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# Bibliography of Pilot Plants for post-combustion carbon capture

TESI DI LAUREA MAGISTRALE IN
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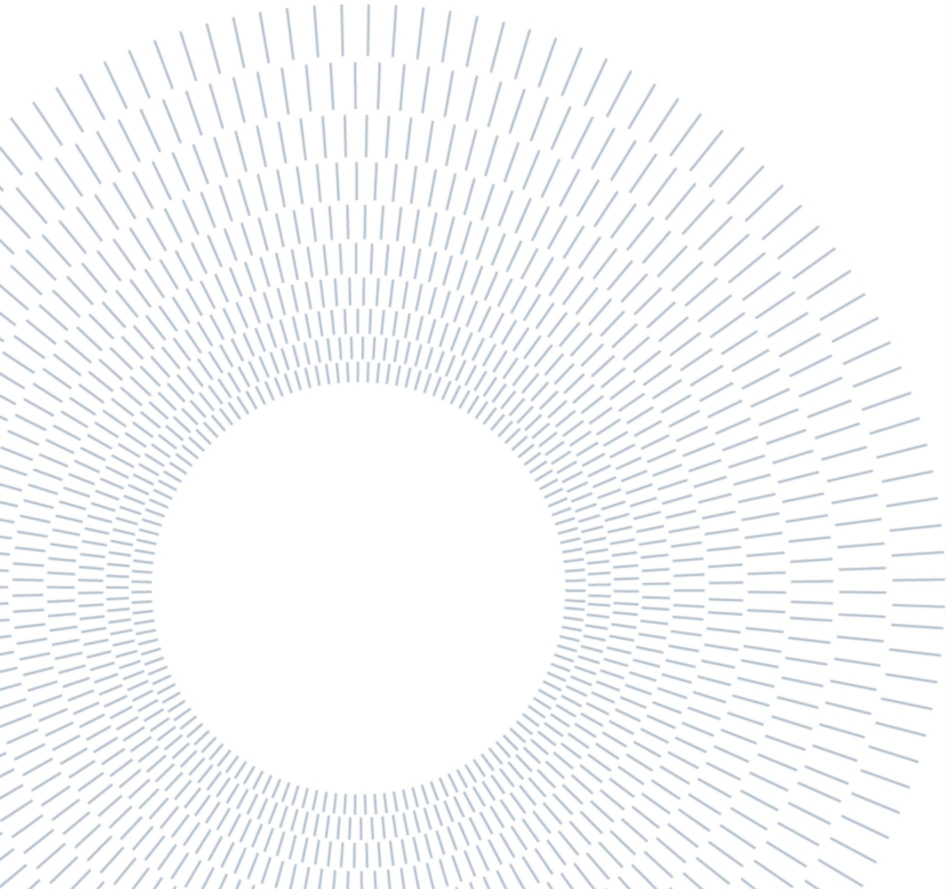


# Abstract

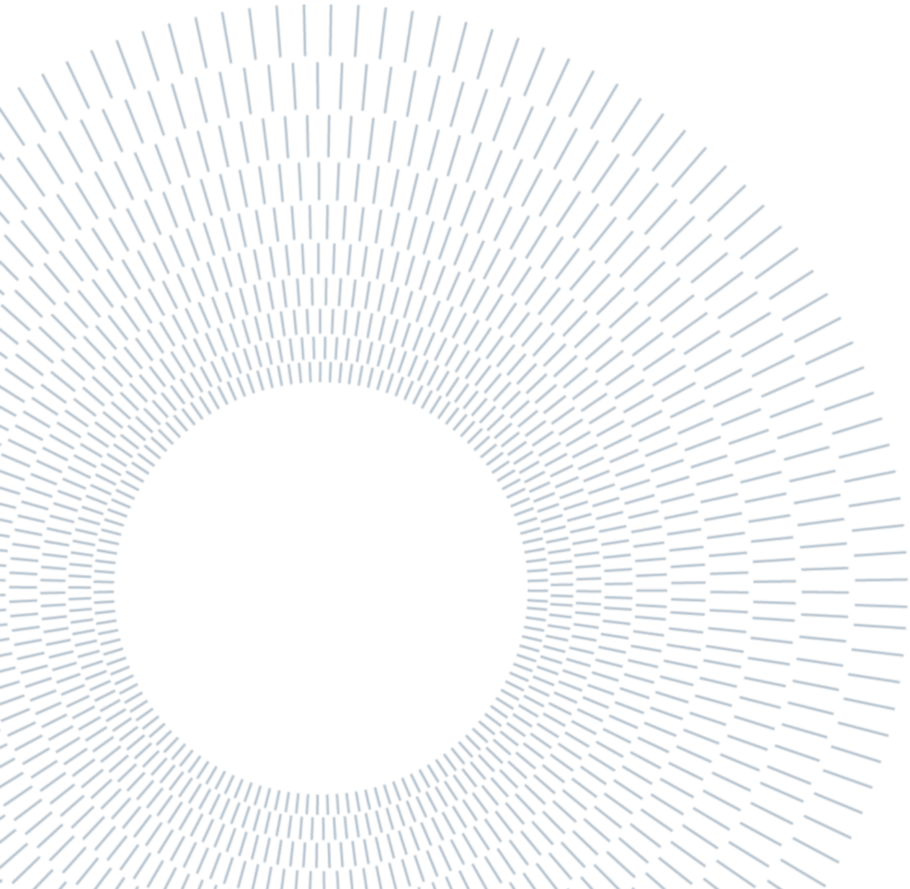
Global warming is increasing every day and despite all attempts and regulations to reduce the dependency on fossil fuels and include more renewables, yet carbon capture is believed to be an effective way to reduce the greenhouse emissions from heavy industries such as cement kiln, waste to energy power plants, coal-fired power plants and many others. This study is dedicated to post-combustion carbon capture from flue gases and in particular, pilot plants that are being used to test new solvents that have much better performance than MEA in terms of higher capture capacity, lower specific regeneration energy, lower degradation rate and lower amine emissions. Pilot plants are being developed towards modular and smaller size units to facilitate the transportation and erecting procedures at the shortest time possible. 13 pilots have been studied and compared in terms of layouts and configurations aimed at decreasing the energy penalty where Technology Center Mongstad (TCM) was taken as a reference in terms of size, instrumentation, performance, and operating parameters. In addition, various scenarios for plants' startup and shutdown have been proposed to reduce the energy penalty while guaranteeing the maximum performance of capture units. Enhancing energy performance was also studied through the new solvents that were tested in addition to the process optimization which included LVC, stripper interstage heating, absorber inter-stage cooling and heat recovery from compressor's cooling system as well as the hot vapor stream from the stripper's top. The main goal of pilot plants is to provide detailed results on the feasibility of implementing large-scale capture unit, and consequently, reduced size, mobility and modularity should be the main goal in designing new pilots which should be equipped with advanced solvents, highly efficient configurations and advanced instrumentation for controlling the emissions and to reduce the mass and heat balance error.

**Keywords:** Pilot plants, Carbon capture, TCM, Technology Center Mongstad, Instrumentation, advanced solvents, Ionic solvents, LVC, Lean Vapor Compression, Energy recovery.

# Abstract in lingua italiana

Il riscaldamento globale aumenta ogni giorno e, nonostante tutti i tentativi e le normative per ridurre la dipendenza dai combustibili fossili e includere più fonti rinnovabili, si ritiene che la cattura del carbonio sia un modo efficace per ridurre le emissioni di gas serra delle industrie pesanti come i forni da cemento, i termovalorizzatori, centrali elettriche a carbone e molti altri. Questo studio è dedicato alla cattura del carbonio in post-combustione dai gas di scarico e in particolare agli impianti pilota che vengono utilizzati per testare nuovi solventi che presentano prestazioni superiore rispetto al solvente di riferimento (MEA), in termini di maggiore capacità di cattura, minore energia specifica di rigenerazione, minore velocità di degradazione e minori emissioni in atmosfera di componenti relativi alle ammine. Gli impianti pilota vengono sviluppati tramite unità modulari e di dimensioni inferiori per facilitare le procedure di trasporto e montaggio nel più breve tempo possibile. Sono stati studiati e confrontati 13 piloti in termini di layout e configurazioni finalizzati alla diminuzione della penalità energetica. In particolare, l'impianto pilota sviluppato presso il Technology Center Mongstad (TCM) è stato preso come riferimento in termini di dimensioni, strumentazione, prestazioni e parametri operativi. Inoltre, sono stati proposti vari scenari per l'avvio e lo spegnimento degli impianti per ridurre la penalizzazione energetica garantendo la massima prestazione dell'unità di cattura. Il miglioramento delle prestazioni energetiche è stato anche studiato attraverso l'utilizzo di solventi innovativi, l'ottimizzazione del processo tramite Lean Vapor Compression (LVC), riscaldamento inter-stadio dello stripper, raffreddamento inter-stadio dell'assorbitore e recupero di calore dal sistema di raffreddamento del compressore, nonché dal flusso di vapore caldo dalla parte superiore dello stripper. L'obiettivo principale degli impianti pilota è fornire risultati dettagliati sulla fattibilità dell'implementazione di unità di cattura su larga scala e, di conseguenza, dimensioni ridotte, mobilità e modularità dovrebbero essere l'obiettivo principale nella progettazione di nuovi impianti pilota che dovrebbero essere dotati di solventi avanzati, configurazioni altamente efficienti e strumentazione avanzata per il controllo delle emissioni e per ridurre l'errore di calcolo sui bilanci di massa e energia.

**Parole chiave:** Impianti pilota, Cattura del carbonio, TCM, Centro tecnologico Mongstad, Strumentazione, solventi avanzati, Solventi ionici, LVC, Lean Vapor Compression, Recupero energetico.



# Contents

# Introduction

## Motivation and context

The sharp increase of the global energy demand has led companies to exploit more new energy sources to satisfy this high demand as well as pushing for increasing energy efficiency on the already existing technologies. Unfortunately, this led to the increase in the gaseous emissions from various sources that are using combustion-based technologies and in particular fossil fuels. Consequently, Global warming has become an important topic in the last few decades specially that we're starting to see its effect on various phenomena that is happing nowadays which includes but not limited to the rise in our oceans temperatures that lead to mass coral bleaching and altered the marine environment as well as the rise in the global average temperature that led to the melting of the icebergs in both North and South Pole. As a result, a rise in the sea level has been noticed which led to floods, Tsunamis and the submerge of various coastal areas and islands. In an attempt to reduce global warming effect, countries have set multiple pathways to reduce the global emissions such as the Net Zero Emissions (NZE) for New Zealand which is due 2050, European Green Deal that aims to make the whole European Union climate-neutral by 2050, the UK's Net Zero Strategy which is also due to 2050, Paris Agreement and the list goes on as many countries have already released long term plans to decrease their carbon footprint. Common measures that can be found among these different plans include increasing the share of renewable energy, improving energy efficiency and transitioning to sustainable mobility which leads to reducing greenhouse gas emissions in various sectors such as energy, transport and industry. Despite the increased efforts towards reducing emissions through increasing the share of renewables such as energy from wind, sun and other sources, it is also important to address the treatment of flue gases that are already being emitted to the atmosphere and in particular the removal of Greenhouse gases such as Carbon dioxide, methane and nitrous oxides. And from here comes the importance of Carbon Capture technology which aims at capturing carbon dioxide from industrial processes and power plants. This technology becomes more convenient the more we increase the share of renewables and in particular in the energy sector because of the need of flexible fossil fired power plants to ramp up and down quickly to provide dispatchable services to cover any gap or surplus in the supply side. Carbon Capture utilization and storage (CCUS) is believed to be one of the fastest and the most important ways to achieve the net zero emissions by 2050. Many $CO_2$ sources can be subjected to CCUS such as aluminum, cement, urea and steel industries as well as waste to energy (WTE) plants and finally fossil fired powerplants that utilize coal and gas. It becomes also important to address $CO_2$ sinks for which the captured $CO_2$ will be used and/or stored which includes storage in depleted oil and gas reservoirs where $CO_2$ is compressed, liquified, transported and pumped at high pressures to be permanently stored under impermeable rocks. Enhanced oil recovery (EOR) is also an interesting solution where liquified $CO_2$ is pumped at high pressures in heavy oil reservoirs to reduce its viscosity and thus facilitate its production. In terms of utilization, $CO_2$ can be used in many industries such as plastic, fish feed, proteins, food and beverage, methanol, algae and greenhouses. Carbon capture induces an energy penalty in power plants and industrial facilities which yields a reduction in the overall efficiency. Moreover, higher investment costs should be considered for both capital and operating costs.

