this work, it can be concluded that for a detailed process design the rate-based approach should be applied.

In addition, the presented results support the idea of extending the use of these two models for benchmarking different $CO_2$ capture solvents and process conditions.

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"Your success will be affected by the quality and quantity of
new ideas you suggest" Brian Tracy

# 5

# CO2 POST-COMBUSTION CAPTURE INTEGRATED WITH CO-PRODUCTION OF H2

*In this chapter, two different Hypogen concepts (electricity generation with co-hydrogen production) based on integrating IGCC and $CO_2$ post-combusting capture are proposed and investigated. In the first concept, hydrogen production is based on syngas water-gas shift reaction with high pressure $CO_2$ capture. While in the second concept, hydrogen is produced based on selective membrane separation from syngas.*

*In the first concept, combining a high-pressure and an ambient-pressure $CO_2$ absorber in one flow sheet and one regeneration column is found to be feasible. However, the advantage of the high $CO_2$ partial pressure in the high-pressure absorber is more obvious if an advanced solvent like 2-amino-2-methyl-1-propanol (AMP) is used instead of monoethanolamine (MEA) solvent kind. The second concept is considered feasible and comparing to the first concept, cost competitive with around 10 % higher overall capital cost. However, the membrane unit does not achieve high hydrogen purity because the investigated membrane is limited to a maximum purity of around 95 %.*

*In addition, the influence of flue gas circulation, gasifier selection and an advanced solvent based on the sterically hindered amine AMP are investigated. The benefit of the flue gas circulation is that absorption equipment become more compact. For AMP type of solvents flue gas circulation result in a substantial reduction in regeneration energy and the overall cost of $CO_2$ avoided. In general, these Hypogen strategies appear to be feasible and the overall costs of these concepts are comparable with the conventional post-combustion capture process.*

## 5.1 Introduction

Nowadays, the world is facing tremendous challenges associated with greenhouse gas emissions, climatic change, and the need for a sustainable energy development. The United Nations Intergovernmental Panel on Climate Change (IPCC) has studied these problems and a general conclusion has been achieved between researchers, industry leaders, and politicians that dramatic reductions in greenhouse gas emissions must be achieved in order to stop climatic changes manufacturing [1]. Post-combustion, pre-combustion, and oxy-fuel are considered as the three main routes for $CO_2$ emission reduction in the power generation [2]. A wide range of technologies currently exist for separation and capture of $CO_2$ from gas streams. These technologies are based on different physical and chemical processes including absorption, adsorption, membranes, and cryogenics [3,4]. The choice of a suitable technology depends on the characteristics of the gas streams, which depends mainly on the power plant technology.

With the growing demand for abatement of $CO_2$ emissions from fossil fuel sources; clean fossil technologies become a viable solution to reduce $CO_2$ emissions while still be able to utilize the available fossil fuel as a main source of energy production. These new clean fossil technologies include clean fossil power plants and the centralized production of clean fossil-based transport fuels for use in mobile and widely distributed sources e.g. $H_2$-fuel cells for transport and heat homes. This concept, which combines both of the clean fossil power production and of transport fuels, is called a Hypogen. This power plant or better a hybrid between a power plant and a chemical factory produces electricity and transport fuels (most likely $H_2$) out of a fossil sources (possibly in combination with renewable) to meet the future energy demands. The idea behind the Hypogen is integrating clean fossil power and transport fuel production into one plant concept, more efficient and flexible plant concept can be developed, which produces clean fossil energy at the lowest cost.

The Hypogen concept has been discussed and evaluated within many researches and commercial applications [5-7]. The purposes of most of these activities are the understanding, developing and evaluating of the Hypogen concept as one of the solutions for sustainable energy and greenhouse gas emission problems. Chiesa et al. 2005 [5], have evaluated the Hypogen concept by coal gasification means, syngas shifting to $H_2/CO_2$ and then separating and purifying the $H_2$ using physical absorption and pressure swing adsorption processes. In their work, they have evaluated the complete chain for hydrogen/electricity production and have evaluated improvement options by varying the $H_2$/electricity production ratios. However, Cormos et al. 2008 [6] have followed the same technical route but they have looked for possible improvements by changing the plant configurations. This proposed improvement considered pressurizing the produced syngas after the gasifier to pressure value of 7200 kPa, which will result in a higher syngas temperature. This high temperature is used in promoting the shift reaction and to raise steam. This use of the available heat in the syngas resulted in a better overall plant efficiency of 0.5-0.75 % points. In addition, Perna 2008 [7] has studied and analyzed the thermodynamic favourable operating conditions to maximize hydrogen production, by varying the gasification pressure, and the steam/carbon ratio in both of the gasifier and the shift reactor. The optimum gasifier steam/carbon ratio was found to be 0.2 and at the water-gas shift reactors 1.2 for the maximum hydrogen production rate.

In all the reviewed references, those are evaluating production or co-production of hydrogen using the coal gasification routes, the syngas will be shifted completely to $CO_2/H_2$ and then use the produced hydrogen partially or completely for electricity production. The main challenge in this concept is the dependency on the availability of hydrogen turbine in the near future, which is not fully guaranteed by the turbine providers or, at least, there is no fixed period for the hydrogen turbine availability.

In this work, which is a part of Dynamis project, a different strategy has been followed. In this strategy, the conventional available syngas turbines will be used for electricity production and a co-production of hydrogen will be achieved using a small shift reactor unit. In this concept, not all the syngas will be shifted to $CO_2/H_2$ but only a small fraction, which is needed for hydrogen co-production, will be shifted. In this way, the dependency on the new hydrogen turbine is not a limiting factor anymore. Dynamis is co-funded by the European Commission project under the Sixth Framework Programme with the objective of identifying the technological routes for large-scale co-production of hydrogen and electricity with integrated $CO_2$ capture based on fossil fuels. One of the aims of the project is to rank the technologies based on maturity and economic feasibility and reduce the risk element for subsequent development of a full-scale demonstration plant by industries in the next decade [8].

The plant concept that the Dynamis project is based upon: Hydrogen output variable between 0 and 50 MW (HHV) and 90% $CO_2$ capture. This low hydrogen production rate has been estimated in a previous Hypogen pre-feasibility study. It was stated that the hydrogen production by the Hypogen plant would be limited due to the small demand for hydrogen in the transport sector [9].

The main target of this work is to assess the Hypogen strategy and two different technology concepts based on post-combustion $CO_2$ capture in combination with co-production of hydrogen. These two concepts will use different techniques for hydrogen production. The first concept will use shift reactors followed by high-pressure $CO_2$ separation and pressure swing adsorption (PSA) unit. However, in the second concept a selective polymeric membrane will be used in producing hydrogen from the syngas. A new flow sheet concept was developed in this work. In this flow sheet, the conventional low-pressure, post-combustion capture route will be used in connection with high-pressure absorber to remove $CO_2$. The idea of this concept is to use one solvent for both high and low pressure separation and to regenerate the rich solvent from both absorbers in one regeneration column. The investigation of possible process developments and improvements has been done in this work by illustrating the effect of circulating the flue gas over the gas turbine and by applying an advanced solvent in the post-combustion process.

## 5.2 Process description

In this section, two different concepts for hydrogen production combined with $CO_2$ management and removal will be conducted. These two concepts are built on using syngas from a coal gasifier for power production and a split stream for hydrogen production. The first concept will produce hydrogen using a high-pressure $CO_2$ absorption after shifting the syngas in the water gas shift reactors to hydrogen and carbon dioxide. However, the second concept will apply selective membrane technology to separate the hydrogen from the syngas. Parallel to the hydrogen production in both concepts, electricity will be produced using a combined cycle power plant followed by post-combustion $CO_2$ capture.

### 5.2.1 Concept I: IGCC with high pressure $H_2/CO_2$ separation and post-combustion capture

In this concept, a split stream from the syngas is used in producing the project requirement of hydrogen (50 MW HHV) using a series of two shift reactors, followed by a high-pressure $CO_2$ absorption column and a PSA unit. The rest of the syngas is combined with off-gases from the hydrogen production unit and is burned in a combined cycle. The conventional post-combustion monoethanolamine process in combination with high-pressure amine absorber is used for $CO_2$ capture. Two different types of gasifiers will be investigated:

1. Low-pressure (LP) dry feed gasifier
2. High-pressure (HP) wet feed gasifier

**Table 5-1: Flow rate, composition of the used syngas cases [10]**

| | LP dry feed gasifier | HP wet feed gasifier |
|---|---|---|
| Mass flow (tonne/hr) | 435.8 | 501 |
| Temperature (°C) | 150 | 44 |
| Pressure (kPa) | 2950 | 5490 |
| Composition (mol. %) | | |
| $H_2$ | 31.83 | 40.57 |
| CO | 60.35 | 41.71 |
| $CO_2$ | 1.62 | 15.52 |
| $N_2$ | 5.17 | 0.98 |
| Ar | 0.75 | 1.11 |
| $H_2O$ | 0.28 | 0.11 |

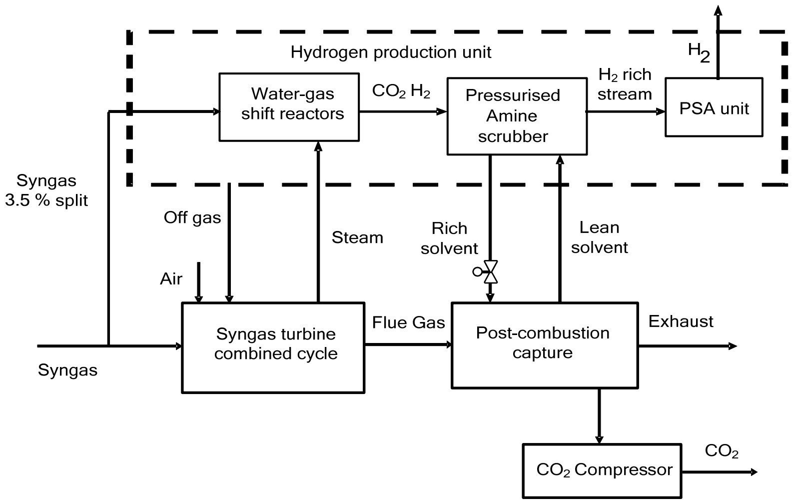

**Figure 5-1: Concept I: Process block diagram**

Table 5-1 shows the composition of the coal gas for these two types of gasifiers. These two syngas compositions are used in the simulation and evaluation activities. The starting point for this work is after the syngas cleaning and treatment units. This means that sulphur and other impurities are removed from the syngas according to the data available in IEA GHG report 2003 [10]. Concept I process block diagram is shown in Figure 5-1. The evaluated process consists of a combination of several process units. The main process components, which are described in more details in this section, are:

1. The syngas combined cycle
2. The hydrogen production unit
3. The $CO_2$ post-combustion capture process
4. The $CO_2$ compression section

#### *5.2.1.1 The syngas combined cycle*

The starting point in this work is conducted after the gasifiers and the syngas pre-treatment units. This means that the used syngas is treated and ready to be used for power generation purposes. Two different types of gasifiers have been used in this work: low-pressure dry feed gasifier and high-pressure wet feed gasifier. The combined cycle power generation unit considered as one of the most effective power generation units. It is similar to the used technology in modern natural gas fired power plants, which maybe needs some modifications to be operated at syngas composition or later on at hydrogen as fuel.

In this activity, the combined cycle power generation unit is simulated as three main parts: The compression system, the combustion step, and the gas turbine unit where expansion takes place to produce electricity. In this cycle the syngas, which is available at a pressure of around 29 bar is burned in the gas chamber with excess air to control the combustion temperature and dilute the flue gas. Then the flue gas is expanded using a gas turbine to produce electrical power and a steam turbine cycle to produce steam for extra electricity production.

The airflow rate is changed to give a specific $CO_2$ content in the flue gas equal to 7.3 mol. % and 8.5 mol. % for the low-pressure and high-pressure processes, respectively. These values for the $CO_2$ content in the flue gas were defined within the base case definitions mentioned in the IEA GHG report 2003 [10].

#### *5.2.1.2 The hydrogen production unit*

The hydrogen production rate is fixed according to the Dynamis project requirement of 0.35 kg/s (50 MW) [9,11]. A syngas split is introduced to use around 4% of the syngas in the hydrogen production unit. The main parts of the hydrogen production unit are the shift reactor, the hydrogen purification by removing the $CO_2$ using a high-pressure absorber and PSA unit to complete the hydrogen purification to 99.999 %. The water gas shift reactor is used to change the chemical composition of the syngas towards more $H_2$ and less CO:

$$CO + H_2O \leftrightarrow H_2 + CO_2 \qquad -41.2\ \text{MJ/kmol} \qquad (5\text{-}1)$$

The reaction is normally carried out in two stages, a high temperature shift, and low temperature shift, with typical operating temperatures are between 200 and 500 $^{o}$C with different catalysts. The typical molar steam/carbon (S/C) ratio, which controls the steam requirement in the shift reactors, is around two [12]. This ratio was proven by the sensitivity analysis in this work. It was found that 2.5 is the optimum ratio after which the carbon monoxide conversion rate is constant, see Figure 5-2. This amount of steam is extracted from the low-pressure steam turbine. This steam extraction will reduce the overall electricity production. However, the reduction in the total electricity production is limited due to the relatively small amount of steam that will be used in the reactors. A high conversion of CO to $CO_2$ could be achieved by applying two serially connected shift reactors. Heat exchangers are placed behind the shift reactors to cool down the converted mixture.

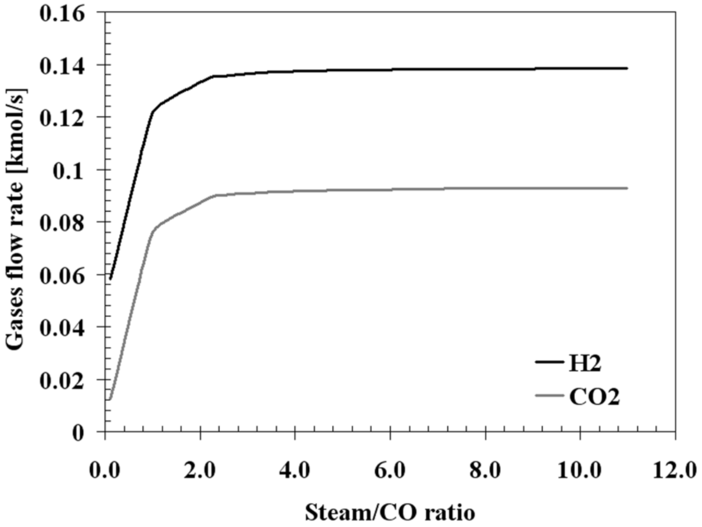

**Figure 5-2: $H_2$ and $CO_2$ production flow rates at different S/C ratios**

The 4 % split high-pressure gas mixture, which is converted to $H_2$ and $CO_2$ in the shift reactors enters a high-pressure absorber where almost 99 % of the $CO_2$ content will be removed using a chemical absorption process. This absorber will be operated at high pressure of 2600 kPa. The new concept in this process is the integration of this high-pressure absorber with the ambient pressure $CO_2$ capture system. The purpose of this integration is to use one type of solvent for both absorption units and to reduce the capital cost by using one regeneration column for both absorption processes. This integration could be achieved by extracting part of the lean solvent as input for the high-pressure absorber. In addition, the rich solvent from the high-pressure absorber together with the rich solvent from the ambient pressure process will be generated in one stripper to release $CO_2$.

The vent gas from the top of the pressurized absorber, which contains almost 90% hydrogen with some other gases, will be fed to the final step in hydrogen production and purification, which is the pressure swing adsorption (PSA) process. The PSA process involves the adsorption of impurities from a hydrogen rich feed gas into a fixed bed of adsorbents at high pressure. The impurities are subsequently desorbed at low pressure into an off gas stream, thereby producing an extremely pure hydrogen product. Product purities in excess of 99.999 % can be achieved [13]. Thus, the final hydrogen product was achieved at purity around 99.999 %.

### *5.2.1.3 The $CO_2$ post-combustion process*

The scheme of the conventional $CO_2$ recovery process using chemical solvents is shown in Figure 5-3.

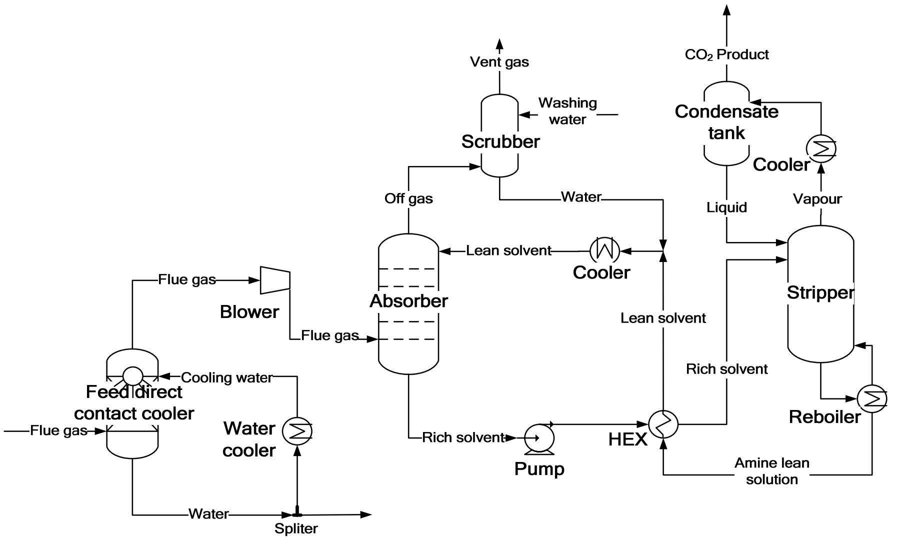

**Figure 5-3: $CO_2$ post-combustion conventional chemical absorption process flow sheet**

The conventional process flow sheet design and description have done using the Econamine FG process, which is described and simulated in different previous studies [14-17]. After cooling the flue gas into temperature between 40 and 60 °C, it enters the absorber where the chemical solvent binds $CO_2$. After passing through, the absorber and before the vent gas leaving the absorber, it undergoes a water wash section to reduce solvent losses in the system. The rich solvent, which contains the chemically bound $CO_2$, is mixed with the rich stream coming from the pressurized absorber and pumped to the top of a stripper, via a heat exchanger. The regeneration of the chemical solvent is carried out in the stripper at elevated temperatures (100 – 125 °C) and pressures slightly higher than atmospheric pressure. Heat is supplied to the reboiler to maintain the regeneration conditions. This heat could be divided into three parts: heating up the solvent, water evaporation and to provide the required desorption heat for removing the chemically bound $CO_2$. Evaporated water will be cooled and condensed partially back to the stripper. The $CO_2$ product is a relatively pure with water vapour being the main other component. The lean solvent, containing far less $CO_2$ is recycled back to the absorber via the lean-rich heat exchanger and a cooler to bring it down to the absorber operating temperature level. Small fraction stream of this lean solvent is pumped to the top of the high-pressure absorber to be used there at high pressure.

### *5.2.1.4 The $CO_2$ compression section*

The produced carbon dioxide will be delivered at 11000 kPa and at around 25 °C [9]. This is achieved by multi-step compression and inter-cooling. $CO_2$ compression scheme, which has been used, was defined in ENCAP and CASTOR projects [18,19]. This scheme consists of three compression steps, three inter-cooling stages and finally a pump as a final step to deliver $CO_2$ product in liquid phase.

### 5.2.2 Concept II: IGCC with polymeric membrane $H_2/CO$ separation and post-combustion capture

A scheme is described for electricity production based on coal gasification with recovery of carbon dioxide and partially hydrogen production from a syngas split stream. The syngas composition, characteristics for low-pressure dry feed gasifier case and high-pressure wet feed gasifier which shown in Table 5-1 are used for this scheme. The main difference between this concept and the first one is using a polymeric membrane for hydrogen production from $H_2/CO$ (syngas) instead of using a shift reactor unit with high pressure $CO_2$ capture. The main advantages of using selective membranes for the hydrogen production are related to the equipment size and complicity reduction.

The simplified process block diagram for concept II is shown in Figure 5-4, where the syngas from the coal gasifier was split into two parts. The main part is used in the combined cycle for electricity generation and the small part (18 %) is sent to the membrane unit to produce hydrogen. However, the retentate syngas from the membrane will be recycled to the syngas combustor. This amount of retentate is equivalent to more than 90% of the syngas that has been used in the membrane unit. The syngas recycles back to the combustion chamber will improve the electricity production by increasing the combusted syngas flow rate.

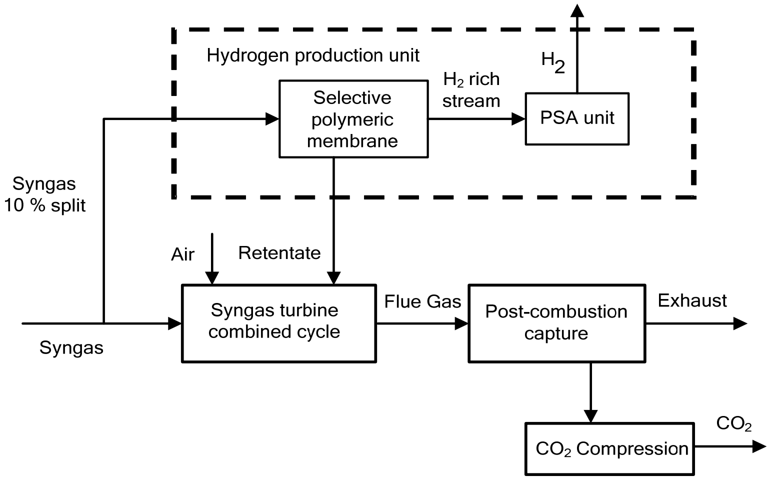

**Figure 5-4: Concept II: Process block diagram**

### 5.2.3 Process modelling and simulation

Both concepts are simulated and analyzed completely using the ASPEN Plus flow-sheeting simulation tools [20]. In the flow sheet simulation, the overall flow sheet has been divided to four main sections: power generation section, hydrogen production, purification section, $CO_2$ capture, and $CO_2$ compression.

The flow sheet was designed and run according to the process description in the previous section. The start point of the flow sheet is the clean syngas after sulphur and water removal, the composition of the syngas is described in Table 5-1. The focus of the flow sheet simulation is on the $CO_2$ capture section and the hydrogen production section. These two sections are controlled by the use of different design specifications to maintain the hydrogen production and purity according to the project requirement and to keep the level of $CO_2$ removal around 90 % of the total $CO_2$ in the flue gas.

Different thermodynamic models are used for the different flow sheet sections. These models have been selected depending on the section operating parameters and conditions, following the general thermodynamic models selection criteria, which are well described by ASPEN Plus reference manual (physical property methods and models [20]). For the power generation, the shift reactors, the hydrogen production and the $CO_2$ compression sections, the general equation of state (Peng-Robinson) is used as a thermodynamic base model. However, for the $CO_2$ capture process, which is considered non-ideal, could be described in the gas phase using the Soave-Redlish-Kwong equation of state [21]. For the liquid phase, electrolyte-NRTL method is considered as a good representation of this system, and all the required data and parameters for the $CO_2$-$H_2O$-MEA system have been developed and presented by Austgen et al. 1989 [22].

## 5.3 Results and discussion

In this section, the results of the different two concepts for hydrogen production combined with $CO_2$ management and removal will be presented and discussed.

### 5.3.1 Concept I: IGCC with high pressure $H_2$/$CO_2$ separation and post-combustion capture

#### *5.3.1.1 Base case results and discussion*

The main syngas stream is used directly in the gas combustion for electricity generation. While the small split of syngas (3.5 %) is used for hydrogen production. The hydrogen production process, using water gas shift reactors, in this work has been described based on the process description of Hendriks 1994 [12].

**Table 5-2: Composition, gas flow rate before and after passing the shift reactors**

| | Feed to first reactor | Product from first reactor | Product from second reactor | Gas mixture after condensers |
|---|---|---|---|---|
| Total flow (kmol/s) | 0.151 | 0.379 | 0.379 | 0.239 |
| Temperature (°C) | 350 | 450 | 330 | 45 |
| Pressure (kPa) | 2950 | 2900 | 2700 | 2670 |
| Composition (mol. %) | | | | |
| $H_2O$ | 0.28 | 38.93 | 37.13 | 0.36 |
| $CO_2$ | 1.62 | 21.96 | 23.77 | 37.66 |
| Ar | 0.75 | 0.3 | 0.3 | 0.47 |
| $N_2$ | 5.17 | 2.06 | 2.06 | 3.27 |
| $H_2$ | 31.83 | 34.01 | 35.81 | 56.76 |
| CO | 60.35 | 2.74 | 0.93 | 1.48 |

The syngas will first be heated up to 350 °C, and mixed with the extracted steam from the steam cycle at the same temperature. This gas stream is fed to the first shift reactor. In this first reactor, the temperature rises to 450 °C. This temperature will be controlled in the reactor by adding more steam to avoid the high temperature side effect on the catalyst. Then the gas mixture is cooled down to 250 °C with heat exchanger, and fed to the second shift reactor.

In the second reactor, the temperature rises to 330 °C. After passing, the second reactor, the gas mixture is cooled down to 45 °C using two step condensers to remove the condensed steam in the gas mixture. Table 5-2 shows as an example, the composition and temperature of the gas mixture before, between, and after the shift reactors for the low-pressure gasifier case.

The $H_2/CO_2$ mixture, which is produced in the shift reactors, will be treated in the high-pressure absorber, where $CO_2$ is separated using monoethanolamine solvent. The outlet gas stream from the top of the HP-absorber is around 90 % hydrogen with some other gases as shown from the gas composition in Table 5-3. The gases impurities were separated from the hydrogen stream using PSA unit to produce 99.999 % pure $H_2$.

**Table 5-3: High-pressure vent gas composition**

| Component | mol. % |
|---|---|
| $H_2O$ | 0.35 |
| $CO_2$ | 0.002 |
| Ar | 0.07 |
| $N_2$ | 5.26 |
| $H_2$ | 91.30 |
| CO | 2.38 |

The off-gas stream from the hydrogen production unit was combined with the main syngas stream and burned in the syngas combined cycle to produce electricity. The flue gas, which produced from the combined cycle, is treated using a conventional amine post-combustion $CO_2$ capture process. This process is a basic absorption/desorption process, which is defined by Fluor Daniel Econamine FG process, Mariz 1998 [14] using 30-wt % Monoethanolamine (MEA) solvent.

The base case process was simulated without flue gas recycle to fix the operating conditions of the process. For low-pressure gasifiers, the $CO_2$ content according to IEA GHG study 2003 is expected to be 7.3 mol. % [10]. This $CO_2$ content in the flue gas was fulfilled in this work by operating gas combustor at 2900 kPa and 1376 °C. Depending on the same IEA GHG report 2003, the expected $CO_2$ content for the high-pressure gasifier process is 8.5 mol. % [10], which was achieved at 2900 kPa and 1424 °C.

The requirements for $CO_2$ capture and compression base case are shown in Table 5-4. From the results, it is clear from the regeneration energy requirement and solvent requirement that treating the flue gas from the IGCC process using MEA post-combustion process is comparable to the expected results for conventional pulverized hard coal-fired plant using MEA post-combustion process for $CO_2$ capture, which has been found in the work of Abu-Zahra et al. [17].

**Table 5-4: Capture base case flue gas specifications and process requirement**

| | **LP gasifier case** | **HP gasifier case** |
|---|---|---|
| Flue gas flow rate (kg/s) | 1457 | 1315 |
| $CO_2$ flue gas content (mol. %) | 7.3 | 8.5 |
| Oxygen flue gas content (mol. %) | 14.2 | 13.0 |
| $CO_2$ produced (tonne/hr) | 545 | 580 |
| Regeneration energy (GJ/tonne $CO_2$) | 3.7 | 3.8 |
| Cooling water, incl. compression inter-cooling ($m^3$/tonne $CO_2$) | 57 | 62 |
| Lean solvent ($m^3$/tonne $CO_2$) | 19 | 19 |
| $CO_2$ compression power requirement (MWe) | 51 | 55 |

### *5.3.1.2 Flue gas recycle analysis*

The effect of the flue gas recycle ratio over the gas turbine is investigated. Figure 5-5, shows the location of the recycled flue gas over the gas turbine. The recycle ratio has been varied in this work in the range between the base case with zero and the maximum ratio of 45 %, this maximum limitation has been considered depending on the process optimization that has been done by Bolland and Undrum 2002 [23]. However, the maximum recycle ratio can be different from one case to another depending on the syngas composition and the flue gas oxygen content.

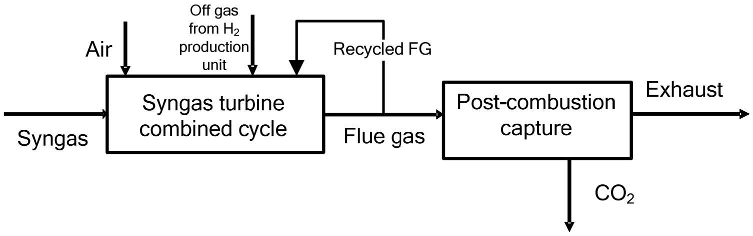

**Figure 5-5: Flue gas recycle block diagram**

While the flue gas recycle ratio has been varied over the gas turbine, all the process-operating conditions are kept the same. The overall air/flue gas flow rate to the syngas combustor is kept constant. The pressure and temperature of the combustor also have been kept the same as defined in the base case for all cases with flue gas recycle. The simulation runs on fixed operating conditions and the $CO_2$ content in the flue gas has been considered as an output of the modelling calculations.

From the analysis with different flue gas recycle ratios; it is found that increasing the recycle ratio will increase the $CO_2$ content in the flue gas. This higher $CO_2$ concentration will reduce the flue gas flow rate and as a result, it is expected that the size of the absorber will decrease.

Figure 5-6, shows the effect of the flue gas recycle ratio changing on the $CO_2$ and $O_2$ concentrations in the flue gas for the low-pressure gasifier case. It is clear that increasing the flue gas recycle ratio to 45 % will increase the $CO_2$ content in the flue gas to 14 mol. %, which is almost two times higher than the base case concentration.