## **Objective**

$CO_2$ capturing can be applied at different stages of combustion process such as pre-combustion capturing, post-combustion capturing and direct air capture. Pre-combustion capture works by gasification of solid fuels such as coal, biomass and Solid Recovered Fuel (SRF) which produce syngas that undergoes a water gas shift reaction to convert CO and $H_2O$ into $CO_2$ and $H_2$ where $CO_2$ is captured and pure hydrogen is used as a clean fuel. On the other hand, post-combustion involves capturing $CO_2$ from flue gases after the complete oxidation of fuel. And finally, direct air capture which works by capturing $CO_2$ that was already emitted to the atmosphere.

In the upcoming pages, carbon capture is addressed to post-combustion capturing process through absorption using liquid solvents. In particular, this study is focused on pilot plants that are being used to verify the feasibility of implementing full-scale capturing units. Pilot plants help in testing new solvents on various types of flue gases with different $CO_2$ levels as well as the different composition of different impurities depending on the type of application and the type of fuel being used. In addition, various scenarios can be applied on these pilot plants to better understand how the capturing performance would change with changing the load (peak and off-peak) specially with the increase of the share of renewables which induces peaks in the energy supply curve due to the prediction errors. These peaks require fossil fired plants to continuously ramp up and down which leads to the increase of $CO_2$ emissions. Finally, pilot plants help in testing new technologies which improves the energy performance of the overall capture unit and thus, reduces the energy penalty.

# 1. Carbon Capture Utilization and storage (CCUS)

## 1.1 An overview

Carbon dioxide is considered one of the most crucial gaseous compounds contributing to the greenhouse emissions. According to global emissions represented in Figure 1.1 based on 2010, Carbon Dioxide from fossil fuels and industrial process holds 65% of the global Greenhouse gas emissions. In addition, $CO_2$ emissions from fossil fuels increased by almost 90% since 1970 as shown in Figure 1.2. Thus, many paths have been paved towards reducing this huge percentage of emissions such as using more renewable and green energy such as wind, solar, geothermal, waves and tides. However, the fact that they are intermittent and not continuous would create a lot of spikes in the supply curve. Moreover, there are many industries in which its $CO_2$ emissions don't include only the fuel being burned, but also $CO_2$ emitted based on its raw materials such as cement. Calcination of limestone in cement kiln alone produces almost 50-60% of the total plant's $CO_2$ emissions [1], so shifting to green or $CO_2$ neutral fuels would only solve half the problem. And finally, with our increased global consumption and the huge global waste generation, the role of waste incinerators becomes essential to avoid emissions of greenhouse gases in dumping sites. This kind of fuel (i.e., waste) would generate a large amount of fossil-based $CO_2$ coming from plastics and petrochemical based products being burned.

Consequently, the idea of carbon capture utilization and storge came into the scene as a more promising technology to fully convert many industries into carbon neutral especially in the recent years. There are several technologies in CCS where each one has its own advantages, limitations and its field of application. They could be listed as post-combustion capture, pre-combustion capture, oxy-fuel combustion, chemical looping combustion, direct air capture and finally carbon utilization and storage.

1. **Post-combustion capture**: This technology mainly targets fossil-fired power plants and industrial plants using nonrenewable fuels such as coal and natural gas but also WTE where fuel undergoes a complete oxidation combustion process. Post-combustion capture units are usually placed downstream of the flue gas treatment units as a final step before being released to the atmosphere. $CO_2$ absorption can be done using chemical solvents but also membranes where solvents are more widely used. However, this technology leads to a reduction in the overall efficiency of these plants because of its huge energy demand. This study is mainly focused on this technology and will be discussed further in more details.
2. **Pre-combustion capture:** This technology basically aims at converting fossil fuels and in particular coal, biomass and SRF into an intermediate product called syngas through gasification. Syngas, which is a mixture of CO, $CO_2$, $H_2O$ and $H_2$ further undergoes a sequence of water-gas shift reactions (WGS) to increase the conversion of CO into $CO_2$ and $H_2O$ into $H_2$. $CO_2$ is then captured through absorption with amines or through membranes. This technology is believed to be more energy efficient than post-combustion. However, a higher capital investment is needed for the gasification unit, the WGS reactors and the capture unit itself.

$$\mathrm{CO + H2O \rightleftharpoons CO2 + H2}$$

3. **Oxy-fuel combustion:** In this technology, fossil fuels are burned with pure oxygen instead of ambient air and thus leading to a flue gas product that consists mainly of $CO_2$ and $H_2O$. Flue gas is cooled and separated from water simply through a sequence of condensing and flashing, therefore eliminating the need of an absorption-stripping unit. However, It involves the presence of an air separation unit that can be retrofitted in already existing power plants.

4. **Chemical looping combustion:** This technology is still at an early stage of development but shows great potential for the future. It involves utilizing metal oxides as oxygen carriers to transfer $O_2$ from air to the fuel. In this way, fuel is combusted with $O_2$ as in oxy-fuel case and a simple flue gas stream is produced with water and $CO_2$.

5. **Direct air capture (DAC):** Capturing $CO_2$ at an efficiency of 90% means that there are 10% emitted to the atmosphere which is not a small quantity when it comes to the global scale. Thus, this technology is dedicated to this 10% in

addition to the $CO_2$ that was already emitted to the atmosphere which is causing the heat to be trapped in our atmosphere. Unlike other technologies that capture $CO_2$ from point sources, DAC captures carbon directly from the atmosphere which makes it a powerful technology as it can be implemented anywhere so it can address various sources of emissions such as transportation and agriculture. Some DAC relies on a chemical solution that reacts with $CO_2$ in the atmosphere and form a solid compound which is heated to release the $CO_2$ being trapped while other technologies rely on adsorption of $CO_2$ on solid sorbent material which is heated afterwards to release the $CO_2$.

6. **Carbon utilization and storage:** The utilization technology on the one hand addresses the post-capture phase of carbon dioxide where $CO_2$ is converted into useful products to be used in various industries such as food and beverage, green houses, fuels, methanol, algae production, fish feed, plastic and Enhanced oil recovery (EOR). On the other hand, storage technology involves the storage of $CO_2$ in depleted reservoirs under high pressure where it is trapped under an impermeable cap rock.

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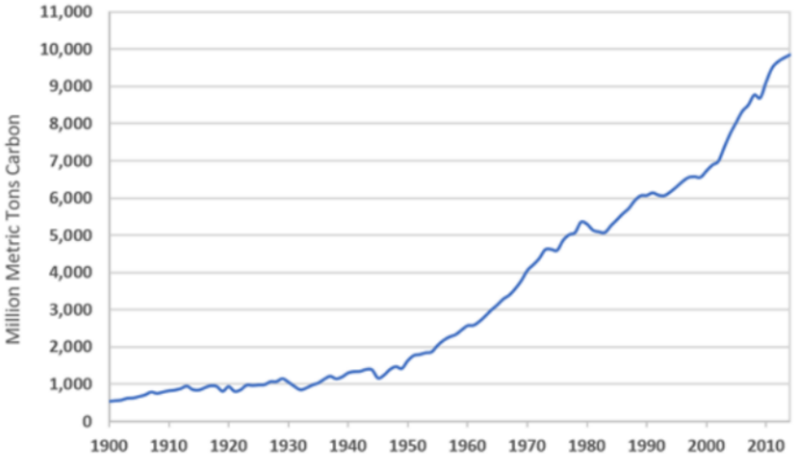

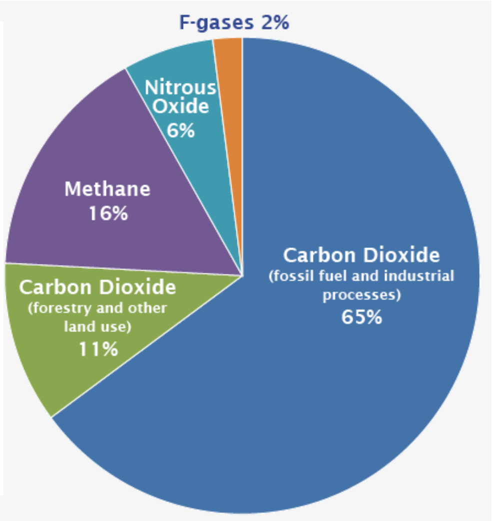

Figure 1.1 Global Carbon Emissions from Fossil Fuels 1900-2014

Figure 1.2 Global greenhouse gas emissions by gas

Source: - Boden, T.A., Marland, G., and Andres, R.J. (2017). Global, Regional, and National Fossil-Fuel CO2Emissions. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A. doi 10.3334/CDIAC/00001_V2017.

## 1.2 Technology Center Mongstad (TCM)

Technology center Mongstad is considered the largest and the most complete $CO_2$ capture testing facility. It was founded in 2012 in Norway as a joint venture between Gassnova (73.9%), Shell (8,7%), Equinor (8,7%) and Total Energies (8,7%) where Gassnova is the main shareholder thus it is owned by the Norwegian state. This facility is built beside the Equinor oil refinery in Mongstad where flue gases from two different sources are being produced where the first is from a combined cycle gas turbine (CCGT) that is providing combined heat and power (CHP) with a $CO_2$ composition of 3.5-4.1 mol%[2] that corresponds to a flow rate of about 80 tons $CO_2$ /day. The other flue gas stream is from Equinor's refinery's Residual Fluid Catalytic Cracker (RFCC) with a $CO_2$ mole fraction of 13-14.5% [2] that corresponds to 200 tons $CO_2$ /day. The P&ID of TCM can be seen in Figure 1.3 [3] where the facility is designed for post combustion capture process with 2 direct contact coolers (DCC) where the smaller one is for CHP flue gases while the larger one is for the RFCC for its higher flow rate. A flue gas blower placed upstream the DCC with a 70,000 $Sm^3/h$ is used to provide the flue gas slip stream with extra pressure that the flue gas will suffer through the DCC, absorber and ducts until it is directed back to the stack for ejection. Flue gas enters the DCC where it comes in contact with water in a counter current configuration for conditioning the flue gas before being introduced to the absorber. In the DCC, the flue

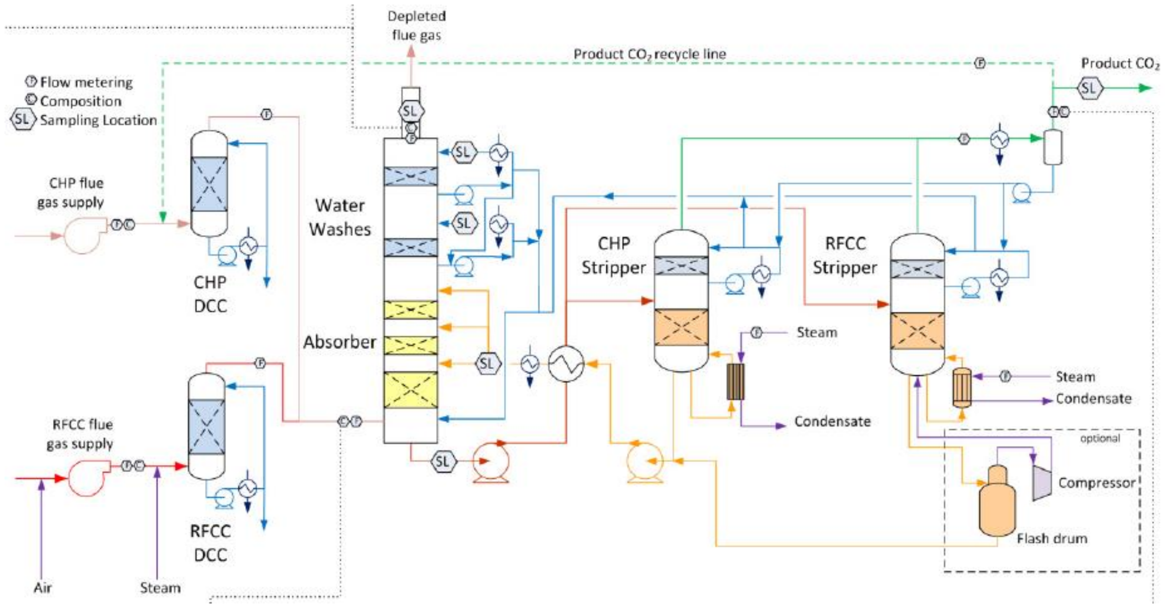

Figure 1.3 P&ID of Technology Center Mongstad for the 2 flue gases configurations

gas temperature is dropped to 25-30 °C which is suitable for the absorption process with Monoethanolamine (MEA) that is an exothermic chemical reaction thus favored at lower temperatures. As the flue gas temperature decreases, the distance between the equilibrium curve and the operating line of the absorber increases which results in a smaller number of stages i.e., a lower height of packing and consequently lower capital costs. Moreover, the flue gas already contains a high-water content, therefore cooling the flue gases would lead to not only the condensation of some of this water, but also saturating the flue gas at the exiting temperature. Saturating the flue gas with water would lead to limiting the absorption of water that is contained within the MEA solvent to avoid solvent losses. And finally, spraying flue gases with water would lead to the further reduction of the $SO_x$ levels to reduce the probability of the reaction of amines with such compounds which can produce sulfamate that is considered one of the degradation products.