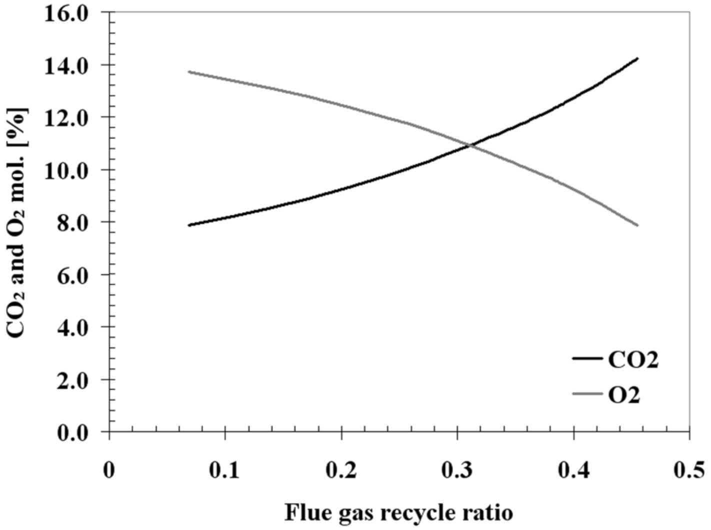

**Figure 5-6: Flue gas recycle ratio Vs. $CO_2$ and $O_2$ mol. % (LP case)**

In addition, increasing the flue gas recycle ratio will decrease the airflow rate required in the syngas combined cycle, since around 13 mol. % $O_2$ is left in the flue gas after the gas turbine, which could be used in the combustion step instead of using $O_2$ from the air. Increasing the flue gas recycle ratio to the maximum of 45 % will reduce the air requirement almost 50%. While the overall inlet flow rate to the gas combustor is kept almost the same. Changing the recycle ratio does not have an effect on the most important capture process requirement (regeneration energy). This is related to the constant amount of carbon dioxide that has been captured in the process. Besides, the MEA solvent capacity is limited by the chemical reaction (theoretically, up to 0.5 mol $CO_2$/mol MEA). However, the increase of the $CO_2$ concentration will have a major effect on the absorber size and as a result on the equipment capital costs, which will clarify more in section 5.5. The $CO_2$ capture process requirements for both gasification processes at different recycle ratios are shown in Table 5-5.

**Table 5-5: Capture process requirements at different flue gas recycle ratio**

| | **LP gasifier case** | | | **HP gasifier case** | | |
|---|---|---|---|---|---|---|
| Recycle ratio | Zero | 0.25 | 0.45 | Zero | 0.25 | 0.45 |
| Flue gas flow rate (kg/s) | 1457 | 1080 | 769 | 1316 | 962 | 679 |
| $CO_2$ content (mol. %) | 7.3 | 9.8 | 14.0 | 8.5 | 11.8 | 17.1 |
| $O_2$ content (mol. %) | 14.2 | 11.8 | 8.0 | 13.0 | 10.2 | 6.0 |
| Regeneration energy (GJ/tonne $CO_2$) | 3.75 | 3.76 | 3.8 | 3.8 | 3.8 | 3.8 |
| Cooling water ($m^3$/tonne $CO_2$) | 57 | 67 | 77 | 62 | 70 | 74 |
| Lean solvent ($m^3$/tonne $CO_2$) | 19 | 19 | 19 | 19 | 19 | 19 |

For the conventional post-combustion process, a direct contact cooler (DCC) is used for flue gas feed cooling, where flue gas and cooling water contact via a large surface area. The gas is cooled to 40 °C using circulating water stream. With flue gas recycle, an extra cooling step is required; because the compressor performance is affected by the inlet temperature. It is necessary to cool the recycled exhaust gas to about ambient temperature (25 °C) before entering the compressor. This extra cooling step is considered as the only improvement that is needed on the gas turbine and the rest of the system is assumed to be not affected by the recycle of the flue gas.

The flue gas cooling power required at different flue gas recycle ratios for the low-pressure gasifier case as an example has been investigated. From this study, it is clear that increasing the recycle ratio will require higher cooling energy. At a recycle ratio of 45 %, a cooling power of around 138 MW is required. The base case process with zero flue gas recycle ratio requires a cooling power of around 51 MW. Increasing the cooling power is expected to have a negative effect on the process by increasing the operating costs. However, the overall effect of the flue gas recycling on the process will be clear in the economic evaluation section, where both operating and capital costs will be estimated and combined in an overall process evaluation.

### 5.3.2 Concept II: IGCC with polymeric membrane $H_2$/CO separation and post-combustion capture

#### *5.3.2.1 Base case results and discussion*

The syngas combined cycle and the carbon dioxide post-combustion capture and compression system have the same specifications as in concept I. However, the difference in this concept is using $H_2$/CO separating polymeric membrane for hydrogen production from the syngas using a split stream. A polyimide membrane is selected, which is produced and developed by UBE 1989 [24]. This membrane has been chosen due to the high hydrogen selectivity and can be operated at temperature up to 150 °C. The permeability values for the main component of the syngas for this membrane are shown in Table 5-6.

**Table 5-6: Permeability coefficients of the selected polyimide membrane (Vendors information [24])**

| **Component** | **Permeability coefficients ($m^3/m^2$.hr.bar)** |
|---|---|
| $H_2O$ | 2.7 |
| $H_2$ | 0.3 |
| CO | $3 * 10^{-3}$ |
| $CO_2$ | $3 * 10^{-2}$ |
| $N_2$ | $1.6 * 10^{-3}$ |
| Ar | $3 * 10^{-3}$ |

The membrane unit was implemented in the Aspen plus flow sheet using a user-FORTRAN model [25]. Having this model connected to the complete flow sheet will help to give results that are more realistic and more flexibility for the flow sheet sensitivity analysis. Using this build in FORTRAN model together with the membrane specifications, so, the maximum hydrogen purity that could be achieved is 95% for the low-pressure gasifier case. This results in a membrane area requirement of 4000 $m^2$ membrane and using a split of 10 % from the total syngas flow rate. However, in the high-pressure gasifier case the membrane area requirement is 1200 $m^2$ and using

18 % of the syngas, which produces hydrogen with around 94 % purity. From the results, an early conclusion could be drawn that membrane unit with this purity will not fulfil the requirement of this work. However, the hydrogen purity could be improved by developing better membranes with higher hydrogen selectivity compared to the present one. Moreover, the produced hydrogen could be further upgraded by adding a pressure swing adsorption unit (PSA) after the membrane unit or by the use of more developed membranes concepts like multistage membranes, which claimed to produce hydrogen with high purity. The option of adding a PSA unit at the end of this route is selected and further investigated in the economic evaluation section.

The syngas combined cycle was operated at conditions to give a flue gas with $CO_2$ composition equal to 7.3 mol. % and 8.5 mol. % for low pressure case and high pressure case respectively, which are the expected flue gas compositions according to IEA GHG study 2003 [10]. The $CO_2$ capture process requirements for the base case in scheme 2 are shown in Table 5-7.

**Table 5-7: Base case post-combustion capture process requirement**

| | **LP case** | **HP case** |
|---|---|---|
| Flue gas flow rate (kg/hr) | 1506 | 1368 |
| $CO_2$ flue gas content (mol. %) | 7.3 | 8.5 |
| $CO_2$ produced (tonne/hr) | 544 | 578 |
| Regeneration energy (GJ/tonne $CO_2$) | 3.73 | 3.8 |
| Cooling water, including compression inter-cooling ($m^3$/tonne $CO_2$) | 66 | 74 |
| Lean solvent ($m^3$/tonne $CO_2$) | 19 | 19 |
| $CO_2$ compression power req. (MWe) | 51 | 54 |

#### *5.3.2.2 Flue gas recycle analysis*

Using the base case results for concept II and the same analysis methodology from concept I, the flue gas recycle ratio over the gas turbine is analyzed. The conclusions in this section are in agreement with the conclusions in the first concept, where the effect of the flue gas recycling is limited to a smaller absorber size.

## 5.4 Capture process: possible improvements

### 5.4.1 Introduction

In previous sections, the conventional post-combustion capture process was used and investigated. Out of the results, it is clear that further improvements are required to make the capture process economically feasible and to meet the Dynamis project targets of reducing the overall capture cost. In this work, the use of a new solvent with a lower energy demand has been investigated, which is expected to have a direct influence on the process requirement and costs.

### 5.4.2 New solvent application

The energy requirement in the capture process is a major contributor in the cost of the capture process. Different researches activities are trying to develop new solvents, which have lower regeneration energy comparing to the conventional solvent (MEA).

Mitsubishi Heavy Industries have developed a new solvent under the name of KS-1, which they claimed that it has a 20 % lower regeneration energy comparing to the conventional MEA process (4 GJ/tonne $CO_2$) Imai 2003 [26]. This new solvent is based on a sterically hindered amine to which an accelerator has been added to improve its reaction kinetics. For that, a preliminary study has been done in this work to estimate the $CO_2$ capture costs and requirements by using 2-amino-2-methyl-1-propanol (AMP) solution as absorption solvent. It is expected that AMP, which is a sterically hindered amine will improve the capture process behaviour by reducing the regeneration energy requirement and increasing the solvent absorption capacity.

This investigation using AMP solvent has been done using the low-pressure dry feed gasifier case as an example to estimate the process requirements and compare it with the conventional process using MEA. This new solvent has been applied for the first scheme, where $H_2$ is produced using the shift reactor unit. The results of this work show a benefit of using AMP by reducing the energy requirement of around 13 % for the base case without flue gas recycle comparing to the conventional MEA process (4 GJ/tonne $CO_2$). An extra reduction on the energy requirement was achieved on the process with flue gas recycle because of the higher $CO_2$ loading that could be reached using AMP solutions. Looking at the MEA case with 45 % flue gas recycle and AMP case with the same recycle ratio, so, it is clear that a reduction of almost 25 % on the regeneration energy could be accomplished.

The main disadvantage of the sterically hindered amines is the slow kinetics. In case of there is no using activator, the absorber size using AMP will be considerably increased compared to faster kinetics solvent, which is expected to influence the overall cost of $CO_2$ removal using AMP as a solvent. The complete technical results of the capture process using 30-wt % AMP solution for the LP gasifier case with different recycle ratios are shown in Table 5-8.

**Table 5-8: Capture process requirements at different flue gas recycle ratio using AMP chemical solvent**

| **Item** | **LP gasifier case** | | |
|---|---|---|---|
| Recycle ratio | Zero | 0.25 | 0.45 |
| Flue gas flow rate (kg/s) | 1457 | 1080 | 769 |
| $CO_2$ content (mol. %) | 7.3 | 9.8 | 14.0 |
| $O_2$ content (mol. %) | 14.2 | 11.8 | 8.0 |
| Regeneration energy (GJ/tonne $CO_2$) | 3.5 | 3.2 | 2.8 |
| Cooling water ($m^3$/tonne $CO_2$) | 72 | 72 | 70 |
| Lean solvent ($m^3$/tonne $CO_2$) | 28 | 25 | 23 |

## 5.5 Concept economic evaluation

### 5.5.1 Introduction

The economic performance of the post-combustion solvent process has been determined for the different concepts and options by the estimation of the main equipment sizes, followed by an estimate of the capital and operating expenses. The procedure and assumptions for the economic evaluation have been built on the previous work of Abu-Zahra et al. [27], which has used the year 2005 as base for the economic calculations. The data from the ASPEN Plus simulation have been used as an input for the processes sizing with 30 wt. % MEA weight concentration at 90 % $CO_2$ removal as a base case. The IEA GHG report baseline power plants cases specifications have been used in performing the analysis [10].

The process economic study and evaluation started by the process equipments sizing and capital cost estimation. However, the hydrogen production system costs, for the first concept, is taken as a constant value (per kg $H_2$ produced), which depends on the production method [13]. The methodology and assumptions that have been used in determining the total capital investment costs (CAPEX), the total manufacturing costs (OPEX) and the overall economic evaluation developed and explained in detail in the previous work of Abu-Zahra et al. 2007 [27].

### 5.5.2 Economic evaluation results: concept I: IGCC with high pressure $H_2/CO_2$ separation and post-combustion capture

The overall techno-economic analyses are done for the two types of gasifiers using MEA as a basic solvent. The carbon dioxide removal is fixed to 90 % and the flue gas recycle ratio over the gas turbine is analyzed.

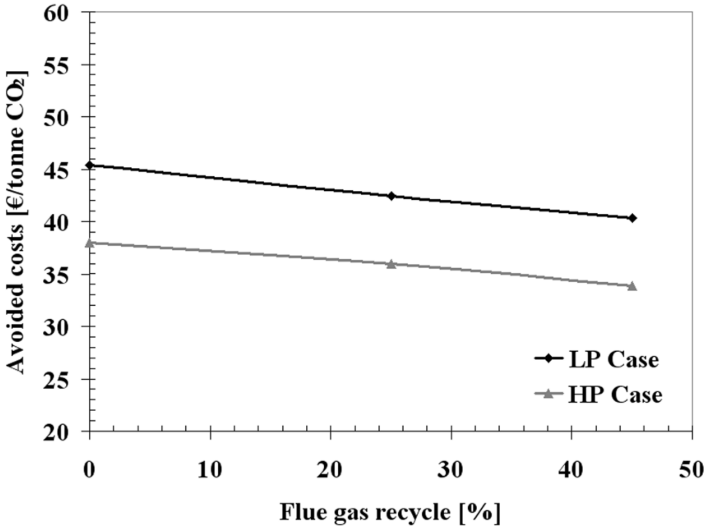

**Figure 5-7: Concept I: Cost per tonne $CO_2$ avoided as a function of flue gas recycle ratio for different gasifiers**

The hydrogen production system costs include: water gas shift reactors and PSA unit was taken as a constant value equal to \$0.92/kg hydrogen [13], which is then added to the overall production costs. The 50 MW thermal, which is produced using the hydrogen stream, is converted into electricity by assuming a conservative low value of 60 % efficiency and then the value of this electricity is added to the overall power plant revenue.

The results of the cost of $CO_2$ avoided show that the cost decreases with increasing the flue gas recycle ratio (see Figure 5-7). This is expected due to the lower flue gas flow rate, which will result in smaller absorption columns. And as a result, reduce the overall capital costs. However, the cost of the gas turbine and the power generation section has been assumed constant and not influenced by the flue gas recycle. The only additional costs are the capital and operational costs for the extra cooler needed to keep recycling flue gas temperature close to ambient.

The overall techno-economic results of this concept are shown in Table 5-9. It is clear from these overall results that using the flue gas recycle concept will improve the overall process economic behaviour by reducing the capital cost and because of that, the overall cost of $CO_2$ avoided and cost of electricity after adding the capture process. By recycling 45 % of the flue gas, the overall capture CAPEX is reduced by 27 % comparing to the base case with no recycle. The cost of $CO_2$ avoided and cost of electricity are reduced but with a factor of 5-10 %.