Conditioned flue gases are then introduced to the absorber column where only one absorber was designed for both flue gases with a 3.55 m × 2 m (Rectangular) shape that is built of concrete and lined with polypropylene that can withstand a maximum temperature of 80°C, a height of 62 meters and 24 meters packing divided into 3 beds of 12m + 6m + 6m of Flexipac 2X structured packing to provide 3 ranges of packing heights of 12, 18 and 24 m depending on the application and the type of test. On the upper part of the absorber, 2 water wash sections with a total of 6m packing height of Flexipac 2Y high-capacity structured packing are placed on the gas side to further wash the depleted flue gases. The absorber is equipped with 96 temperature sensors with 4 sensors placed every 1 m of the 24 m of packing where these 4 sensors are separated by a 1 m horizontal distance. Placing multiple temperature probes at the same level can tell a lot about liquid distribution along the absorber and as we can see in Figure 1.4 [4] the difference in readings between B, C &D is mainly because of poor & uneven distribution of gas & solvent on packing.

Post-absorption water washing has two main objectives: 1) to capture the water and amines entrained with the flue gases and thus keeping the water balance of the solvent and avoid solvent emissions/losses and, 2) reduce the concentration of amines and its degradation products that could be present on the gas phase side such as formaldehydes, acetaldehydes or acetone and keep the volatile organic compounds (VOC)'s concentration as low as possible. On the other hand, $CO_2$ rich solvent is extracted from the absorber's sump and pumped through a lean-rich heat exchanger for heat recovery from the lean stream exiting the stripper's sump. Hot rich solvent is then introduced to one of the two strippers available on the site where a smaller diameter one (1.3 m) is used for CHP configuration while the larger diameter one (2.2 m) is used for the RFCC configuration given its higher solvent flowrate. Both strippers are 30 m high with 8 m of Flexipac 2X structured packing fitted with a welded plate thermosiphon reboiler at the bottom that is fed with low pressure steam extracted from the L-P steam turbine at a temperature between 140-160 °C with a steam flow rate ranging between 1000–5000 kg/hr. The temperature of the reboiler is kept in the range of 110-125°C where above this temperature thermal degradation products of amines will be formed which will result in the decrease of the efficiency of the solvent along with economic losses. Several campaigns were done to evaluate the overall energy performance of the capture unit at different stripper pressures which went up to 4.5 bara. However, average pressure was kept between the range of 1.9 to 2 bara. In section 3.2.5 the effect of increasing stripper pressure will be discussed in detail. It is good also to mention that the stripper was equipped with 28 temperature probes in a 4 sensors every 1.14 m with a 1 m horizontal distance for further studying the stripping performance with respect to the energy provided at the reboiler. Figure 1.5 [4] shows three different cases of stripping processes where the left graph shows the stripper being operated below optimum conditions while the middle one shows an optimum operating condition and finally the right one shows an operating point above the optimum conditions.

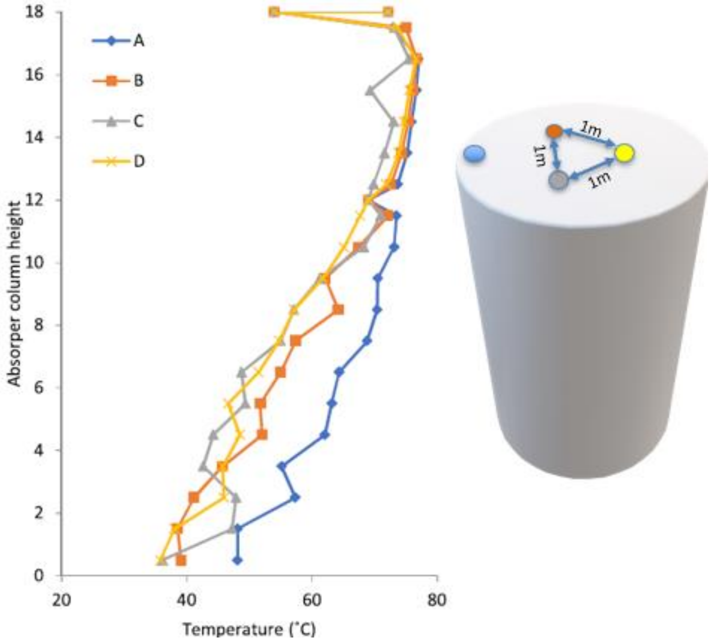

Figure 1.4 Absorber temperature profile in TCM

A comparison between those three cases can be seen in Table 1.1 [4] where it should be useful specially for advanced solvents where a lot of information about the solvent's performance is still to be studied to better understand the optimal operating points for these solvents.

| Below optimal conditions (left) | At optimal conditions (middle) | Above optimal conditions (right) |
|---|---|---|
| o Receiving little energy<br>o Boil up is much smaller than the overall solvent flow.<br>o Stripping of CO2 takes place at the top & bottom while in between is inefficient. | o Receiving the exact amount of energy<br>o Constant driving force along stripper height<br>o Good balance between water condensation & CO2 desorption | o Receiving too much energy<br>o The temperature drop in the top part is steep.<br>o Most of the $CO_2$ stripping takes place at the top part mainly through water condensation |

Table 1.1 Comparison between various operating conditions of the stripper in TCM

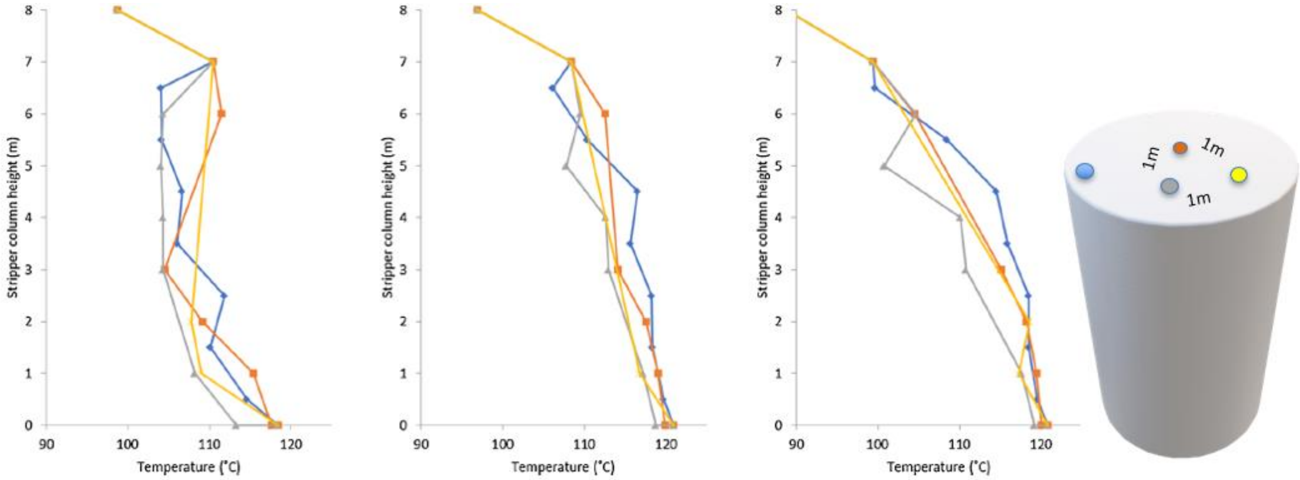

Figure 1.5 Stripper Temperature profile in TCM

A lean vapor compression (LVC) unit was also included in this facility but was not adopted in all the campaigns. Lean solvent stream exiting the sump of the stripper is still carrying a percentage of vapor and $CO_2$ which if extracted from the solvent and reintroduced to the stripper would result in a lower amount of steam required at the reboiler to generate enough vapor to strip the solvent of its $CO_2$ i.e., the reboiler duty. Further information about the LVC should be discussed in section 3.2.3. Lean solvent exiting the desorber's sump or the flash tank in case of LVC configuration is then pumped to the Lean-Rich heat exchanger to heat up the rich solvent that is about to be introduced to the stripper while the lean solvent is further cooled in a water-cooled heat exchanger to be conditioned to the appropriate absorption temperature. TCM is also equipped with carbon filters placed on the lean solvent side before being introduced to the absorber were depending on the type of amine being used and its thermal and chemical stability, lean solvent can contain some degradation solid products and heat stable salts (HHS) that needs to be removed. Different kinds of filters have been adopted in different pilot plants and will be discussed later in section 2.8.3. The upper part of the stripper is basically a water wash section that consists of 1 bed of Flexipac 2Y high capacity structured packing of height of 1.6 m which is made to further wash and cool down the vapors rising from the reboiler which has entrained and vaporized solvent along with $CO_2$ that was being stripped from the rich solvent thus, the water wash section is crucial from the environmental point of view as it controls the total amount of VOC being released to the atmosphere. Vapors that consist mainly of $CO_2$ and water are then passed through a demister to remove liquid droplets of solvents being entrained before it passes through a condenser where the stream is cooled and flashed producing a liquid stream that is redirected to the stripper and a gas stream of a high purity $CO_2$ which is sent to compression and storage.

TCM has more than 400 online instruments and around 100 sampling points distributed along the whole units which are used mainly for performing test campaigns with MEA solvent. However, they encourage various companies to test newly developed solvents that have a much better performance in terms of cycle capacity, regeneration duty and lower degradation rate. Moreover, companies with mobile pilot plants such as Aker solution MTU were brought on site to perform further tests using their technology and advanced solvents while benefiting from the wide range of equipment and facilities available there.

Amine emissions have always been a great concern when it comes to $CO_2$ capture with solvents as these solvents react with different compounds and impurities in flue gases and produce a wide range of products such as sulfates, nitrosamines, nitramines in addition to a wide range of degradation products that includes but not limited to acetaldehydes, acetone and ammonia of which some are carcinogenic and cause health problems. TCM is equipped with various gas and liquid analyzers that are used to monitor the composition of different streams to ensure that the emissions are being withing the allowable limits.