**Table 5-9: Concept I: Techno-economic results for the three different gasifiers with different flue gas recycle ratio**

| Item | LP gasifier case | | | |
|---|---|---|---|---|
| | Before capture | after capture | | |
| | | Zero Recycle | 25% Recycle | 45% Recycle |
| Capacity (tonne $CO_2$/hr) | - | 545 | 543 | 544 |
| Gross power output (MWe) | 910 | 910 | 910 | 910 |
| Fuel price (€/tonne) | 38.8 | 38.8 | 38.8 | 38.8 |
| Net power output (MWe) | 776 | 567 | 570 | 571 |
| Thermal efficiency, % (LHV) | 43.1 | 31.5 | 31.7 | 31.7 |
| $CO_2$ emission (kg/MWh) | 763 | 105 | 108 | 106 |
| Capture Investment (mil. €) | - | 246 | 207 | 178 |
| Total Investment (€/kWe) | 1372 | 2311 | 2229 | 2176 |
| O&M costs (mil. €/yr) | 140 | 172 | 170 | 168 |
| Cost of Electricity (€/MWh) | 46 | 76 | 74 | 73 |
| Cost of $CO_2$ Avoided (€/tonne) | - | 45 | 42 | 40 |
| | HP gasifier case | | | |
| Capacity (tonne $CO_2$/hr) | - | 580 | 581 | 586 |
| Gross power output (MWe) | 989 | 989 | 989 | 989 |
| Fuel price (€/tonne) | 38.8 | 38.8 | 38.8 | 38.8 |
| Net power output (MWe) | 827 | 603 | 605 | 609 |
| Thermal efficiency, % (LHV) | 38.0 | 27.7 | 27.8 | 28.0 |
| $CO_2$ emission (kg/MWh) | 833 | 102 | 100 | 93 |
| Capture Investment (mil. €) | - | 224 | 196 | 174 |
| Total Investment (€/kWe) | 1187 | 2000 | 1945 | 1887 |
| O&M costs (mil. €/yr) | 153 | 184 | 182 | 181 |
| Cost of Electricity (€/MWh) | 44 | 72 | 70 | 69 |
| Cost of $CO_2$ Avoided (€/tonne) | - | 38 | 36 | 34 |

This reduction in the overall capital investment and the overall capture cost is related to the smaller absorber column, which is a result of increasing the $CO_2$ partial pressure (increasing driving force) with applying the flue gas recycles. However, the capacity of the MEA solvent is limited by the stoichiometric of the chemical reaction (~ 0.5 mol $CO_2$/mol MEA) this will result in a limited influence of the flue gas recycle on the capture process when using MEA like solvent.

Comparing the two different types of gasifiers, the high-pressure gasifier process results in a lower cost of $CO_2$ avoided, comparing with the low-pressure gasifier process. This lower cost could be related to the higher hydrogen content in the syngas and the higher $CO_2$ content in the flue gas, which will improve the absorber behaviour and contribute to reduce the overall capital costs.

### 5.5.3 Economic evaluation results: concept II: IGCC with polymeric membrane $H_2$/CO separation and post-combustion capture

The economic analysis and evaluation method used in this concept are the same as in the first concept. The cost of the membrane depends on the membrane development and the scale of the membrane module. Since there is no specific cost estimation available, it is assumed in this work to use 100 €/$m^2$ as installed cost for the membrane unit (this price includes costs of both the membrane and the membrane module). The membrane life of stability is assumed to be five years, which means that the capital cost of the membrane will be added to the process overall cost every five years. Moreover, the hydrogen purity produced using the membrane unit does not qualify with the project requirement of 99.999%. To achieve the high purity, a PSA unit is added in the process after the membrane unit and included in this economic evaluation.

The total capital investment of the PSA unit is estimated separately and added to the overall capital investment of the capture process. For this estimation, Kreutz et al. 2005 [28] present a scale factor equation, which is applied and used in the current calculation. This economic evaluation is done for the two gasification technologies on different flue gas recycle ratios over the gas turbine. The overall results show a reduction of the avoided costs between 12 and 14 % by increasing the flue gas recycle ratio up to 45 %. The avoided cost is reduced from 43 to 38 €/tonne $CO_2$ for the LP gasifier case and from 36 to 31 €/tonne $CO_2$ for the HP gasifier case by applying 45 % flue gas recycle ratio comparing to the base case with no recycle.

The overall techno-economic results are shown in Table 5-10. The main benefit of the flue gas recycle ratio could be seen clearly in the capture investment, which is well connected to the reduction of the absorber size by recycling the flue gas over the gas turbine. For the low-pressure gasifier case, increasing the recycle ratio from zero up to 25 and 45 % will result in a reduction of 16 % and 28 % in the capture investment costs, respectively. In addition, the total operating costs of the power plant are decreased in a small value with increasing the flue gas recycle ratio, this small reduction is expected due to the reduction of the power required in the flue gas blower. Again, the same conclusion could be drawn here by comparing the high-pressure gasifier technology and low-pressure technology. A lower cost of $CO_2$ avoided is found for the high-pressure gasifier technology, which could be related to the higher $CO_2$ partial pressure in the flue gas.

However, comparing the two concepts shows clearly that the first concept has a lower overall power plant efficiency with around one-percentage points in all cases. This lower efficiency is resulted out of the steam extraction for the water gas shift reactors and due to the higher amount of syngas that has been used for hydrogen production in the first concept.

**Table 5-10: Concept II: Techno-economic results for the two different gasifiers with different flue gas recycle ratio**

| Item | Before capture | LP gasifier case<br>after capture<br>Zero Recycle | 25% Recycle | 45% Recycle |
|---|---|---|---|---|
| Capacity (tonne/hr) | - | 544 | 543 | 542 |
| Gross power output (MWe) | 910 | 910 | 910 | 910 |
| Fuel price (€/tonne) | 38.8 | 38.8 | 38.8 | 38.8 |
| Net power output (MWe) | 776 | 585 | 587 | 588 |
| Thermal efficiency, % (LHV) | 43.1 | 32.5 | 32.6 | 32.7 |
| $CO_2$ emission (kg/MWh) | 763 | 102 | 104 | 105 |
| Capture Investment (mil. €) | - | 270 | 228 | 195 |
| Total Investment (€/kWe) | 1372 | 2279 | 2201 | 2140 |
| O&M costs (mil. €/yr) | 140 | 174 | 171 | 169 |
| Cost of Electricity (€/MWh) | 46 | 75 | 73 | 71 |
| Cost of $CO_2$ Avoided (€/tonne) | - | 43 | 40 | 38 |
| | | HP gasifier case | | |
| Capacity (tonne/hr) | - | 578 | 579 | 583 |
| Gross power output (MWe) | 989 | 989 | 989 | 989 |
| Fuel price (€/tonne) | 38.8 | 38.8 | 38.8 | 38.8 |
| Net power output (MWe) | 827 | 626 | 628 | 630 |
| Thermal efficiency, % (LHV) | 38.0 | 28.8 | 28.9 | 29.0 |
| $CO_2$ emission (kg/MWh) | 833 | 106 | 104 | 98 |
| Capture Investment (mil. €) | - | 240 | 205 | 180 |
| Total Investment (€/kWe) | 1187 | 1952 | 1890 | 1842 |
| O&M costs (mil. €/yr) | 153 | 185 | 183 | 182 |
| Cost of Electricity (€/MWh) | 44 | 70 | 68 | 67 |
| Cost of $CO_2$ Avoided (€/tonne) | - | 36 | 33 | 31 |

On the other hand, the second concept using polymeric membrane is found to be feasible and cost competitive with the first concept with a relatively lower capital investment. However, these results have been achieved assuming a membrane installation cost of 100 €/m$^2$. If the price of the membrane has been increased, it is expected that the total capital and avoided costs for the second concept will increase. Assuming that the membrane price is 200 €/m$^2$, then the total capital investment and the avoided costs for the base case without flue gas recycle have been found to be 2307 €/kW and 44 €/tonne $CO_2$, respectively. It is clear from these calculations that the influence of the membrane cost on the total capture cost is limited due to the relatively small contribution of the membrane unit in the overall process (only 10 % of the total syngas has been treated using the membrane unit).

### 5.5.4 Economic evaluation results: new chemical solvent integrated within concept I

The economic and overall evaluation of the process in concept I have been evaluated using AMP as the main chemical solvent. The overall evaluation shows the combined effect of lower energy requirement and the larger size of the absorber column. At a flue gas recycle ratio of 45 % , the overall process economic in terms of cost of $CO_2$ avoided is almost the same as the conventional MEA process, but with significantly lower energy penalty. The complete techno-economic results of the capture process using 30-wt % AMP solution for the LP gasifier case are shown in Table 5-11.

**Table 5-11: Techno-economic results with different flue gas recycle ratio using AMP solution**

| Item | LP Case with AMP | | | |
|---|---|---|---|---|
| | Before capture | after capture | | |
| | | Zero Recycle | 25% Recycle | 45% Recycle |
| Capacity (tonne/hr) | - | 546 | 548 | 547 |
| Gross power output (MWe) | 910 | 910 | 910 | 910 |
| Fuel price (€/tonne) | 38.8 | 38.8 | 38.8 | 38.8 |
| Net power output (MWe) | 776 | 571 | 587 | 604 |
| Thermal efficiency, % (LHV) | 43.1 | 31.7 | 32.6 | 33.5 |
| $CO_2$ emission (kg/MWh) | 763 | 102 | 95 | 95 |
| Capture Inv. (mil. €) | - | 500 | 407 | 268 |
| Total Inv. (€/kWe) | 1372 | 2739 | 2507 | 2206 |
| O&M costs (mil. €/yr) | 140 | 193 | 185 | 174 |
| Cost of Electricity (€/MWh) | 46 | 87 | 80 | 73 |
| Cost of $CO_2$ Avoided (€/tonne) | - | 62 | 52 | 39 |

Using a solvent like AMP, improves the capture process economics by reducing the operating cost. This operating cost has been reduced due to the lower energy requirement for the AMP solvent regeneration. However, the main drawback of this kind of solvent is the relatively slow reaction kinetics comparing with the primary amine solvents. This slow kinetics resulted in a large absorber column and increased the overall capital investment. The reaction kinetics of AMP solvent could be improved by using an accelerator like piperazine, which will result in a major reduction on the size of the absorber column. Adding an activator will undoubtedly reduce the energy performance of AMP a little but this is expected to be minor. However, the faster reaction kinetics will improve the size of the absorber and the overall cost of the capture process.

It has been seen clearly that the influence of the flue gas recycle has a large influence on the capture cost when using the AMP type of solvents comparing the primary amine (MEA). This larger influence of the flue gas recycle is due to the AMP solvent ability to absorb more $CO_2$ at higher $CO_2$ partial pressure. This solvent capacity will be increased by increasing the $CO_2$ content in the flue gas and it is not limited to 0.5 as in the MEA case.

## 5.6 Conclusions

Two different Hypogen concepts with $CO_2$ capture were proposed and investigated. In the first concept, two different gasification technologies were investigated: low-pressure dry feed gasifier and high-pressure wet feed gasifier. It is clearly found that the high-pressure case shows a better economic performance. This lower overall capture cost for the high-pressure case is expected due to the higher carbon dioxide content in the flue gas and the higher hydrogen content in the syngas. In the second concept, polymeric membrane is used for hydrogen production. It is found that the concept of using membrane is feasible and cost competitive. However, the membrane unit does not achieve high hydrogen purity. As a result, using the membrane unit requires an extra hydrogen purification step e.g. extra membrane separation steps or a PSA, which increases the system complicity and the overall cost. In addition, using membrane for hydrogen production will increase the capital cost due to the high membrane capital cost. On the other hand, using membrane will improve the overall thermal efficiency in the power plant because no steam is needed for hydrogen production comparing with the regular water gas shift reaction route.

The flue gas recycle ratio over the gas turbine is beneficial for the overall process behaviour. The total flue gas flow rate is reduced with increasing the flue gas recycle ratio (the $CO_2$ content in the flue gas was increased), this reduction in the flow rate results in a smaller absorber column. As an overall result the capital investment, the cost of electricity and cost of $CO_2$ avoided are reduced with increasing the flue gas recycle ratio. There is no effect of the flue gas recycle ratio on the solvent regeneration energy in the stripper using the conventional MEA solvent. This could be explained by the solvent loading limitation of the MEA solvent. However, the effect of the flue gas recycle ratio on the energy requirement and the overall cost is more obvious using a different solvent with higher loading capacity (AMP). The energy requirement is reduced by increasing the flue gas recycle ratio with AMP solvent, which could be related to the higher solvent loading with AMP at higher $CO_2$ partial pressure.

Generally, it can be stated that the Hypogen strategy is feasible and the overall cost of these concepts for combining $CO_2$ capture with co-production of hydrogen is comparable to the conventional post-combustion capture process.

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"For an idea that does not at first seem insane, there is no hope"
Albert Einstein

# 6

# TWO-STEP SEPARATION CONCEPT FOR CO2 POST-COMBUSTION CAPTURE

*$CO_2$ post-combustion capture from flue gas typically employs a reactive absorption liquid in a single absorption/desorption process. However, the desorption energy requirement is a significant burden for large-scale applications. To overcome the high-energy demand and to increase the operational flexibility, a new process concept is investigated in this chapter. This process concept is based on dividing the $CO_2$ capture process into a bulk removal step and a deep removal step using two different solvent/systems.*

*This two-step concept is evaluated for two different cases. Both cases are based on the use of the primary amine monoethanolamine (MEA) in the first step. In the second step, either the sterically hindered amine 2-amino-2-methyl-1-propanol (AMP) or coal is used for the removal of the remaining $CO_2$. The results show that the removal of $CO_2$ using coal is not advantageous due to the large quantity of coal needed. Using activated carbon instead of coal can lead to an improved process. Still, with the current $CO_2$ adsorption capacity, even activated carbon is not an attractive option for $CO_2$ removal at low pressure.*

*Employing AMP in the second step, however, can lead to a 15% reduction of the total energy requirement. The overall costs of $CO_2$ mitigation for this two-step concept are comparable to the conventional capture process due to the low energy requirement and the relatively higher capital investment.*

## 6.1 Introduction

The Fourth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) [1] has directed public awareness towards the issues of climate change and rising greenhouse emissions. Several governments adjusted their targets for lowering greenhouse emissions. The European Union is committed to a 20 %-reduction and even considers a 30%-reduction of their $CO_2$ emissions (as compared to the 1990-level) by the year 2020 [2]. Emission control and thus, carbon capture and storage (CCS) within the energy sector is considered a key target for reaching these objectives [3].

To keep up with future energy demands, while avoiding a sharp increase of carbon dioxide emissions, there is a strong need for further developing carbon capture technologies. Accordingly, efforts are taken to increase the efficiency of carbon capture technologies [4,5].

Chemical absorption processes based on aqueous monoethanolamine (MEA) solutions are the state-of-the-art technology for removing carbon dioxide from flue gas streams. A detailed description of the technology and its application can be found elsewhere [6-16]. Rao and Rubin 2002 [9] showed that amine-based $CO_2$ absorption systems are the most suitable systems for combustion-based power plants. The authors argue that these systems are, in particular, suitable for low $CO_2$ concentrations. Furthermore, the technology is commercially available, easy to use and can be retrofitted to existing power plants. At the same time, several disadvantages have to be faced. The energy-intensive desorption step (steam at temperatures up to 140°C is required), as well as solvent losses due to deactivation and evaporation are main obstacles for large-scale implementations [11]. Therefore, research is focussed on increasing the energy efficiency of capturing technology with a low consumption of chemicals. Improvements can be obtained by either changing the solvent itself as well as by adjusting the process conditions [24] or changing the process concept.