# 2. Pilot plants for post-combustion applications

13 pilot plants applied to different utilities have been reviewed throughout this work. In a dedicated excel, working parameters, equipment dimensions, various solvents, flue gas source, composition and flowrate have been listed and compared for all the pilot plants in addition to various technologies, configurations and energy performance and consumption. Table 2.1 lists down their locations and to which flue gas source they are assigned.

| Pilot plant | Location | Flue gas source |
|---|---|---|
| **Next Generation Carbon Capture Technology (PDVU)** | United Kingdom | Waste, CCGT |
| **Niederaussem pilot plant** | Niederaussem (Germany) | Lignite |
| **Fagerlund Cansolv WTE Fortum** | Klemetsrud (Oslo, Norway) | Waste |
| **Technology Centre Mongstad (TCM)** | Mongstad, Norway. | natural gas |
| | | refinery residual fluid catalytic cracker |
| **Aker Solutions' Mobile Test Unit (MTU) NORCEM** | Brevik, Norway | flue gas from the cement kiln |
| **Imperial College carbon capture pilot** | London, UK | Not specified |
| **CASTOR- Esbjerg Pilot Plant** | Esbjerg, Denmark | Pulverized Bituminous Coal |
| **CESAR- Esbjerg Pilot plant** | | |
| **UK CCSRC PACT facility** | United Kingdom | Coal |

| Pilot plant | Location | Flue gas source |
|---|---|---|
| **NCCC pilot plant** | Wilsonville, Alabama USA | Illinois No. 6 bituminous coal |
| **RECODEH2020** | Greece | flue gas from the cement kiln |
| **LTD pilot plant University of Kaiserslautern pilot** | Germany | gas fired (Set I) |
| | | Coal fired (Set II) |
| **UK CAER, University of Kentucky** | Harrodsburg, Kentucky, USA | Pulverized coal |

Table 2.1 Pilot plants names, locations and flue gas source.

## 2.1 General classification

Pilot plants can be classified into different categories, depending on their scale, Technology Readiness Level (TRL) and the type of application. University and research centers-based pilot plants are mainly for research and validation of new technologies such as University of Kaiserslautern, Imperial College carbon capture pilot plant and PACT facility. In those pilots there is no actual flue gas source but rather, ambient air is mixed with $CO_2$ and Nitrogen to arrive at a final composition that simulates flue gas of waste, coal or gas fired plants. Despite the usefulness of these pilots, it can be hard to estimate solvent degradation rate and thus the need of a reclamation unit and the amount of makeup needed for compensation. On the other hand, industrial based pilot plants are more realistic because it can follow the various scenarios induced by the power plant such as unsteady states during ramping up and down which results in a sharp increase in the emissions which would influence the solvent emission and degradation rate. Moreover, impurities present in flue gases would help in addressing solvent degradation rates, foaming problems, reclamation neediness and makeup rate. Industrial based pilot plants also help in testing the effect of energy integration using waste heat from the process itself such as in cement kilns which could limit the need of steam or the load of electric heaters in the reboiler to regenerate solvents which is the case in Norcem cement kiln [1]. Moreover, energy integration concept was widely explored in the UK CAER, University of Kentucky pilot plant [5] where multiple heat exchangers were placed to recover heat from the vapors leaving the primary and the secondary air stripper which will carefully be reviewed later.

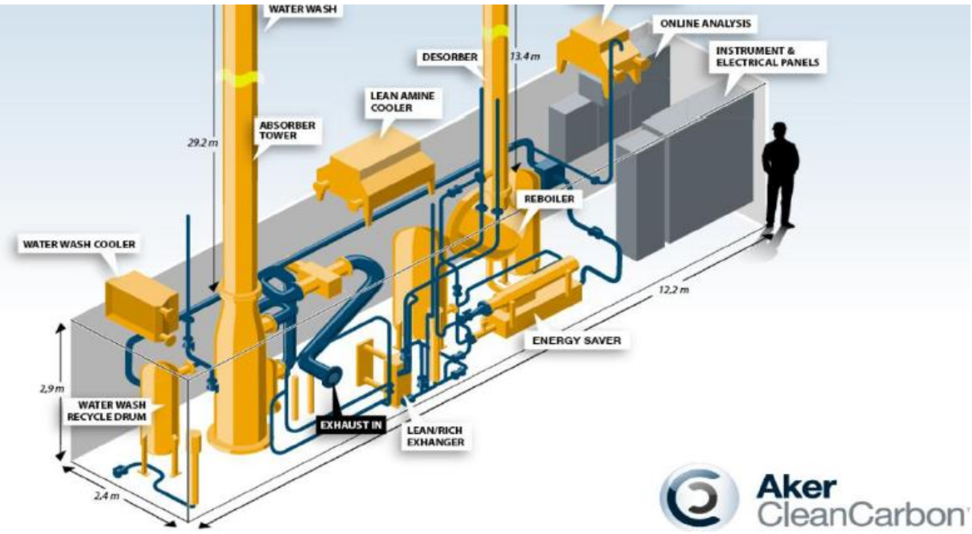

Figure 2.1 Aker Solution's MTU

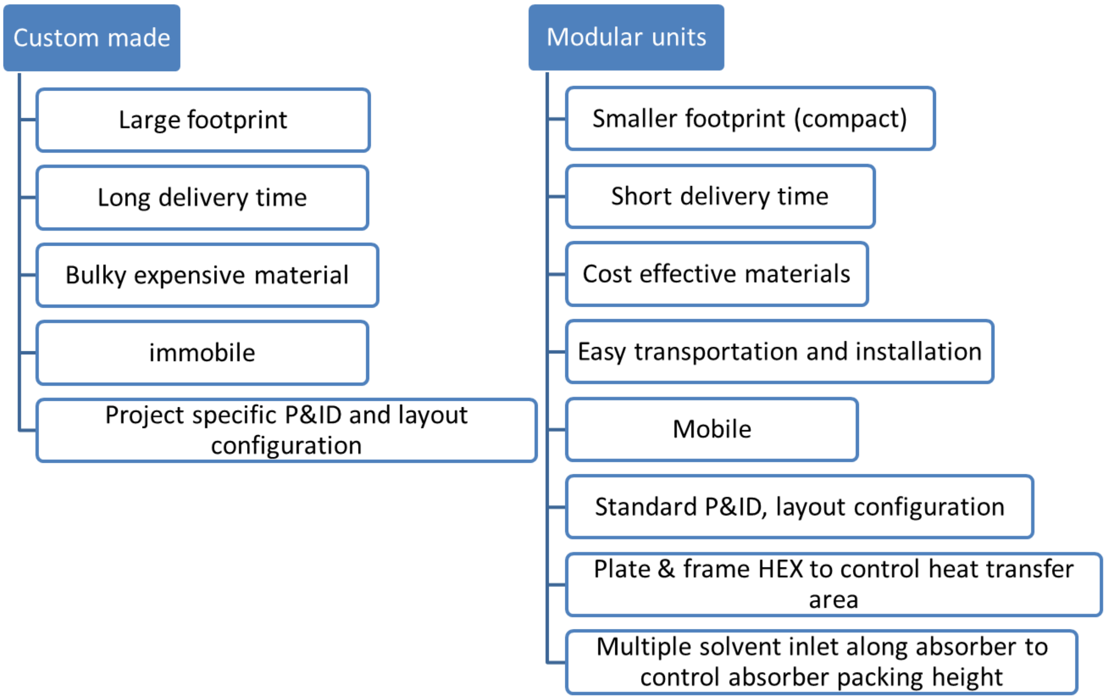

Figure 2.2 Modular Vs Non-Modular pilot plants

Another classification of pilot plants can be seen in Figure 2.2 along with the advantages of modular above non modular ones. Modular pilot plants such as Aker Solutions Mobile Test Units (MTU) Figure 2.1 [6] is considered an effective solution for testing pilot plants on power plants, industrial and chemical plants as well as offshore plants without the need to size specific equipment for each plant which can lead to a huge cost reduction. So far, the MTU has been used in coal and gas fired power plants as well as Waste to Energy (WTE), cement, heavy oil cracker and hydrogen [7][1][8] for over 20,000 operating hours. To further reduce carbon capture costs, Aker solutions launched its new modular pilot plant "Just Catch" that is smaller in size than its MTU which can be seen clearly in Figure 2.3 [9] which compares this new modular unit with TCM.

$CO_2$ capture technology must be available at the lowest cost possible to encourage plant owners to invest in it. Costs include the construction, delivery and erection costs and time that it takes until the unit is ready for testing which could take up to 2 years. Modular Plants have already solved such problems and it is becoming more promising for the future of carbon capture technology as those units are relatively smaller in size which guarantees mobility and consequently those pilots can be rented instead of being bought.

Figure 2.4 Just catch modular pilot plant.

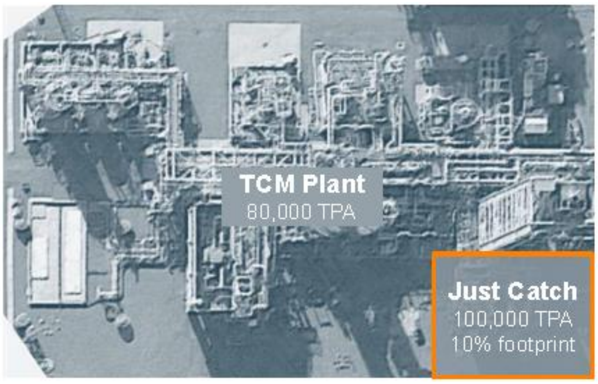

Figure 2.3 Aker solution's Just Catch new modular pilot plant compared to TCM.

Just catch modular plant has various advantages which can be summarized in:

- Capture capacity of 100,000 tons $CO_2$ per year
- Fully controlled remotely and automatically
- Flexibility to work on different flue gas sources, flowrates and compositions.
- Short delivery time "15 months"

- TRL level 8
- Usage of robust solvents S26
    - ❖ low degradation,
    - ❖ low emission
    - ❖ low waste to be disposed.
- Higher efficiency than standard plants

## 2.2 Test duration

Testing new technologies of carbon capture require a lot of hours to test various configurations, solvents, operating conditions and operating scenarios and see their effect on the overall capture rate, specific reboiler duty, the Levelized Cost Of Electricity (LCOE) and the emissions. Different utilities have different flue gas properties including different $CO_2$ concentrations and flow rates in addition to different concentration of impurities which depend on the type of fuel being burned and the air to fuel ratio. These differences will result in a different impact on the solvent's regeneration energy, solvent circulation rates, solvent degradation and consequently the need of solvent reclamation and make up as well as the amine emissions at the absorber's top. Thus, a long period of testing should be dedicated to each pilot plant to be able to study various scenarios and better understand the behavior of these pilot plants with respect to each utility whether it's a power plant or a chemical refinery or a cement plant. Pilot plants and specifically the ones using new solvents have to run a primary test campaign with MEA 30% as it's considered the reference on which they compare their results of the new solvents. Table E.1 shows the duration of each test campaign done in the University of Kentucky [10] where 4 solvents have been used to test different operating parameters and their effect on the overall performance of the capture unit. Table E.2 reports the test duration of each pilot plant

## 2.3 Capture capacity and capture efficiency.

Pilot plants work on a slip stream of the flue gases exiting the flue gas treatment units which depends on the design and the sizing of the equipment. Capture capacity is defined as the amount of $CO_2$ captured per day or hour which is a function of the composition of the flue gas as well as the flow rate. Higher $CO_2$ content flue gases coming from cement, waste and Residual Catalytic Cracker (RCC) would yield in higher capture rates. Moreover, it's a function of the type of solvent being used where fast solvents would react with more $CO_2$ and produce a higher flow rate of $CO_2$ at the top of the stripper. Sometimes it becomes hard to compare this capture rate per day or per year as it depends on the number of equivalent hours for each unit per day. Capture efficiency on the other hand is a function of how much energy is available at the reboiler either through steam extracted from the low-pressure turbine or through an external steam generator or an electrical reboiler. The higher the energy available at the reboiler the leaner the solvent that exits the stripper's sump. However, that would lead to a higher energy penalty. Most of the capture units are designed to capture about 90% as seen in Figure H.1. However, aiming for capture efficiency beyond 90% was achieved in some campaigns to test the limits of their technologies in terms of the thermal stability of the solvent as the reboiler temperature goes beyond 120°C. Moreover, other opinions on carbon capture was that if we can capture carbon we should capture it all because the other 10% of $CO_2$ in the flue gases will still be emitted to the atmosphere which is will add to global warming. Achieving 95+ capture efficiency with MEA is possible but will cause a huge energy penalty in the power plants due to its high SRD in addition to its high thermal degradation rate. Consequently, shifting towards new advanced solvents that could withstand such high regeneration temperatures while having a lower SRD could be a way to reduce the capture cost and thus encourage more industries to implement such technology.

## 2.4 P&ID

All the pilot plants are based on conventional (absorption-stripping) layouts with some differences in :-

1) Dimensions of units
2) Configurations of different technologies
3) Presence/absence of:
   - Amine reclaiming unit.
   - lean solvent mechanical vapor recompression (MVR)
   - Absorber intercooler
   - Stripper interstage heating
   - DCC (pre-scrubbing unit)
   - Solvent filters
4) Fluid sampling points & Temperature sensors
5) Type of reboiler and its heat source.

Pilot plants reported here have adopted various sizes of equipment based on the flue gas capacity being treated and tested. For instance, TCM Mongstad adopted a rectangular shape absorber because of its high flue gas capacity that reaches up to 60000 scm/hr while the rest of the pilot plants had circular shape with a diameter ranging between 0.4-1.1 meter. Absorber height also was a clear comparison point where most of the pilot plants had one single absorber except the Pre Deployment Verification Unit (PDVU) Figure 2.5 [11] which had the absorber divided into three columns to facilitate the mobility of such a unit because transferring columns with more than 30 meters heigh is a very challenging and expensive operation that requires a lot of time and attention. Height of packing and the number of packing also varied between a pilot plant and another depending on the type of solvent being used, type and capacity of flue gas being treated and various technologies available in the pilot which can have an impact on the height of the packing such as the absorber interstage cooler which can decrease the overall mass transfer are i.e., the packing height.

Most of the pilot plants adopted the interstage cooler except UK CCSRC PACT facility Figure 2.7 [12]and the CASTOR- Esbjerg Pilot Plant Figure 2.6 [13][14]. While post-absorption washing section is considered a must in all carbon capture units, yet it was seen as an interesting point of comparison between different pilots. A different number of beds was adopted varying between 1 and 2 beds which was mainly dedicated to washing the $CO_2$ depleted flue gases with water to remove any evaporated or entrained amines. However, Aker solution's MTU included an additional acid wash section to further reduce any sulfur dioxide (SO2) and nitrogen oxides (NOx) which is suitable for flue gases with high sulfur oxide content such as the RFCC in Mongstad Figure 2.8 [8] and Norcem Cement Kiln [1] [15] as well as the PDVU which used sulfuric acid. Washing stages are usually imbedded in the same column of the absorber for better heat integration and to avoid additional costs of piping and connections needed for a separate vessel> However it was seen in the Next Generation Carbon Capture PDVU, UK CCSRC PACT facility, The pilot solvent test unit (PSTU) at the National Carbon Capture Centre (NCCC) Figure 2.9 [16] and LTD pilot plant University of Kaiserslautern Figure 2.10 [17] that the absorber was separated from the absorber in a dedicated column where a reasonable explanation to this could be limiting the height of absorber to facilitate its manufacturing, transportation and erecting..