It can be shown (see section 2), that the energy required for the absorption-desorption unit (based on the MEA solvent) does not increase linearly with the percentage of $CO_2$ removed from the flue gas. To avoid the increased energy demand for deep $CO_2$ removal, a new two-step absorption concept is presented in this chapter that differentiates between the $CO_2$ bulk removal and the removal of $CO_2$ at low concentrations. For high $CO_2$ concentrations, a conventional chemical solvent is applied. However, as the $CO_2$ concentration within the flue gas stream diminishes, the effort for removal increases and the use of primary amines such as MEA becomes exceedingly energy intensive. Therefore, this work proposes to introduce the flue gas to a second unit for low concentration $CO_2$ removal, which applying a capture system with lower regeneration energy. The aim is to improve the energy efficiency of the $CO_2$ capture process by introducing a second capture step. The feasibility of the concept is evaluated with physical adsorption using coal within the second $CO_2$ removal step and is extended towards the application of a sterically hindered amine as the second $CO_2$ absorption step. The division of the $CO_2$ capture process into two separation steps will increase the process flexibility and allow the use of different regeneration conditions for both absorbents. This might make it possible to use low steam quality or waste heat for the purposes of solvent regeneration at low temperature.

## 6.2 Process description

In continuation of [24], Aspen flow sheeting simulations have been carried out with the flue gas specified in Table 6-1. All parameters (temperatures, pressures, solvent concentration, number of theoretical stages, degree of solvent regeneration, flue gas flow rate, and composition) except the solvent flow rate were kept constant. For the different solvent flow rates, both the amount of $CO_2$ removed and the required energy of solvent regeneration can be quantified. This allows expressing the regeneration energy as a function of carbon dioxide removal. One could expect that the regeneration energy depends linearly on the quantity of $CO_2$ removed from the flue gas. At low $CO_2$ removal, this relation holds. Figure 6-1 shows the linear relation that describes the energy requirements at different $CO_2$ removal percentages. However, as the carbon dioxide removal increases, the simulations indicate an increasing deviation from the linear behaviour, which become clearly pronounced beyond 80% $CO_2$ removal.

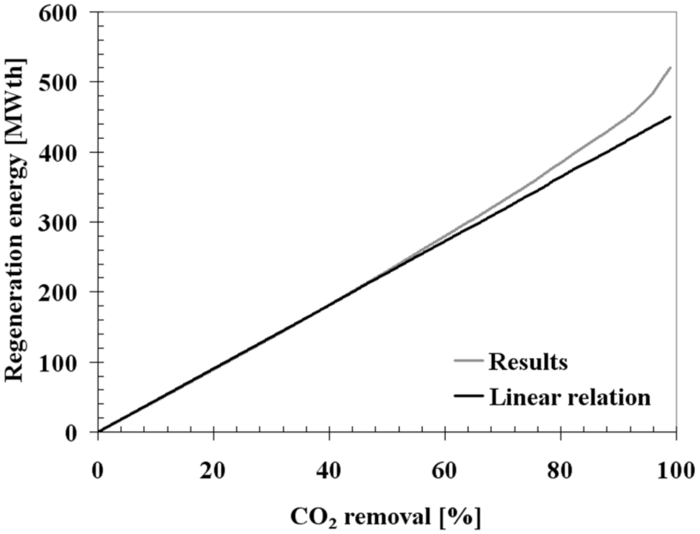

**Figure 6-1: Regeneration energy function of $CO_2$ removal percentage**

The higher energy demand is related to the necessity of regenerating the absorption solvent to a greater extend (higher cyclic capacity). An improved regeneration concept should focus on the reduction of the energetic effort, which is required at higher levels of $CO_2$ removal. Therefore, a process that does not require regeneration or a solvent with low desorption enthalpy can be an interesting choice as the second $CO_2$ removal step.

### 6.2.1 The coal adsorption concept

A significant step towards energy efficient $CO_2$ capture for coal-fired power plants could be achieved by applying a $CO_2$ removal system within the second absorption step, which does not require regeneration. It has been observed that $CO_2$ shows high affinity for coal adsorption. Many research groups are currently investigating the possibility of storing $CO_2$ in deep unmineable coal layers [17-23]. The maximum amount of adsorbed $CO_2$ depends on the water content as well as on the composition and the size of the coal lumps. Clarkson and Bustin [20] showed that, depending on the water content, up to 32 cc $CO_2$ per gram coal (0.063g/g) could be adsorbed at 40 bar. Sun et al. [23] performed adsorption experiments with $CO_2$ on activated carbon. Wet activated carbon adsorbs up to 1.5 g $CO_2$ per gram coal, which is considered as the maximum adsorption capacity. Moreover, in mixtures with nitrogen or methane, carbon dioxide is selectively adsorbed [20-22].

Hence, coal or activated carbon can be applied to selectively remove carbon dioxide from flue gas. The clear advantage of this concept is that coal does not need to be regenerated, but can be used as a feed stream to the combustion chamber in a coal fired power plant (see Figure 6-2). In principle, only the bulk (higher concentrated) $CO_2$ has to be removed using the conventional capture process. In addition, the remaining $CO_2$ is recycled and is introduced back to the system. In this concept, the flue gas is first introduced to a MEA based absorption unit. Then, the treated flue gas is fed into the second treatment step, which uses coal as a physical adsorbent.

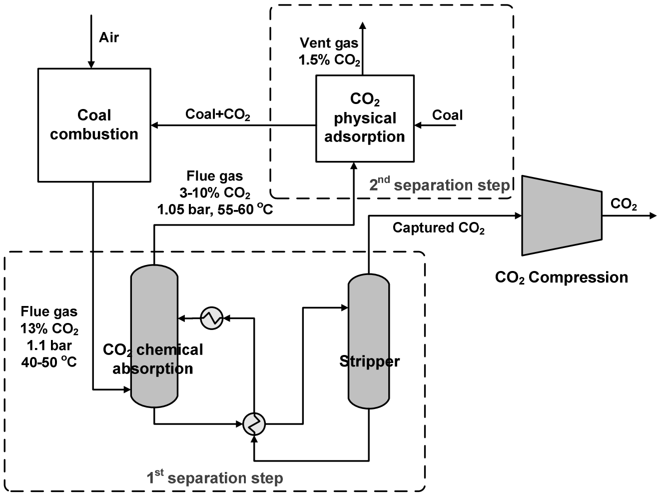

**Figure 6-2: $CO_2$ capture process flow sheet for the combined chemical absorption and physical adsorption concept**

### 6.2.2 The two step chemical absorption concept

The simplified process flow sheet in Figure 6-3 shows two complete post-combustion cycles. As can be observed, the solvents are regenerated in separate columns. Therefore, both regeneration steps can be kept at different process conditions leading to an increase in operational flexibility. These different conditions could result from the development of the solvent absorption systems. An example is that different regeneration temperatures can be used to further optimise cost versus $CO_2$ removal. In addition, more flexibility is gained with the use of two different solvent classes (e.g. aqueous and/or organic solutions). These different solvents might require completely different operating conditions in the process. Moreover, dividing the $CO_2$ capture plant into two sections will help in the operation elasticity, especially if the plant needs to be run on partial loads rather than full loads.

The potential of the two-step process has been evaluated using process as described below. Flue gas with 13.3 wt-percent $CO_2$ is treated in the first absorption column using the conventional MEA chemical solvent. The $CO_2$ loaded solvent leaves at the bottom of the absorber and is pumped via the lean/rich heat exchanger to the top of the regeneration column. In the regeneration column, the carbon dioxide is released from the solvent by steam heating up to 120 °C. The energy requirement for the $CO_2$ desorption sums up to ~ 4.0 GJ/tonne $CO_2$ [6-11,14]. The lean solvent from the bottom of the stripper is cooled to the absorber conditions (40-50 °C) by using a series of heat exchangers and is re-fed into the absorber.

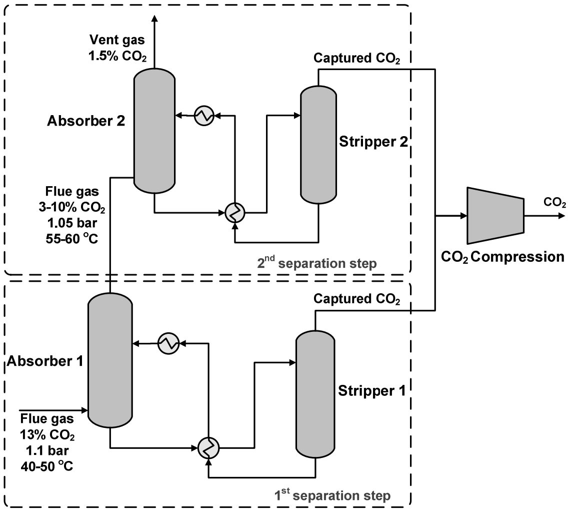

**Figure 6-3: $CO_2$ capture process flow sheet for the two-step chemical absorption concept**

The flue gas (minus the bulk quantity of $CO_2$) leaves the top of the first absorber column and, subsequently, enters the second absorber to remove the remaining $CO_2$. Within this second unit the sterically hindered amine solvent 2-amino-2-methyl-1-propanol (AMP), which has a lower reaction enthalpy comparing to MEA, is used as an absorption solvent to reach a total $CO_2$ removal of 90 %. Different removal ratios can be realized based on the amount of $CO_2$ removed in each step.

AMP has been investigated earlier as an alternative to the primary amines for the $CO_2$ capture process [28-33]. The advantage of applying AMP compared to MEA is the lower reaction enthalpy [28]. Furthermore, AMP exhibits a higher solvent capacity, which is not limited to 0.5 mol $CO_2$/mol amine as in the MEA case, but could reach up to 1 mol $CO_2$/mol amine [30,33]. The disadvantage of ternary amines is the slower reaction kinetics compared to primary amines (e.g. MEA).

In short, this process concept consists of two separated conventional post-combustion capture cycles. The difficult and energy demanding task of removing carbon dioxide at low concentrations is, thus, performed with a solvent exhibiting a higher $CO_2$ capacity and a lower heat of reaction than conventional chemical solvents.

## 6.3 Simulation and analysis methods

The conventional $CO_2$ post-combustion capture process based on monoethanolamine (MEA) has been analyzed in previous works [11-13,24]. Flue gas from a conventional pulverized coal power plant after the sulphur removal and cooling steps, as specified in Table 6-1, is used for the current evaluation.

**Table 6-1: Flue gas specifications**

| | |
|---|---|
| Mass Flow (kg/s) | 616.0 |
| Pressure (kPa) | 101.6 |
| Temperature (°C) | 48 |
| Composition | Volume % wet gas |
| $N_2$+Ar | 71.62 |
| $CO_2$ | 13.30 |
| $H_2O$ | 11.25 |
| $O_2$ | 3.81 |
| $SO_2$ | 0.005 |
| $NO_x$ | 0.0097 |

### 6.3.1 The coal physical adsorption concept

The coal concept is based on the use of coal in the second removal step for the deep carbon removal. The coal that is loaded with $CO_2$ is burned in the combustion chamber to produce electricity and steam. Therefore, the regeneration energy required for the second $CO_2$ capture step can be saved.

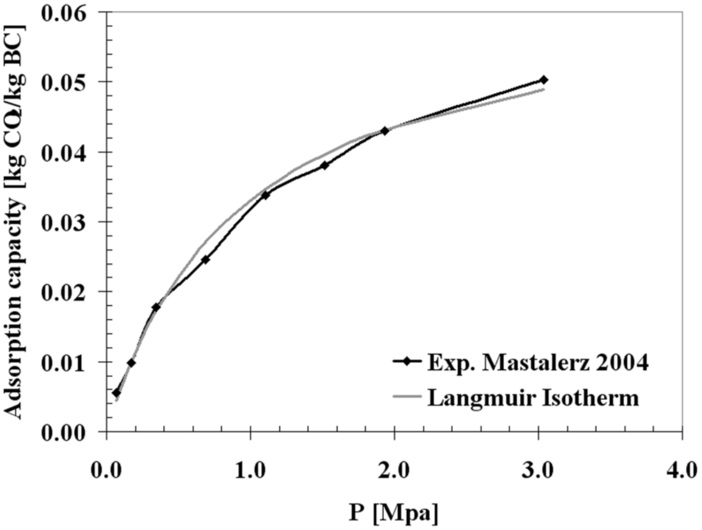

**Figure 6-4: Bituminous adsorption capacity of $CO_2$ as a function of $CO_2$ pressure [22]**

Mastalerz et al. [22] have investigated the bituminous coal adsorption capacity of $CO_2$. These adsorption isotherms have been analysed, fitted to a Langmuir model and, subsequently, been used in this work as an estimate for the amount of coal required to achieve a certain $CO_2$

removal capacity. Figure 6-4 shows the experimental results of the adsorption capacity of $CO_2$ on bituminous coal with the Langmuir isotherm fitting given as:

$$q = \frac{0.068 * p}{1 + 1.067 * p} \tag{6-1}$$

Where p is the adsorption pressure [MPa], and q is the adsorption capacity [kg $CO_2$/kg coal].

The adsorption capacity has been evaluated at a pressure level close to the $CO_2$ pressure at the exit of the first absorption unit (0.03-0.1 bar/0.003-0.01 MPa). Depending on the bituminous coal adsorption capacity of $CO_2$ at this pressure, the required coal quantity to reach a certain $CO_2$ removal within the second unit is calculated.

As a best-case example, the use of activated carbon for $CO_2$ adsorption is investigated. Sun et al. [23] performed adsorption isotherm measurements for activated carbon. The adsorption capacity data has been used to fit the Langmuir isotherm (see Figure 6-5).

$$q = \frac{1.74 * p}{1 + 1.86 * p} \tag{6-2}$$

Where p is the adsorption pressure [MPa], and q is the adsorption capacity [kg $CO_2$/kg coal].

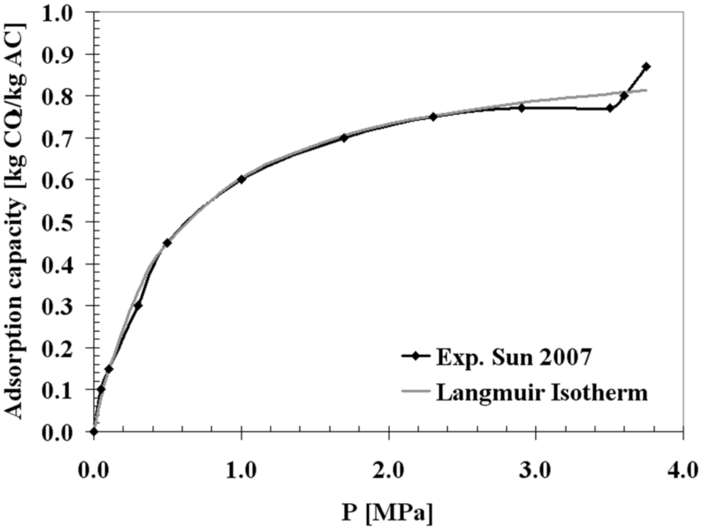

**Figure 6-5: Dry activated carbon adsorption capacity of $CO_2$ as a function of $CO_2$ pressure [23]**

The coal concept is evaluated by fixing the overall $CO_2$ removal to 90%. The total required coal quantity for the deep carbon dioxide removal in the second step is calculated. For this purpose, equilibrium conditions were assumed for the $CO_2$ adsorption on coal and activated carbon. In addition, maximum coal and activated carbon loading are assumed and adsorption kinetics is neglected.