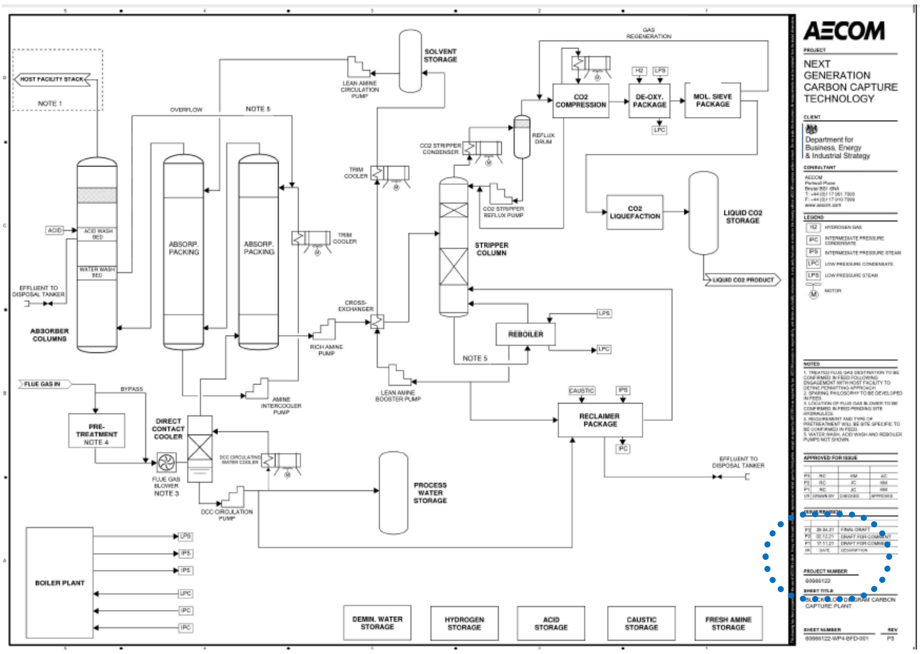

Figure 2.5 Next Generation Carbon Capture PDVU's P&ID

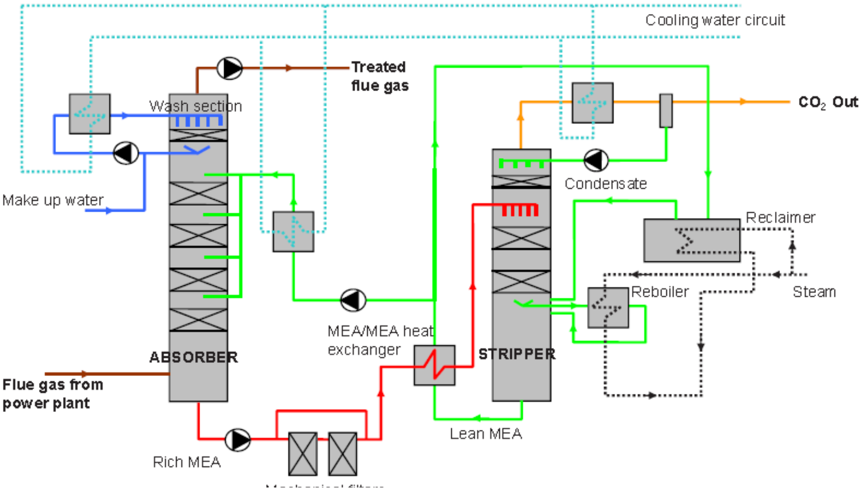

Figure 2.6 Esbjerg pilot plant (CASTOR project) P&ID

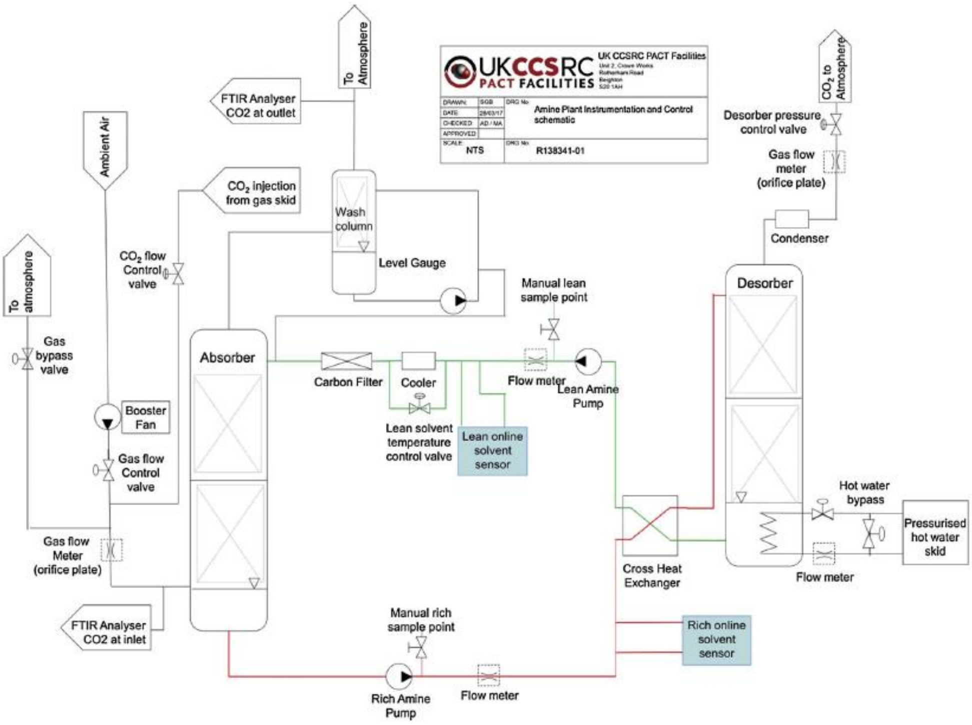

Figure 2.7 PACT facility of the UKCCSRC at the University of Sheffield P&ID

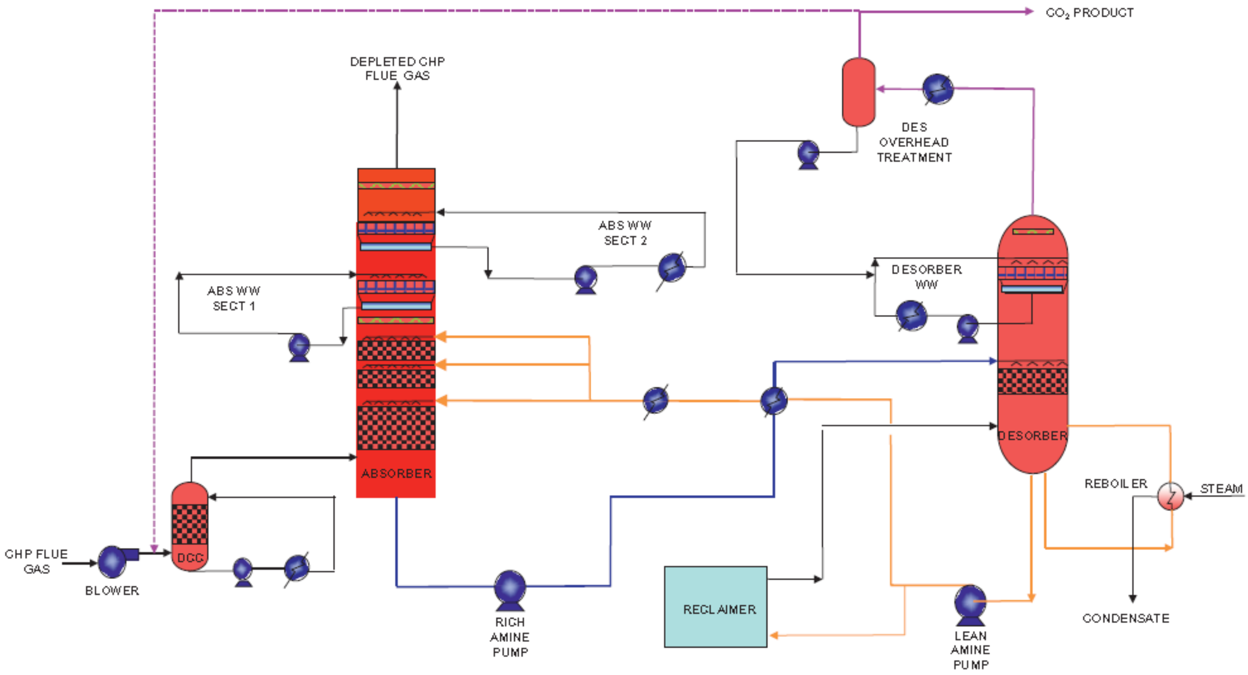

Figure 2.8 Aker Solution's MTU in TCM P&ID

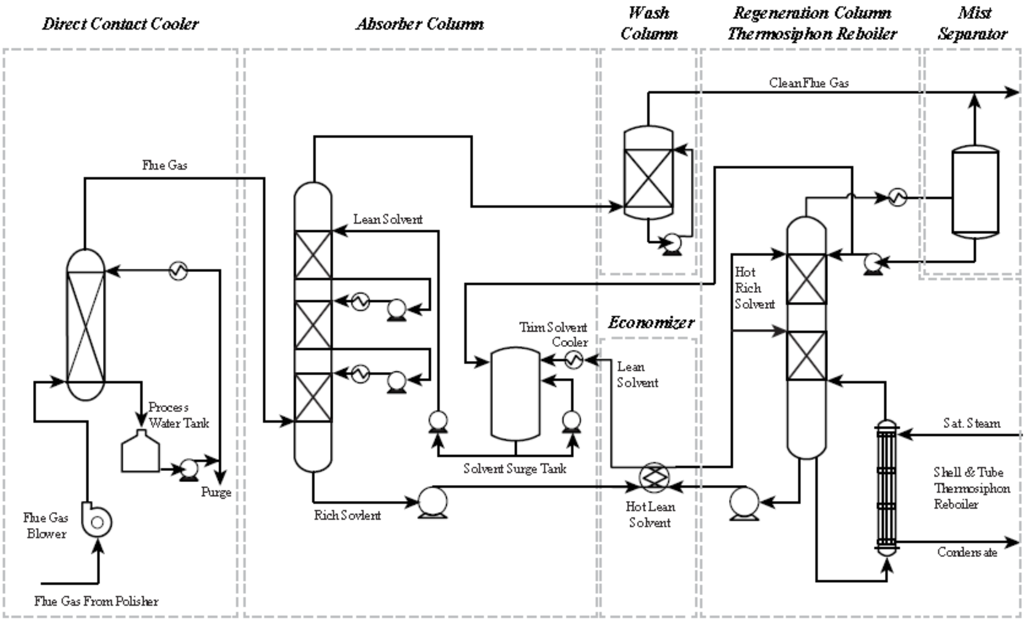

Figure 2.9 PSTU at the National Carbon Capture Center

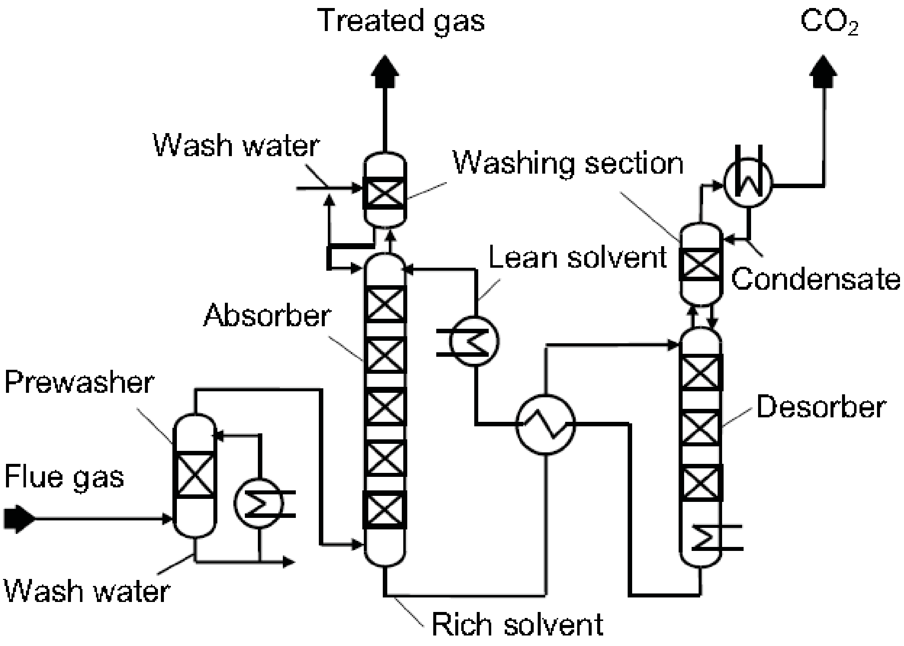

Figure 2.10 LTD pilot plant University of Kaiserslautern P&ID

The DCC was only absent in the CASTOR-Esbjerg pilot plant and the PACT facility and was integrated within the absorber in one single tall tower that has the DCC, absorber and water wash in the Linde- BASF NCCC pilot plant Figure 2.11 [18]. The number of heat exchangers and their position varied from one place to another depending on the configuration being adopted where the more they exist, the more heat recovery and integration available which leads to the reduction of the steam extraction from the steam turbine or the reboiler's duty in general (in case electric reboiler was used) which was clear in Linde-BASF NCCC pilot and UK CAER, University of Kentucky Pilot plant Figure 2.12 [5].

The stripper in the 13 pilot plants was an interesting unit for comparison that varies mostly in its diameter between 0.125- 2.2 m as well as its height. All the strippers had a single water wash section that varied in height depending on the volume of solvent being used. Pilot plants of carbon capture absorption-stripping are usually equipped with 1 conventional stripper that uses steam in the reboiler to heat up the solvent to liberate it from $CO_2$ and excess water. However, the UK CAER, University of Kentucky Pilot plant was the only pilot plant that adopted 2 stripping stages i.e., 2 strippers where the first is a primary conventional stripper fed at the bottom with steam through its reboiler to heat the solvent and strip it of its $CO_2$ and water vapor while the secondary stripper is using combustion air to further strip the solvent of its $CO_2$ to produce a much leaner solvent to be introduced in the absorber while the $CO_2$ rich air is the directed to the boiler to increase the concentration of $CO_2$ in the flue gas stream which has a positive effect on reducing the overall energy penalty of the capture unit as it leads to increasing the driving force of mass transfer.

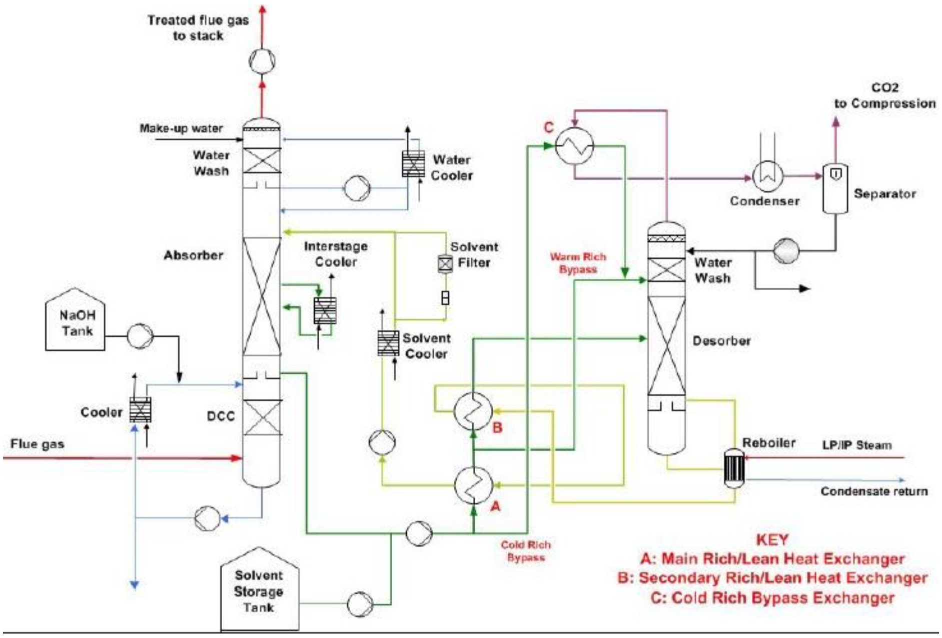

Figure 2.11 Linde-BASF NCCC pilot plant P&ID **Configuration-3 "LB1-CREB"**

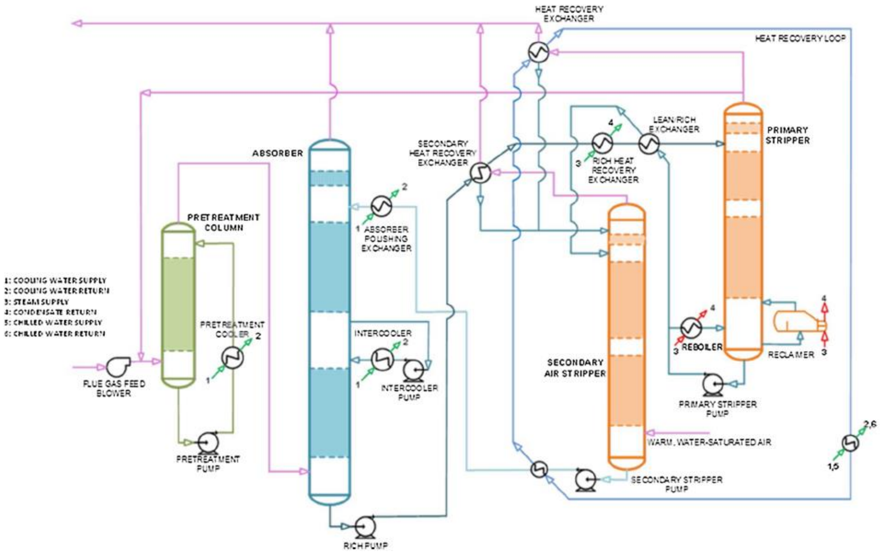

Figure 2.12 UK CAER, University of Kentucky Pilot P&ID

The reboiler as well was reported in this study where they varied between Welded plate thermosiphon HX, Shell & tube and kettle-type reboiler. Usually, the reboiler is fed with steam extracted from the steam turbine which is the main source of penalty in the power plant. However, in power plants that is not planning to extract steam from its turbine which is the case of Niederaussem pilot plant Figure 2.13 [19] or in university/lab based pilot plants where the steam turbine is not available which is the case of LTD pilot plant University of Kaiserslautern pilot or in mobile test units of Aker solutions, electrical steam generators were used to generate steam to heat up the solvent. A comparison between different types of reboilers can be found in Table 2.2 while keeping in mind that choosing the type of reboiler has many factors affecting this decision such as the cost and its tendency to fouling and the need to maintain it.

| **Thermosiphon Reboiler** | **Shell and tube reboiler** | **Kettle-type reboiler** |
|---|---|---|
| • Very simple to design<br>• Based on the natural circulation of fluids to produce vapor<br>• Better for small scale projects<br>• A relatively low heat transfer coefficient<br>• Needs more heat transfer area→ not suitable for mobile units & offshore applications.<br>• For small scale pilot plants, it could be effective cost wise.<br>• For large scale it might not be the best option | • Heat transfer coefficient is higher than thermosiphon.<br>• More efficient<br>• suitable for high capacities<br>• Complex design<br>• Requires More maintenance.<br>• More expensive than Thermosiphon | • High heat transfer coefficient<br>• Steam heating coil<br>• Self-contained equipment i.e., no external parts.<br>• Highest maintenance cost<br>• Most expensive |

Table 2.2 A comparison between different types of reboilers found in the studied pilots.

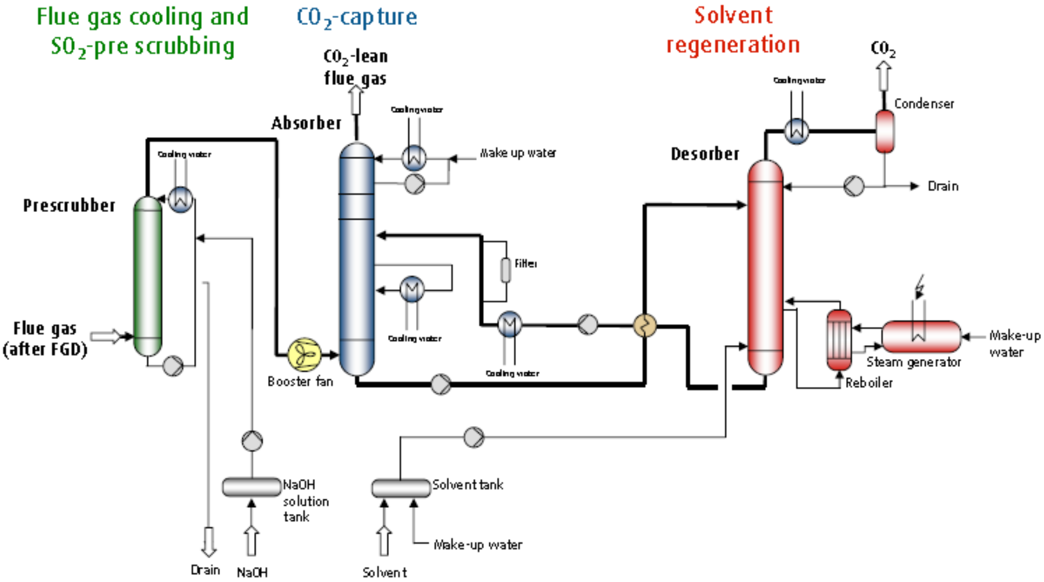

Figure 2.13 Niederaussem Pilot plant P&ID

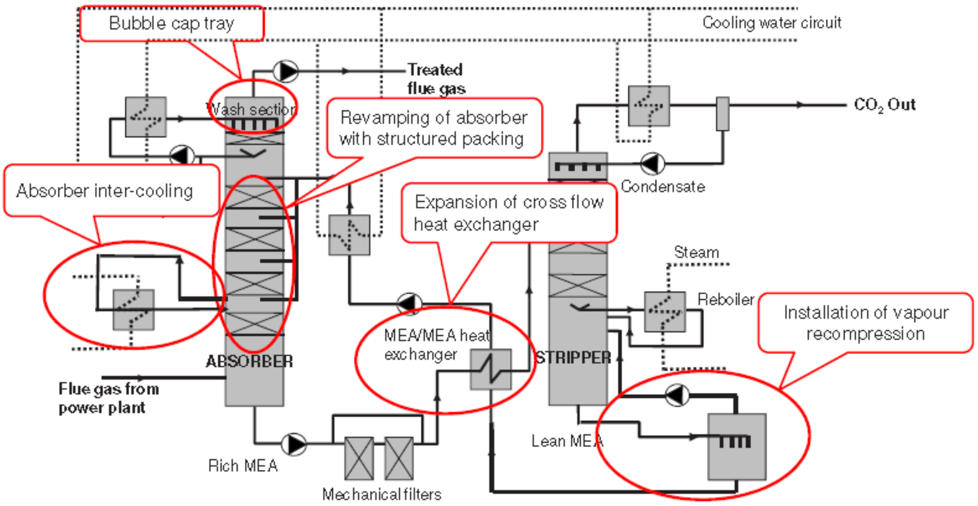

Figure 2.14 Esbjerg pilot plant (CESAR project) P&ID

It's good to know also that CESAER project Figure 2.14 [13] is an upgrade to the CASTOR project done in Esbjerg power plant where changes can be seen in:

- the addition of an absorber interstage cooler between the second and the first bed from the bottom.
- Installation of a lean vapor recompression (LVC) unit on the lean solvent exiting the stripper's sump.

- Changing the IMTP50 Random Packing in the absorber with Mellapak 2X Structured packing to enhance mass transfer and increase the absorption efficiency.
- Changing the packing of the water wash section on the absorber side from Mellapack 250Y structured packing to Bubble cap trays for better washing performance.

A comparison between 4 different packing types has been reported in Table 2.3

| **Mellapak 2X Structured Packing** | **IMTP50 Random Packing** | **Sulzer Mellapak CC3** | **Flexipac 2X** |
|---|---|---|---|
| higher efficiency and better mass transfer performance than Mellapak 2X<br>Large surface area<br>Better and more uniform distribution of liquid and gas<br>Less probability of channeling<br>Very Expensive due to complexity of design and installation<br>More susceptible to fouling and requires more maintenance | Less expensive<br>Better choice if the budget is a crucial factor.<br>Easier installation<br>Lower mass transfer performance than structured packing<br>More effective than structured packing at high Liquid flowrates i.e., less tendency to flooding.<br>Less susceptible to fouling and easier to clean.<br>If the choice was made for small absorbers→ better use random packings [lower pressure drops] | corrugated sheet packing<br>More compact design than Mellapak 2X<br>Higher liquid and gas capacity<br>More suitable for high gas and liquid flow rates<br>Provides a lower pressure drop.<br>Very Expensive and not suitable for budget restricted projects. | • corrugated sheet packing<br>• More flexible design than Mellapak 2X<br>• Lower pressure drop than Mellapak 2X→ energy savings<br>• Very Expensive |

Table 2.3 Packing types used in the absorber in different pilots.

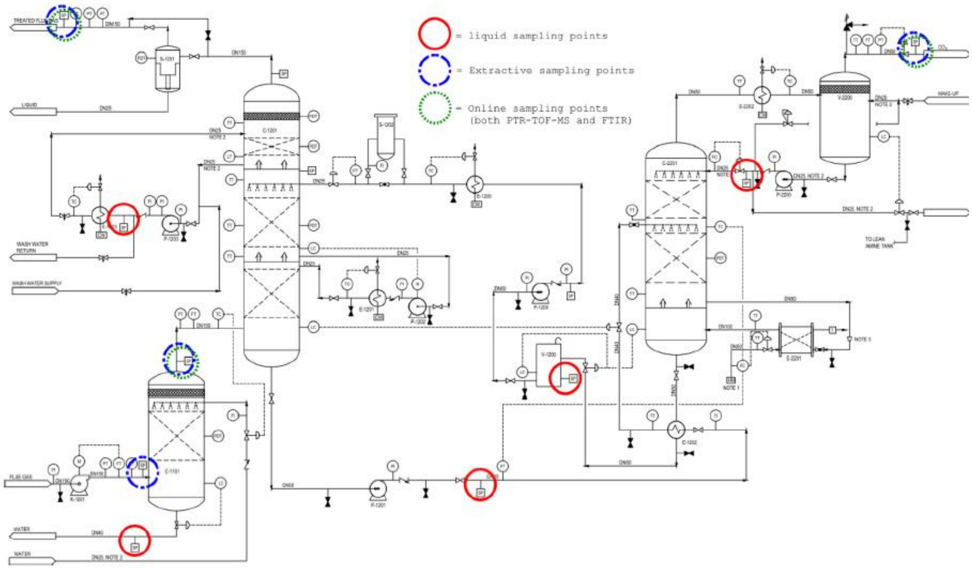

Figure 2.15 WTE Fortum Oslo Varme (FOV's pilot) P&ID

Figure 2.15 [20] shows a conventional absorption a conventional absorption-stripping P&ID of the Fortum Oslo Varme WTE pilot plant while Table A.1 listed all the absorber side features such as the number of absorbers, absorber's diameter and height as well as the type of packing and the number of packing beds and height of packing. It is to be noted that not all the data was available as some of it was not explicitly written in the references and was difficult to get. It is also to note that almost all the absorbers were operated at atmospheric pressure of slightly above.

Table B.1 on the other hand includes most of the stripper aspects that were collected from all the references listed in the Bibliography including number of strippers, stripper diameter and height, as well as the type of packing in the stripper and the height of the packing beds. Stripper interstage heating was only adopted in the Linde-BASF NCCC. However, among 3 tentative configurations for the Linde-BASF NCCC pilot plant, only the 3rd layout Figure 2.11 with the heat recovery was chosen to be implemented.

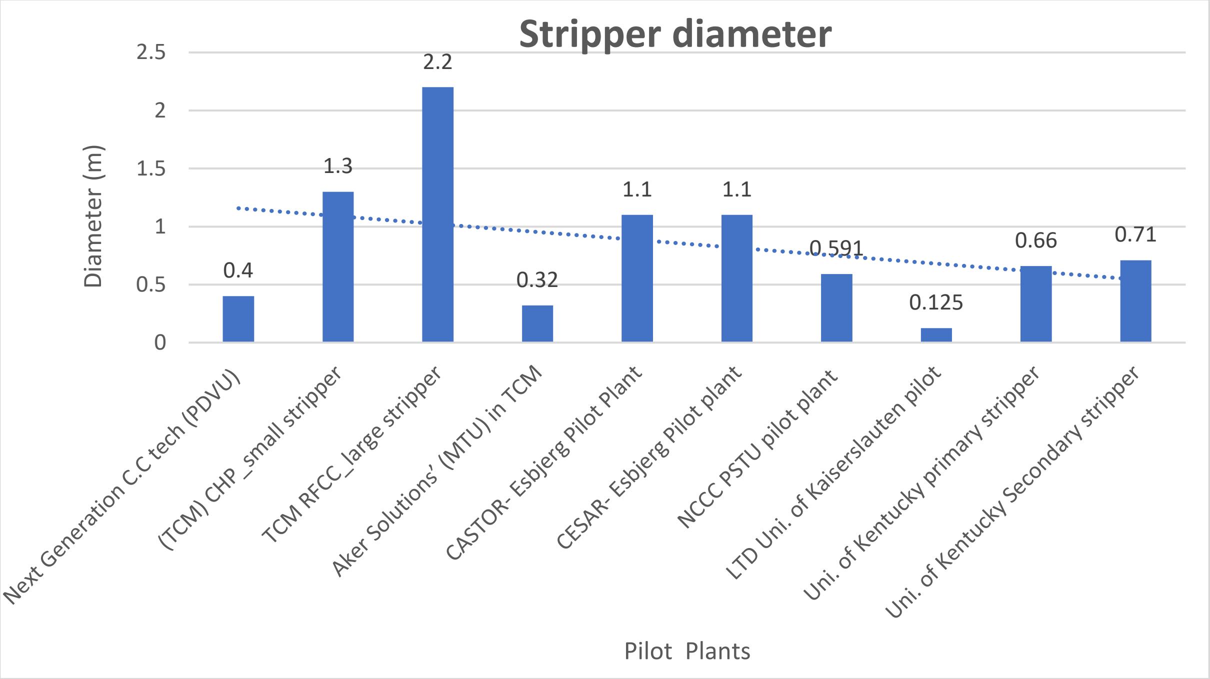

Figure 2.16 Stripper diameter in different pilot plants

Trends are going towards smaller stripper diameters as seen in Figure 2.16 which is matches with the trend towards mobile units which aims at reducing cost of construction but also transportation and erecting. Moreover, strippers now are being operated at high pressures even up to 10 bars which is believed to have an overall positive benefit over the total capture cost.

## 2.5 CO2 compression units

The main goal of the whole carbon capture unit is to produce a high purity stream of $CO_2$ which is produced by cooling the vapor stream leaving the stripper and flashing it to remove water/condensate then the vapor stream passes through a train of compression, cooling and flashing to further separate the condensate that contain impurities and keep a high purity $CO_2$ stream that is compressed and liquified which is to be either stored in depleted reservoirs or to be used in EOR applications or to be shipped to other locations where it can be used in other industries. However, in smaller scale applications such as pilot plants that still test the feasibility of applying a full-scale unit, a relatively small amount of $CO_2$ is being captured which is not economically enough to be shipped and used due to the high compression energy. Consequently, $CO_2$ compression units are eliminated from the whole unit and thus saving a large capital cost needed for the compressors, coolers and the flashing tanks.

The $CO_2$ captured is either sent to the stack to be ejected along with the depleted flue gases or recycled back to the flue gas absorber inlet to increase the concentration of $CO_2$ in the flue gas. The higher the concentration of carbon dioxide available in the flue gas, the easier it is to capture it due to the increase in the mass transfer driving force which means that post combustion capture process is more suitable for high $CO_2$ content flue gases resulting from coal combustion, cement kilns, waste to energy power plants and RFCC in refineries.

Many pilot plants tested the effect of the increase od $CO_2$ content on the reduction of the specific reboiler duty such as the UK CAER, University of Kentucky Table E.1 as well as NCCC. Unfortunately, increasing $CO_2$ concentration can have a negative effect on the solvent's lifetime as it can lead to an increase in the degradation rate of the solvent and thus leads to an increase in the operating costs. In large scale applications were recycling the already captured $CO_2$ is not the case not only due to its economic value but also the capacity of the absorber, a typical secondary stripper configuration can be adopted such as the one in the UK CAER, University of Kentucky where the combustion air is further heated and introduced to this secondary stripper resulting in a much leaner solvent while the combustion air which is so rich in $CO_2$ is directed to the boiler where it takes part in the combustion process while guaranteeing a a flue gas stream with higher $CO_2$ content. This configuration for sure requires a higher capital cost needed to purchase a secondary stripper but could lead to a much lower energy penalty if combined with one of the new solvents which are considered fast solvents in terms of capturing and regeneration as well as having a higher cyclic capacity to capture more $CO_2$ with less solvents.

## 2.6 Flue gases

Flue gas emitted from different power plants, chemical plants, refineries and cement kilns have different compositions, flow rates and concentration of pollutants depending on the type of fuel being combusted as well as the combustion technology adopted. Moreover, the operating mood plays a great role in the concentration of pollutants, $CO_2$, and oxygen levels in the flue gases. For instance, off peak moods require that those plants and in particular power plants continuously ramp up or down to follow and satisfy the demand side which requires operating at excess air and consequently a higher concentration of oxygen in the flue gases which leads to the higher oxidation rate of the amine solvents i.e., a higher solvent's degradation rate. In addition, starting up and shutting down those power plants has a great influence on the rate of emissions and in particular the amine emissions and VOC due to the deviation from optimal working conditions.