### 6.3.2 Two-step chemical concept

The two-step chemical concept is simulated and analyzed using the ASPEN Plus flow-sheeting simulation tools [25]. Within the simulation, the overall flow sheet has been divided into three main sections: the $CO_2$ removal step using MEA solvent, the $CO_2$ removal step using AMP solvent and the $CO_2$ compression system. The flow sheet is designed according to the process description in the previous section. Moreover, the process flow sheet is simulated and designed assuming the conventional $CO_2$ capture process with no extra process improvements or modifications (e.g. split flow, absorber inter-cooling) [6,24]. The solvent flow rates and the solvent degree of regeneration are modified and controlled to remove 90 wt-% of the $CO_2$ in the flue gas. The $CO_2$ removal has been divided between the two absorption units. The ratio of $CO_2$ absorption between the different absorption units can, thus, be varied to optimize the process performance.

Different thermodynamic models are used in the flow sheet sections. The gas phase is described by the Soave-Redlish-Kwong equation of state. For the liquid phase, the electrolyte-NRTL model has been applied as a representation of the system. All required data and parameters have been developed and presented by Austgen et al. [26]. In addition, the properties sets for both systems, $CO_2$-$H_2O$-MEA and $CO_2$-$H_2O$-AMP, are built in the ASPEN Plus simulation database [25].

Based on the process description, the flow sheet simulation is used to solve the energy and mass balances. These results are the input for the process equipment design and sizing. The absorber and stripper columns in the two different steps have been designed in detail using stage-by-stage calculation method. The effect of the reaction kinetics for both solvents (MEA and AMP) and the mass transfer resistances have been incorporated into the equilibrium stage results from ASPEN Plus simulations. This implementation of the kinetics and the mass transfer coefficients is essential for the estimation of the columns height. In addition, for the remaining process equipment the main dimensions are determined. The equipment design and sizing are used in the economic evaluation model to estimate the capital investment, operating costs and the overall $CO_2$ mitigation costs [27].

## 6.4 Results and discussion

### 6.4.1 The coal concept

The two-step concept has been evaluated for the use of a physical adsorption as the second step in the $CO_2$ post-combustion capture process. A reduction of the capital cost is foreseen by integrating the adsorption step into the currently available power plant components. This concept is expected to reduce the operational cost by preventing the use of the energy intensive regeneration within the adsorption step.

The quantity of coal required in the adsorption step to recover carbon dioxide is calculated from the adsorption isotherms of bituminous coal (Figure 6-4). The quantity of coal required for the removal of 10 % of the $CO_2$ (i.e. 13 kg $CO_2$/s) in the second step is orders of magnitude higher than the coal required for a conventional 600 MWe power plant. Thus, capturing $CO_2$ with conventional bituminous coal cannot be realized at post-combustion low-pressure conditions.

It is well known that the $CO_2$ capacity of coal can be increased by means of activation. To set a theoretical best-case boundary for the coal adsorption concept, the use of activated carbon is examined. The activated carbon is, thus, considered as a feed for the coal combustion that can be obtained at the expenses of common bituminous coal. The adsorption capacity of activated carbon for $CO_2$ at low adsorption pressures is almost 100 times higher than the capacity of bituminous coal. The activated carbon requirement for a 10 % $CO_2$ removal in the second capture step (physical adsorption) at 0.003 MPa is found to be 2500 kg/s, which is also much higher than the coal requirement for a standard 600 MWe power plant.

Due to the limited coal and activated carbon adsorption capacities, the amount of coal required for the second step capture exceeds the coal requirements of the power plant significantly. Therefore, the process concept using coal/activated carbon will not be economically evaluated.

### 6.4.2 The two step chemical concept

**Table 6-2: Two steps concept-overall technical results**

| **Parameters** | **Unit** | **MEA case** | **$CO_2$ removal ratio 70:20** | | |
|---|---|---|---|---|---|
| | | | **1st step** | **2nd step** | **Overall** |
| $CO_2$ removal % | % | 90 | 70 | 20 | 90 |
| Flue gas flow rate | kg/s | 616 | 616 | 536 | 616 |
| $CO_2$ feed content | mol fraction | 0.13 | 0.13 | 0.04 | 0.13 |
| $CO_2$ captured | kg/s | 114 | 88 | 28 | 115 |
| Solvent used | - | MEA | MEA | AMP | MEA/AMP |
| Solvent concentration | wt. % | 0.30 | 0.30 | 0.27 | 0.30/0.27 |
| Solvent demand | $m^3$/tonne $CO_2$ | 20 | 19 | 35 | 23 |
| Energy requirement | GJ/tonne $CO_2$ | 4.05 | 3.75 | 3.35 | 3.65 |
| Cooling water Required | $m^3$/tonne $CO_2$ | 69 | 58 | 105 | 69 |

| **Parameters** | **Unit** | **$CO_2$ removal ratio 50:40** | | | **$CO_2$ removal ratio 25:65** | | |
|---|---|---|---|---|---|---|---|
| | | **1st step** | **2nd step** | **Overall** | **1st step** | **2nd step** | **Overall** |
| $CO_2$ removal % | % | 50 | 40 | 90 | 25 | 65 | 90 |
| Flue gas flow rate | kg/s | 616 | 559 | 616 | 616 | 583 | 616 |
| $CO_2$ feed content | mol fraction | 0.13 | 0.07 | 0.13 | 0.13 | 0.10 | 0.13 |
| $CO_2$ captured | kg/s | 63 | 49 | 112 | 32 | 79 | 111 |
| Solvent used | - | MEA | AMP | MEA/AMP | MEA | AMP | MEA/AMP |
| Solvent concentration | wt. % | 0.30 | 0.27 | 0.30/0.27 | 0.30 | 0.27 | 0.30/0.27 |
| Solvent demand | $m^3$/tonne $CO_2$ | 19 | 31 | 24 | 19 | 27 | 25 |
| Energy requirement | GJ/tonne $CO_2$ | 3.64 | 3.05 | 3.40 | 3.55 | 2.83 | 3.05 |
| Cooling water Required | $m^3$/tonne $CO_2$ | 56 | 81 | 67 | 63 | 65 | 64 |

A MEA solvent reference case with 90 % $CO_2$ removal is defined as a benchmark. The overall process requirements are evaluated for the reference case and three other options with varying $CO_2$ removal ratios in the two steps. The main process input and results for each step and the overall capture process can be found in Table 6-2.

It can be observed from Figure 6-6 that an increased removal split within the second step (using AMP as a solvent) leads to lower specific energy requirements. The regeneration energy requirements for the MEA reference case sum up to 4.05 GJ/tonne $CO_2$. The application of the two-step concept leads to a reduction of the overall regeneration energy demand to 3.03 GJ/tonne $CO_2$ with a first step $CO_2$ removal of 25 %. At the same time, the solvent demands will increase (see Figure 6-6).

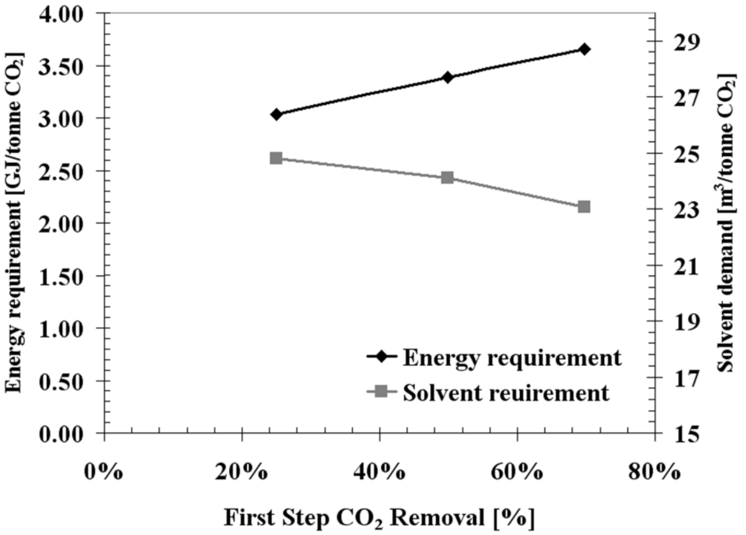

**Figure 6-6: Energy and solvent requirement at different first step removal percentage**

The trade-off between the overall energy requirements and the remaining process operational requirements can be visualized by the process economic evaluation. A detailed description of the process economic evaluation can be found elsewhere [27]. The overall process capital and operating investment are estimated and are used to calculate the $CO_2$ avoided costs as well as the price per MWh of delivered electrical energy.

The process overall economic results are shown in Table 6-3. As expected, applying the capture process will reduce the overall power plant net efficiency. Using MEA solvent reduces the overall plant efficiency by 12 percentage points. Applying the two-step concept saves up to 16 % of the overall regeneration energy requirement However, using a tertiary-amine-based solvent in the second step also causes the overall solvent demand to increase. This leads to higher solvent pumping power demands for the capture process. Combining these two trends results in a net power plant efficiency improvement of one percentage point compared to the MEA reference case.

The economic results of the two-step concept show that the optimum-splitting ratio between the first and the second capture step is approximately 50:40. At this ratio, the reduction in the operational costs due to the lower energy requirement has exceeded the cost increase from the higher solvent requirement and the pumping energy. As a result, an optimum splitting ratio has been found with the lowest capture operating costs comparing to the other splitting ratios. For this optimum case, a 38 %-increase of the capture capital investments comparing to the MEA reference case, which is mainly related to the large absorber column required for the second step. As a result, the cost of $CO_2$ avoided in the two-step concept is estimated to be 13 % higher than in the MEA reference case, as can be shown in Figure 6-7.

**Table 6-3: Overall economic results: two-step concept compared to MEA base case**

| **Parameters** | **Units** | **Power plant no capture** | **Power plant with capture** | | | |
|---|---|---|---|---|---|---|
| | | | **MEA case** | **Two-step concept (MEA/AMP)** | | |
| | | | | **70:20** | **50:40** | **25:65** |
| Net Electricity output | MWe | 575 | 422 | 413 | 435 | 437 |
| Efficiency | % | 45 | 33 | 32 | 34 | 34 |
| $CO_2$ emitted | kg/MWh | 772 | 105 | 118 | 108 | 93 |
| $CO_2$ captured | tonne/yr | - | 3.1E+06 | 3.1E+06 | 3.0E+06 | 3.0E+06 |
| Total capital investment | €/kW | 980 | 1819 | 2080 | 2023 | 2078 |
| Capture investment | mln€ | - | 180 | 270 | 292 | 321 |
| Operating costs | mln€/yr | 119 | 145 | 152 | 153 | 155 |
| Capture operating costs | mln€/yr | - | 64 | 74 | 69 | 71 |
| Fuel price | €/GJ | 2.9 | 2.9 | 2.9 | 2.9 | 2.9 |
| Cost of electricity | €/MWh | 42 | 71 | 78 | 74 | 76 |
| Cost of $CO_2$ avoided | €/tonne $CO_2$ | - | 44 | 55 | 49 | 50 |

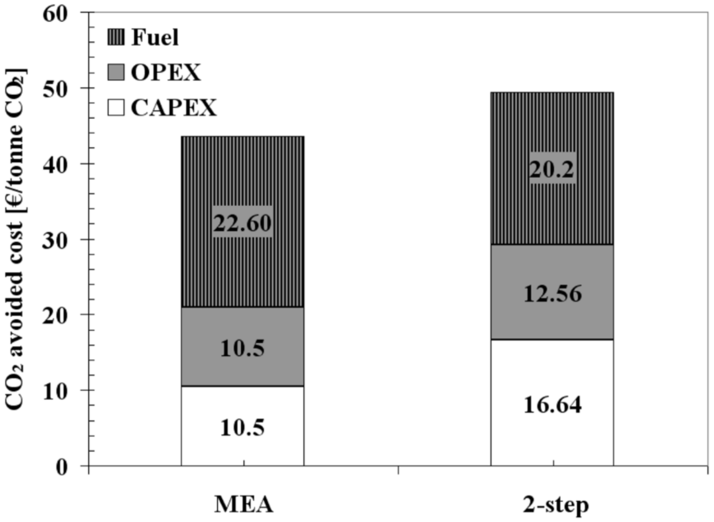

**Figure 6-7: Cost of $CO_2$ avoided for the two-step concept (50:40 splitting case) and MEA base case. The contributions are Fuel, operational cost (OPEX) and capital costs (CAPEX).**

On the other hand, the fuel contribution in the overall avoided cost is reduced by 11% when applying the two-step treatment, which is connected to the lower regeneration energy demand in the second absorption unit. Moreover, the operational cost and the capital cost per tonne $CO_2$ avoided for the two-step concept are considerably higher than the costs for the MEA reference case.

The two-step concept could be further enhanced by introducing an activator to the second absorption step to improve the solvent system. This will lead to a reduction of the size of the absorber column and the solvent requirement. Consequently, the economic competitiveness of the two-step concept might be significantly increased.

## 6.5 Conclusions

A two-step $CO_2$ post-combustion capture concept has been introduced, analysed and evaluated. Two flow sheet configurations are presented. In the first one, the flow sheet is based on a combination of the conventional chemical absorption (with MEA) and physical adsorption on coal is evaluated.

To reach a target of 10 % $CO_2$ removal within the coal adsorption unit, a huge quantity of coal is required, that exceeds the coal stream to the combustion chamber. The results indicate that the application of bituminous coal for $CO_2$ adsorption at the given process conditions is not feasible. Even though the use of the activated carbon results in a decrease of the overall coal requirement, the amount of activated carbon required for $CO_2$ capture still exceeds the coal that is fed to the power plan, significantly.

In the second concept, two chemical absorption cycles are applied. The conventional MEA solvent has been used for the bulk $CO_2$ removal in the first step. In addition, AMP has been applied for the second chemical absorption step. The operating costs of the process are dominated by the solvent and energy requirements. A minimum for the operational costs can be found by applying 50 % carbon dioxide removal in the MEA unit and a 40 % removal in the AMP unit. With this division, the overall energy requirements can be reduced by 16 % as compared to the MEA reference case (~ 4 GJ/tonne $CO_2$).

Due to the higher capital costs as well as the increased solvent requirement, the overall cost of carbon dioxide avoided in the 2-step concept increases by 13 %. Still, increasing the capture process flexibility is a clear advantage of the 2-step concept. This flexibility allows the application of different operating conditions and/or process systems in the different absorption-desorption units. This benefit could be seen by operating each regeneration step on different temperature. The different temperature might make it possible to operate one of the columns on low temperature, which will allow the use of waste heat streams for the purposes of $CO_2$ regeneration. Further improvement of this concept is expected by the addition of an activator to the AMP solvent, which could reduce the capital investment.

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"If there must be trouble let it be in my day, that my child may
have peace" Thomas Paine

# 7

# FUTURE OUTLOOK

*One of the main global challenges in the years to come is to reduce the $CO_2$ emissions, which is considered as one of the main reasons for global warming. An intermediate solution towards sustainable energy systems in the long term is carbon dioxide capture, transport and storage (CCS). However, CCS is still facing some challenges, such as large scale implementation leads to high cost. This leads to extra pressure on the technology providers and developers to come with breakthrough technologies in the coming years.*

*In this chapter, a perspective is given on the development lines for the $CO_2$ post-combustion capture technology. In this future outlook, guidelines for cost reductions and suggestions for future research on solvent and process development can be found.*

## 7.1 General introduction

The research activities presented in this thesis have been focused on the process improvement on the $CO_2$ post-combustion capture. These improvements have been evaluated in two major parts: the first one by investigating possible process optimization and techno-economic improvement on the conventional capture process (30 wt-% MEA), which have been done in chapter two and three in this thesis [1,2]. For the second part, new process concepts were investigated as alternatives or improvements for the conventional process flow sheet, as presented in chapter five and six [3,4].

From the analysis of the post-combustion capture process, it has came apparent that to achieve significant reduction of the capture process cost, multiple process parameters need to be improved. In this chapter, a future outlook on the development directions of the capture process will be presented. Based on this outlook, general guidelines and recommendations for improving the absorption solvent and process conditions are discussed.

### 7.1.1 $CO_2$ capture systems current developments

The process for $CO_2$ post-combustion capture using an aqueous solution of 30 wt-% Monoethanolamine (MEA) as the active ingredient is considered as the state-of-art capture technology [1,5], which has been described in chapter one and two in this thesis. In addition, it is acknowledged that the developments in solvents for $CO_2$ post-combustion capture are accelerating with the expectation of future $CO_2$ emissions constraints. Fluor Daniel has claimed the following improvement on the conventional MEA process by various means, including modifications of the capture solvent and process [11]:

- Enhanced solvent formulation (faster reaction kinetics and higher solvent capacity)
- Flue gas pre-treatment (integrated with the flue gas direct contact cooler)
- Absorber inter-cooling
- Lean vapour compression and split flow configuration
- Advanced reclaiming technologies
- Heat integration with the power plant
- Low regeneration energy consumption (1270 Btu/lb $CO_2$ = 2.95 GJ/tonne $CO_2$)

Mitsubishi Heavy Industries is marketing their KS-(1, 2, and 3) solvents group [6-8,12]. The following improvements for the KS-2 solvent, which have been defined as factors comparing to the MEA conventional capture process, are claimed by MHI:

| | |
|---|---|
| Solvent circulation rate | 0.6 |
| Regeneration energy | 0.8 |
| Solvent losses | 0.1 |
| Corrosion inhibitor | No |

These improvements are expected to influence the overall capital and operating costs of the $CO_2$ capture process. However, the higher price of the KS-2 solvent (3.6 times the cost for MEA) will limit the reduction of the overall operating costs.

The above mentioned systems are considered to be proven systems for smaller scale $CO_2$ post-combustion removal. However, there are several other systems under development. For instance, TNO has developed a new class of solvents (CORAL), which is currently tested on a pilot scale [9]. This class of solvents is based on the use of aqueous solution of amino acid salts as absorption liquid. Another interesting system is the so called Chilled Ammonia process, currently developed by the Alstom [10]. However, analysing these newly developed systems will be limited to the data published by the vendors.

## 7.2 Guidelines for capture cost reduction

In this section, guidelines for further development are given with the conventional MEA system as reference capture process. The economics for this reference process have been analysed in great detail in chapter two, three and six of this thesis [1,2,4]. Based on this analysis, the major contributors of the overall capture cost are identified.

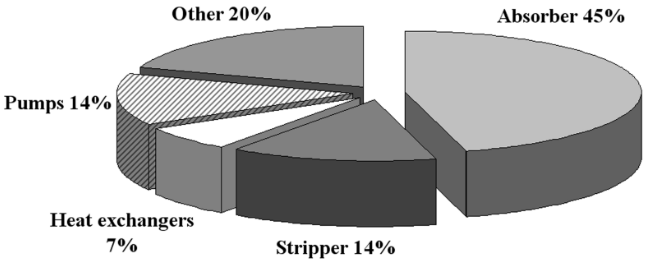

**Figure 7-1: The contribution of the different equipments on the overall conventional capture process equipments costs**

Based on the capital expenditure, the absorption column is the principal component. The cost for this component is around 50% of the total equipment costs for the coal power plant case (see Figure 7-1). This can exceed 60% for the natural gas power plant case [2]. In addition, the analysis of the overall capital investment of the capture process including the $CO_2$ compression system has shown that the $CO_2$ compression is responsible for around 30% of the total investment cost. This makes the compression system one of the major cost contributors in the capture process. However, most of the research activities focus on the capture process without giving the required attention to the $CO_2$ compression section. The capital and operational cost of the $CO_2$ compression can be improved by increasing the stripper operating pressure.

Looking for the operational expenditure, the analysis based on the overall $CO_2$ avoided cost shows that the fuel requirement for regeneration energy and electricity is responsible for more than 50% of the overall cost (see Figure 7-2). Within the fuel requirement, 55 to 70% is needed for the solvent regeneration heat. The rest of the fuel consumption is divided between the $CO_2$ compression and solvent pumping power. It is important to note that the contribution in the overall cost for each component will vary depending on flue gas specifications and the economic values.

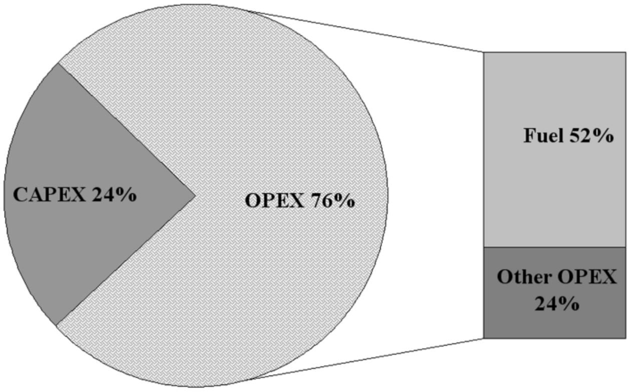

**Figure 7-2: Major contributions of the cost of $CO_2$ avoided for the conventional capture process**

Based on the capture process cost analysis, the future solvent research and development activities should be focussed on the following parameters in order to reduce the overall capture costs:

- Regeneration energy requirement: a reduction in the regeneration energy requirement will decrease the cost of $CO_2$ avoided, the cost of electricity and the power plant efficiency penalty. The regeneration energy requirement is connected to the solvent properties (e.g. reaction enthalpy and solvent capacity) and to the capture process operating conditions (e.g. regeneration conditions and heat exchangers efficiencies). The total regeneration energy is divided into three parts: the reaction enthalpy, the sensible heat and the heat of steam evaporation. In this guideline investigation, the reduction on energy requirement will be investigated by considering two parts: the reaction enthalpy, which will be investigated as a separate process parameter. The sensible heat (heat required to increase the solvent temperature), which will be included in the solvent capacity because it is connected to the amount of solvent needed in the process.
- The solvent capacity: increasing the solvent capacity will reduce the overall solvent circulation and improve the absorption process. This increase in the solvent capacity is expected to reduce the overall capital cost and to improve the cost of $CO_2$ avoided.
- The reaction kinetics: the reaction kinetics is an important parameter in designing the absorber and stripper columns. Accelerating the reaction kinetics will reduce the size (height) of the columns. As a result, the overall capital investment and cost of $CO_2$ avoided will be reduced. In this work, the impact of improving the reaction kinetics for the absorption step is investigated.
- The solvent stability: this is related to the solvent losses and degradation. Improving the solvent stability has a major influence on the environmental effect of the capture process. In addition, reducing the solvent losses will have some influence on the overall cost of $CO_2$ avoided.
- The stripper pressure: increasing the stripper pressure is expected to reduce the $CO_2$ compression cost and requirement due to the higher starting pressure.

The guidelines for the capture process improvement are divided into two parts. The first part is related to the solvent development by investigating the effect of the above mentioned solvent parameters. The second part is related to the capture process improvement by changing the stripper operating pressure. Finally, the overall cost reduction target for a generally designed solvent will be evaluated and compared with different vendors improved capture processes.

### 7.2.1 Solvent related development

In this section, scenarios for solvent improvement are investigated from a process economic perspective. The calculations are based on the MEA base case techno-economic evaluation that has been discussed in this thesis [1,2]. The results of the different investigated improvements are presented as relative values to the MEA process (MEA is used as a benchmark). The evaluation of the impact of different solvent properties and process parameters has been done by changing one parameter at the time.

#### *7.2.1.1 Reaction enthalpy*

In general, the reaction enthalpy is considered responsible of around 30% of the total regeneration energy requirement. Reducing the reaction enthalpy is expected to reduce the overall regeneration energy requirement and the capture process costs. In Figure 7-3, the impacts of improving the reaction enthalpy on the overall costs and efficiency penalty are presented.

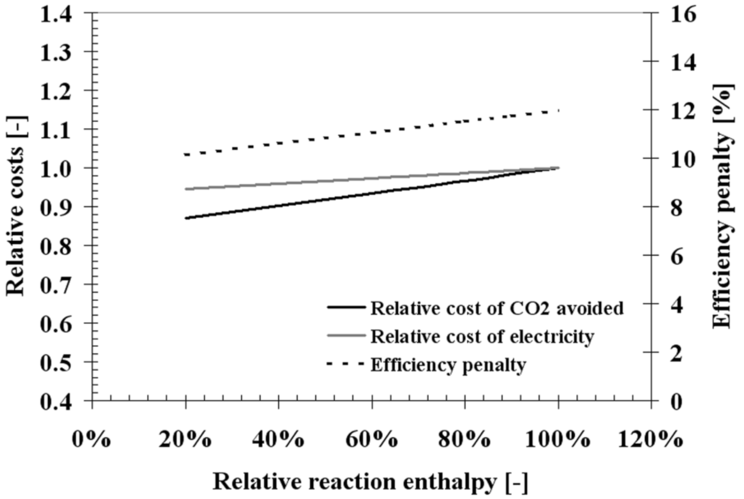

**Figure 7-3: Influence of the reaction enthalpy improvement on the cost of $CO_2$ avoided, cost of electricity and efficiency penalty relative to MEA benchmarking process (benchmark MEA= 100%)**

As expected, it can be seen that improvements related to the reaction enthalpy have major influences on the cost of $CO_2$ avoided and the overall cost of electricity. A decrease of the reaction enthalpy by 50% leads to a 10% and 5% reduction on the cost of $CO_2$ avoided and cost of electricity, respectively. The reaction enthalpy has a clear influence on the overall net power plant efficiency. Improving the regeneration energy by 50% will reduce the efficiency penalty by 1.5 percentage points (12% of the overall energy penalty for the conventional benchmarking process). Most of the solvent development activities are aiming to reduce the overall regeneration energy requirement to values lower than 2.5 GJ/tonne $CO_2$, which is almost 60% of the energy requirement for the conventional MEA process. Out of the presented results, it can be seen that such a development step cannot be achieved by improving only the reaction enthalpy.

### *7.2.1.2 Capacity*

The solvent circulation, which is connected to solvent capacity (increasing the solvent capacity reduces the solvent circulation rate), has a major influence on the overall cost of $CO_2$ avoided, cost of electricity and efficiency penalty (see Figure 7-4). Reducing the solvent circulation by 50% (meaning doubling the solvent capacity) will decrease the overall avoided cost by around 15%. This reduction in the overall cost results mainly from the reduction in the solvent cost, electricity required for solvent pumping and the reduction in the sensible heat required in the regeneration step to heat up the solvent to the stripper temperature.

The solvent circulation has a large influence on the power plant efficiency penalty. Reducing the solvent circulation by 50%, results in a reduction in the efficiency penalty of 2 percentage points. This makes the overall influence of solvent capacity equivalent or even larger than the effect of the reaction enthalpy. This is because the combined effect of the pumping power and sensible heat. In this study, the effect of the solvent capacity (circulation rate) on the size of the absorber has been excluded. Reducing the solvent circulation rate is expected to reduce the volume of packing required, which will result in a reduction in the overall capital investment. Therefore, the effect of higher solvent capacity is expected to be more beneficial.

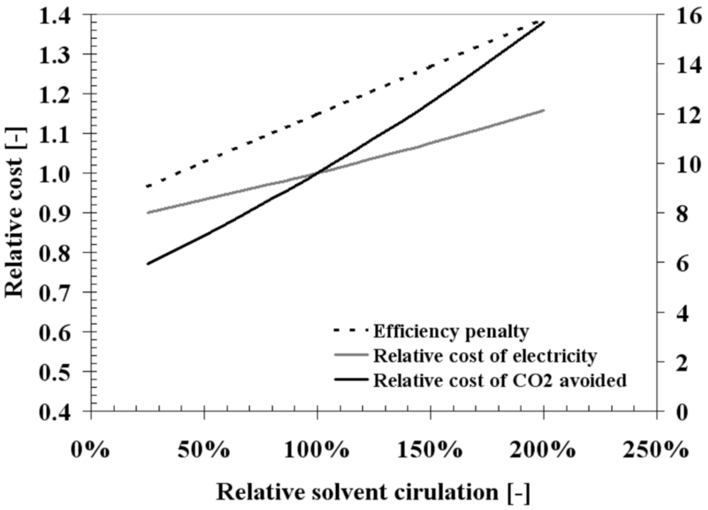

**Figure 7-4: Influence of the solvent circulation improvement on the overall capital investment and the cost of $CO_2$ avoided relative to MEA benchmarking process**

### *7.2.1.3 Kinetics*

The absorption reaction kinetics has an influence on the capital expenditure. Faster solvent kinetics leads to a smaller (shorter) and, therefore, cheaper absorption column. In Figure 7-5, it can be observed that going to a faster solvent kinetics compared to MEA leads to strong reduction on the overall capital investment. However, this reduction is limited by 10% on the overall cost of $CO_2$ avoided. Solvents faster than three times MEA has a lower influence on the overall cost. In reality solvents with a fast kinetics are expected to have higher regeneration energy requirement.

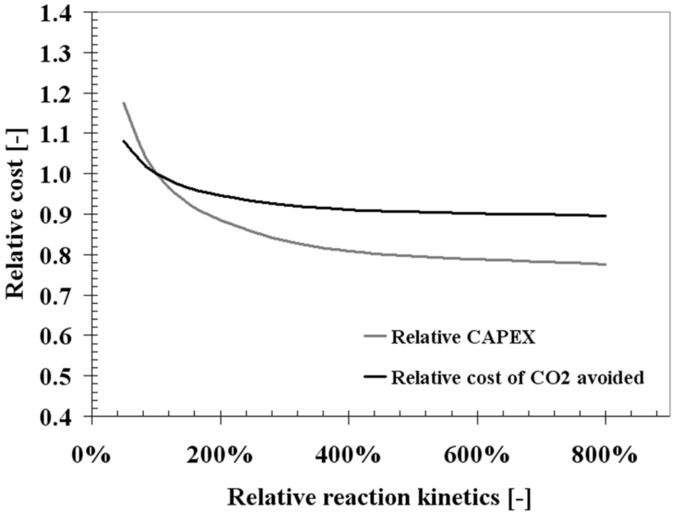

**Figure 7-5: Influence of the solvent reaction kinetics improvement on the overall capital investment and the cost of $CO_2$ avoided relative to MEA benchmarking process**

### *7.2.1.4 Stability*

The solvent losses have been investigated in the overall economic evaluation as the cost of the makeup solvent that needs to be added to the capture process. As can be seen in Figure 7-6, the influence of the solvent losses on the reduction of the overall avoided cost is very limited to values less than 5%.

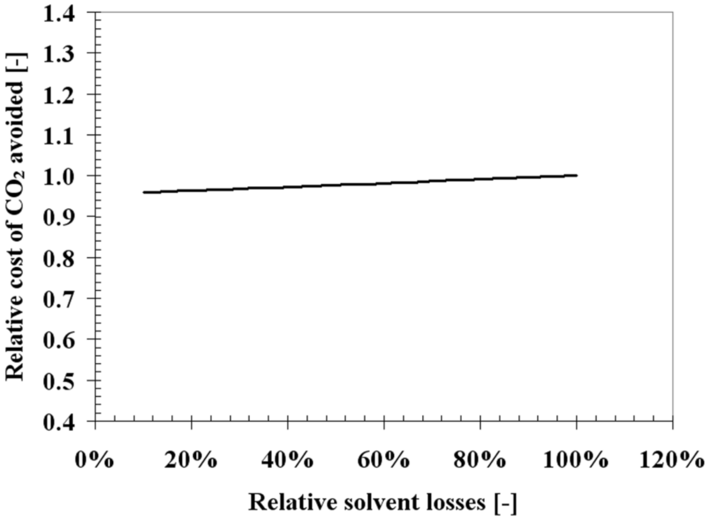

**Figure 7-6: Influence of the solvent losses improvement on the cost of $CO_2$ avoided relative to MEA benchmarking process**

However, this does not mean that this is not an important topic for the capture process development. In light of the expected demands on the environmental impact, it will be a crucial item.

It can be expected that the direction for improved solvents is focussed on low environment impact solvents and enhanced solvent behaviour (i.e. higher capacity and lower regeneration energy). However, this development might lead to more expensive solvents compared to the current MEA solvent. From Figure 7-7, it can be seen that the solvent price has a large influence on the overall cost of $CO_2$ avoided. A four times more expensive solvent will lead to an increase of the avoided cost by 15%. However, it is important to note that a more expensive solvent can have advantages (e.g. higher capacity, lower losses, faster kinetics), which will limit the overall influence of the higher solvent price.

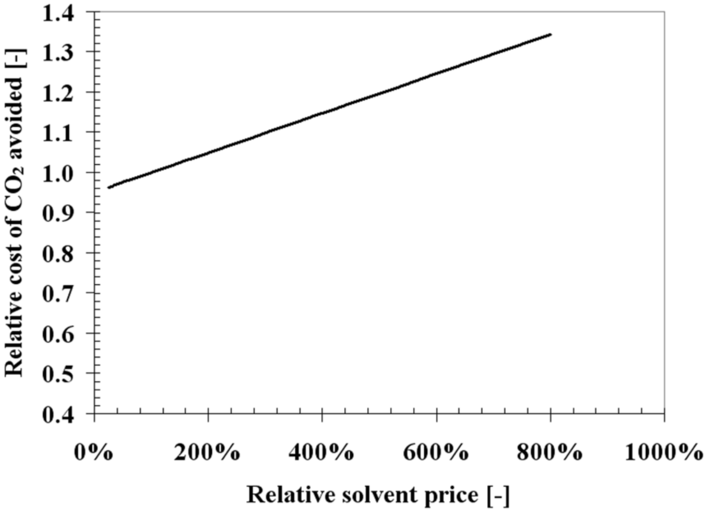

**Figure 7-7: Influence of the solvent price on the cost of $CO_2$ avoided relative to MEA benchmarking process**

### 7.2.2 Process related development: increasing stripper pressure

In this section, a scenario for process improvement by increasing the stripper pressure is presented from the economic prospective. The influence of the stripper pressure on the power plant net efficiency and the overall capture economics is investigated (see Figure 7-8). The stripper pressure has a clear direct influence on the net power plant efficiency. By increasing the stripper pressure less electrical power is required for the $CO_2$ compression, which will result in lower efficiency penalty. In general, 3-4 penalty points are the contribution of the $CO_2$ compression above 100 bar (10 MPa) to the overall efficiency penalty. Increasing the stripper pressure from the conventional process (1.5 bar/150 kPa) to 20 bar (2 MPa) will save two penalty points (50% of the total compression energy penalty).

In addition, increasing the stripper pressure reduces the overall cost of $CO_2$ avoided and cost of electricity. For a stripper pressure of 20 bar (2 MPa), the overall cost of $CO_2$ avoided is reduced by 14% comparing to the conventional process, which is mainly related to the reduction in energy requirement. After this pressure, these costs became constant. In addition, increasing the stripper pressure above 20 bar (2 MPa) results in a higher overall capital investment. This can be explained by the fact that at higher stripper pressure, a thicker columns' wall is needed, which will result in higher capital cost of the stripper column. The conclusion can be that a future development on the capture process should not exceed 20 bar (2 MPa) as stripper pressure to keep the economic benefit of the lower energy requirement and to avoid the disadvantage of the more expensive stripper column.

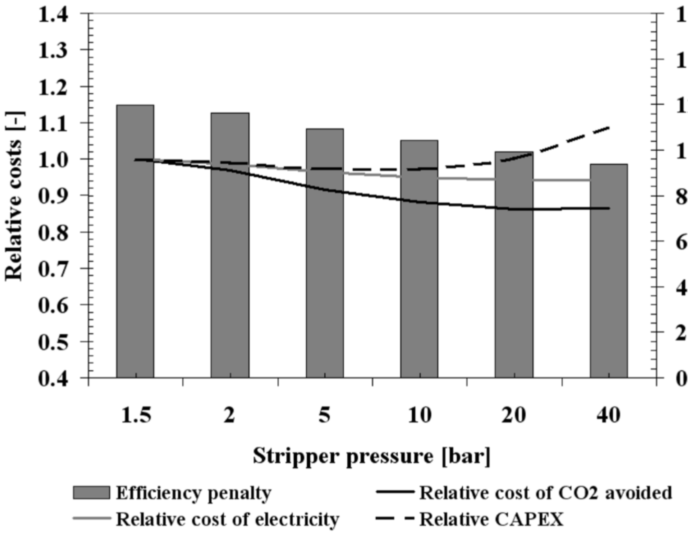

**Figure 7-8: Influence of increasing the stripper pressure on the cost of $CO_2$ avoided, cost of electricity, overall capital investment and efficiency penalty relative to MEA benchmarking process**

### 7.2.3 The evaluation of improved post-combustion capture systems

In this section, the targets to reduce the cost of $CO_2$ post-combustion capture will be evaluated. This will be done by designing a capture generic solvent/system with improved properties. In addition, numbers of newly developed solvent systems are evaluated using the vendors' available information. These different systems and a generic designed solvent system are benchmarked with the conventional MEA process

Specific targets for the reduction on the cost of $CO_2$ emission reduction (presented as cost of $CO_2$ avoided) have been set in different research and industrial project. These targets have been designed to enable the application of the full-scale capture process in the near future. The general target for the European CCS projects is to reduce the cost of $CO_2$ avoided to 20-30 Euro/tonne $CO_2$, which is almost 50% lower than the current avoided cost. This target cannot be achieved only by solvent development but by combining it with process integration and improvement.

This targeted avoided cost seems too optimistic, however, it has been shown earlier in this chapter that the combination of different improvement on the capture process will achieve a major cost reduction. The results of the cost reduction investigation have shown that the improvements of the following parameters will reduce the cost of $CO_2$ avoided dramatically:

- The reaction enthalpy: reducing the reaction enthalpy has a direct influence on the cost of $CO_2$ avoided. A realistic target for the reaction enthalpy for the newly developed solvent can be

50% lower than the conventional MEA process. This reduction of the reaction enthalpy will be translated into 10% reduction on the cost of $CO_2$ avoided.

- The solvent capacity: A possible improvement on the solvent capacity can be by doubling the cyclic loading comparing to the conventional MEA process. This looks realistic target looking into the available tertiary amines and other types of solvents. The double capacity will result in 50% lower solvent circulation rate and this will be translated into around 15% reduction on the cost of $CO_2$ avoided. This reduction in costs includes the effect of reducing sensible heat.
- The solvent chemical reaction kinetics: as stated before, improving the kinetics will reduce the capital cost of the absorber column. Accelerating the reaction kinetics together with improving the regeneration energy and solvent capacity is challenging to achieve. However, introducing solvent activators and improved solvent classes (e.g. TNO's CORAL) might make it possible to improve the reaction kinetics together with the rest of the solvent parameters. A reasonable target can be doubling the reaction kinetics comparing to the conventional MEA solvent. This faster kinetics will reduce the size of the absorber and will be seen as a total reduction of around 8% on the total cost of $CO_2$ avoided.
- The stripper operating pressure: increasing the stripper pressure will reduce the cost of the $CO_2$ compression system. Keeping in mind that the cost of the stripper will increase by increasing the operating pressure, the overall avoided cost will be reduced at higher regeneration pressure. A targeted operating stripper pressure of 10 bar (1 MPa) will result in an overall reduction of more than 10% on the cost of $CO_2$ avoided.

Table 7-1 presents the summary of these different improvements and its effect on the overall cost of $CO_2$ avoided. It can be seen that combining the improvement on these different parameters will reduce the cost of $CO_2$ avoided by almost 45%. This improvement is still did not match the targeted reduction on the overall cost (50%). In addition, it is expected that extra costs related to process modifications and more expensive solvent will have a negative effect on the overall cost, which is not included in this summary. However, the price of the solvent might have a large negative influence on the overall avoided cost if it is 4 times higher than the price of the conventional MEA solvent. In Figure 7-9, the overall $CO_2$ avoided cost and efficiency penalty are presented for different $CO_2$ absorption systems. These different systems together with the generic designed solvent system are compared in relation to the conventional MEA. It can be seen that for the generic solvent with lower solvent regeneration energy and the compression power, the overall efficiency penalty is 6 percentage points (50% of the conventional MEA).

**Table 7-1: Capture process summary of improvement s**

| Parameter | Targeted improvement | Reduction on $CO_2$ avoided cost |
|---|---|---|
| Reaction enthalpy | 50%<MEA | 10% |
| Solvent capacity | 200%>MEA | 15% |
| Reaction kinetics | 200%>MEA | 8% |
| Stripper pressure | 10 bar (650%>MEA) | 12% |
| **Overall effect** | - | **45%** |

Based on this analysis, it can be seen that to achieve the targeted reduction on the cost of the $CO_2$ post-combustion capture process a combination of multiple parameters and components needs to be improved. In addition to the solvent development, a step of improvement on the process flow sheet is required. This process development might lead to a further reduction on the overall cost of $CO_2$ avoided. In general, it can be concluded that, for breakthroughs in the $CO_2$ post-combustion capture more than one process parameter need to be addressed and improved.

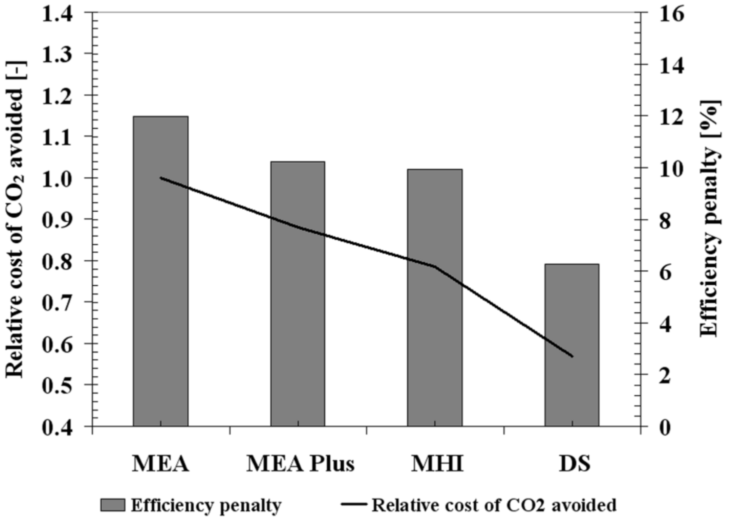

**Figure 7-9: Efficiency penalty and relative cost of $CO_2$ avoided in relation to MEA process for different solvent systems,** ***MEA: the conventional benchmarking process, MEA Plus: Fluor improved process, MHI: Mitsubishi Heavy Industry KS-2 solvent process and DS: Generic designed solvent***

## 7.3 What to focus on!!

Through the work in this thesis, there are number of subjects encountered that have been considered as interesting subjects. However, some of these subjects are outside the scope of this thesis. Therefore, it was difficult to give them the required attention. In this section, recommendations for future research in these subjects are presented with general advice for future research directions:

- The conventional capture process using MEA still has a room of improvement and optimization. This improvement can be done by improving the solvent properties (increase concentration, the addition of inhibitors to avoid corrosion and solvent degradation) or by improving the process concept. An extended experimental study is needed to evaluate the solvent behaviour at higher concentrations and to come with the exact figures in relation to solvent degradation rate and corrosively.

- Heat integration within the capture process and with the power plant is expected to provide an extra reduction on the capture process energy requirement. Different process concepts can be investigated using suitable modelling/simulation tools to give a first impression on the advantage of these integration concepts.

- The conventional coal power plant is capable of reducing the sulphur content in the flue gas to levels between 40-60 ppmv. However, this sulphur content is expected to reduce the solvent absorption capacity of most of the available post-combustion solvent, which are not able to handle sulphur content higher than 10 ppmv. As a result, there is a clear need to either improve the $CO_2$ absorbent or install an additional flue gas desulphurization unit, which is considered as an additional $CO_2$ capture cost. Another option can be there to investigate new solvent generation that can removal both $SO_2$ and $CO_2$ (combined sulphur and carbon removal). There are couple of research groups investigating this option and it is expected to have more attention in the near future.

- An extended study of the capture process scale-up challenges and requirement is a must to be able to apply the capture process in full scale. These scale-up challenges are varied from direct requirement (e.g. available space at the power plant), challenges related to the process operation (e.g. chemical supply, source of steam and power, process operation flexibility) and environmental challenges (e.g. water treatment, other types of emission, governmental regulations).

- The best method to understand the capture process is by real operation. Large-scale capture process demonstrations are required to gain more operational and process understanding experience. In addition, these demonstrations can be used for accelerating the political decision and the industrial adoption of the technology.

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"Blessed are those who can give without remembering and take
without forgetting" Elizabeth Bibesco

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Thank you very much

**شكراً**

Dank u wel

ABU
Mohama

Mohammad Abu Zahra

September, 2009 in Delft

# RESUME

Mohammad Abu Zahra was born on the 27th of January 1979 in Amman, Jordan. In 2002, he finished his B.Sc in chemical engineering from the University of Jordan with the graduation project on the production of crude oil from tar sand. One year after, he has joint the process design and development school at the University of Twente – Netherlands. With his final thesis "the design and economic analysis of carbon dioxide capture with MEA-processes", he obtained his master in chemical engineering together with the professional doctorate in engineering (PDEng) diploma in 2005. Later in 2005, Mohammad started his job as an innovator and later as a senior process engineer at the separation technology department within TNO science and Industry. In his work he contributed in different projects and studies related to the gas treatment specially the carbon dioxide post-combustion capture. Within this area, he has been involved in developing and evaluating $CO_2$ post-combustion processes and concepts, using process modelling tools and economic evaluation. He has done this work in different $CO_2$ capture European and national projects, for example CASTOR, CATO and Dynamis. His work in the $CO_2$ post-combustion capture process development has resulted in this PhD thesis. On August 1st, 2009, Mohammad has joint the International Energy Agency Greenhouse Gas R&D Programme (IEA GHG) in Cheltenham – United Kingdom as a project manager.

# PUBLICATIONS AND PRESENTATIONS

## Journal publications

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