### 2.6.1 Source

In this study, 13 pilot plants were studied which were applied to different flue gas types. The performance of these pilots as well as the design and type of solvent depends greatly on the source of fuel being burned as seen in Table 2.1. Moreover, the type of instrumentation adopted and in particular for gas and liquid analysis depends on the type and concentration of some compounds such as $SO_3$ and other pollutants. For instance, coal-fired power plants flue gases are rich in carbon dioxide as well as $SO_2$ and $NO_x$. Moreover, combusting this type of fuel is done at a high air to fuel ratio which makes the stream rich in oxygen. High concentration of oxygen requires a more robust solvent that has a low degradation rate or in other words less reactivity with oxygen. A high $SO_3$ concentration requires a specific pre-treatment in the DCC through water and acid wash sections to avoid solvent degradation as well as destroying the FTIR sensors due to the sulfuric acid produced. Particulate matter is also another concern as it can lead to an increased amine emission in the form of aerosols condensed on those fine particles.

WTE, cement kilns and RFCC from refineries are characterized by high VOC emissions in addition to a high concentration of hydrogen chloride (HCl), oxygen, $SO_2$ as well as heavy metals. Despite the advantage of having a high concentration of $CO_2$ in the flue gases that helps in increasing the driving force for mass transfer and thus, reducing the SRD, this type of flue gas needs a specific pre-treatment due to the high degradation rate that it can induce on the solvent. Consequently, carbon capture from these types of plants has to be done using advanced solvents that have proven better results compared to MEA 30%. Flue gases from WTE, cement kilns, coal and biomass fired power plants should be treated and cleaned with high efficiency flue gas cleaning systems such as selective non-catalytic reduction (SNCR), selective catalytic reduction (SCR), electrostatic precipitators (ESPs), fabric filters (FFs), and flue gas desulfurization (FGD) systems before being introduced to the carbon capture units.

Flue gases from natural gas fired plants on the other hand are easier to treat due to the absence of particulate matter as well as the low concentration of $SO_x$ and $NO_x$. For this type of flue gases, MEA solvent combined with some technologies dedicated for enhancing energy performance such as absorber interstage cooler and a LVC can be a good match if new solvents are not available.

### 2.6.2 Pretreatment and conditioning

Flue gases leaving the last stage of the flue gas cleaning system are still at a relatively high temperature. Moreover, water levels there are not in saturation condition which can cause a loss in the solvent due to the absorption of water that is contained within the solvent. Finally, even though flue gases have been passed through desulfurization and de-NOx systems, they still have significant amounts of $SO_x$ and $NO_x$ which can lead to corrosion in the absorber as well as in other equipment of the capture units. These $SO_x$ and $NO_x$ can also lead to the formation of aerosols which can lead to the loss of amines due to the deposit of amines on those fine droplets. Consequently, flue gases have to be conditioned and prepared for the absorption process through a DCC where flue gases are washed with water to lower its temperature, remove some of the $SO_x$ and $NO_x$ and saturate the flue gas with water to avoid solvent loss. As seen in Table G.1, most of the pilot plants included a DCC with only water. However, plants that use coal as a source of fuel included also acid wash such as Niederaussem pilot plant which used NaOH acid wash to treat the flue gases from lignite coal as well as UK CAER University of Kentucky used soda Ash to treat flue gas in DCC. In fact, the $SO_2$ concentration in the flue gases was adjusted to a low concentration of lower than 5 ppm [10] [5] before being introduced to the absorber.

On the other hand, PACT facility and CASTOR pilot plant excluded the DCC from their design where PACT facility is still on a lab base scale, and they are not actually treating flue gases but instead mixing gases to simulate the flue gas composition of coal and thus there is no NOx or SOx present. Esbjerg pilot on the other hand is actually treating flue gases and the exclusion of the DCC could be made intentionally to test the effect of the impurities in the flue gases on the advanced solvents in terms of degradation rate and make-up and reclamation.

NCCC Linde-BASF pilot plant was the only pilot that included the DCC along with the absorber column with its post-absorption washing beds all in one column. This was done for better heat integration and to reduce the footprint of the whole unit to facilitate transportation and reduce the installation costs.

### 2.6.3 Position of flue gas blower

The flue gas blower is considered a significant load in carbon capture due to the huge volume of flue gases present at a high temperature before the DCC. Moreover, the presence of SOx and NOx in flue gases from WTE and coal fired plants causes corrosion in those blowers. Consequently, attempts were made to reduce this power consumption by simply shifting the position of the fan from upstream the DCC to downstream the DCC or even downstream the absorber as seen in Table G.1. Flue gases at the exit of the DCC are at a lower temperature (~40°C) and consequently the volume flowrate is reduced accordingly. Downstream the absorber, and in particular after the water wash section, flue gases are at a similar temperature as the absorber inlet (for water balance closure) but it is much lower in terms of mass flowrate due to the $CO_2$ that was captured as well as the excess water and the other pollutants. The NCCC Linde-BASF pilot plant which placed the flue gas fan at the exit of the reboiler reported a reduction in the blower duty by ~13% [21]. Moreover, Corrosion in the fan blades and casing can be reduced significantly with adopting such configuration.

### 2.6.4 $CO_2$ Concentration

Carbon capture process is a mass transfer dependent, and the main driving force is the concentration of $CO_2$ in the flue gases which means that flue gases with higher $CO_2$ concentrations will result in a higher driving force and consequently, a better mass transfer and a lower absorption surface area needed for absorption. This means a lower cost needed for the packing beds, lower absorber diameter and a lower flowrate of solvents. Thus, carbon capture is very advantageous for highly $CO_2$ concentrated flue gases from WTE, coal-fired plants, cement kilns and refineries' RFCC despite all the challenges resulting from the other contaminants and pollutants present in those types of flue gases. However, for low $CO_2$ applications such as natural gas fired power plants and other industries that depend on clean fossil fuels, increasing the $CO_2$ in the flue gas stream is still possible by adopting the University of Kentucky's layout Figure 2.11 and Figure 2.12 where a secondary stripper was adopted to further reduce the loading of the lean solvent to very low levels. The secondary air stripper which is described in detail in section 3.2.1 where the lean solvent leaving the primary stripper's sump is directed to the further stripper in a secondary column with preheated air. At the top of the secondary stripper, the air stream becomes highly rich in $CO_2$ while the solvent at the bottom is pumped to the polishing condenser with a very low $CO_2$ loading which helps increase the cyclic capacity of the solvent. The $CO_2$-laden air is then directed to the main boiler to be used in combustion and by doing so the flame temperature of the burners is reduced, which helps in reducing the thermal NOx. Moreover, the concentration of $CO_2$ in flue gases is increased which will positively affect the performance of the capture unit. Figure 2.18 and Figure 2.17 [5] represent the campaigns performed in the University of Kentucky to test the effect of increasing the $CO_2$ concentration in the flue gas on the energy consumption. In the higher $CO_2$ concentrations, more steam had to be injected in the reboiler to further reduce the solvent's $CO_2$ loading. This will lead to increase of the cyclic capacity to capture the additional $CO_2$.

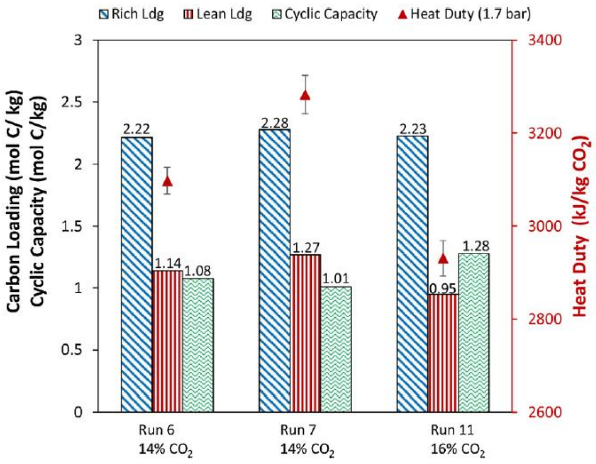

Figure 2.17 Solvent performance comparison for inlet CO2 concentrations of 14 and 16 vol% at a stripper pressure of 1.7 bar.

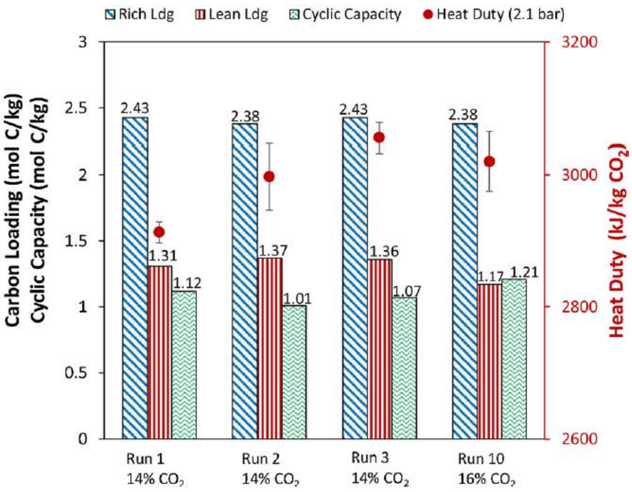

Figure 2.18 Solvent performance comparison for inlet CO2 concentrations of 14 and 16 vol% at a stripper pressure of 2.1

## 2.7 Dynamic scenarios

Several dynamic scenarios were implemented in a study in PACT facility [11] to simulate real operations that can occur to a CO2 capture unit associated to a coal fired power plant. As mentioned before starting up and shutting down large power plants is not an easy operation that requires operating the power plants in an off-design mode which influences the overall performance of the power plant and consequently the CO2 capture unit attached to it. Thus, efforts are made to increase the flexibility of these capture units to cope with the effects of the increase of the share of intermittent energy produced from renewable sources.

### 2.7.1 Plant shutdown

For big power plants such as coal fired ones to shut down, the plant first ramps down to the minimum stable generation load which is in this case 30% of the baseload. Below this limit the combustion becomes incomplete and the flue gases start to be rich in pollutants resulting from this inefficient combustion which will consequently damage the solvent due to the high concentration of NOx, SOx and O2. Once the flue gas flowrate becomes zero, two main actions are taken:

1) hot water/ steam is continuously fed at a progressively lower rate to the reboiler to regenerate the solvent and liberate the CO2 captured within it and prepare the solvent for the next startup.

2) Solvent flowrate is reduced to 50% and is kept circulating till the rich and lean solvent CO2 loading converges and becomes equal.

As soon as the shutdown starts, the $CO_2$ capture efficiency increases because the L/G ratio is increasing (same Solvent flow rate with a reduced gas flowrate while keeping the same regenerating steam flowrate). Consequently, the rich solvent loading decreases because less amount of $CO_2$ is captured with the same amount of solvent. Once the steam flowrate starts to decrease, the lean loading starts to increase till it converges with the rich one. Moreover, the temperature profile of the absorber changes continuously with a temperature peak shifting from top part to the lower part of the packing.

### 2.7.2 Plant startup

Two startup scenarios were studied here which are preceded by a single shutdown scenario discussed before in the same study at PACT facility which are later summarized and compared in Table 2.4

| | **Scenario-1** | **Scenario-2** |
|---|---|---|
| **Steam extraction** | After the LP steam reaches full load | Once the Flue gases are introduced to the absorber |
| **$CO_2$ emissions over the startup stabilization time** | 25.1 kg m $CO_2$ | 10.3 kg m $CO_2$ |
| **Steam consumption** | - | 23.6% more than in Scenario-1 |
| **$CO_2$ efficiency drop-off** | 33% | 70% |
| **Stripping temperature** | Reached after 120 mins | Reached after 60 mins |
| **Total residual $CO_2$ emissions over 16 hrs shift** | 79.4 Kg | 64.6 Kg |

Table 2.4 Comparison between the 2 startup scenarios

### Scenario 1

Here steam is not bled from the low-pressure steam turbine unless it reaches full load which requires a long time before $CO_2$ capture efficiency reaches the desired level. As illustrated in Figure 2.19 and Figure 2.20 [12], once the gas is introduced to the absorber at **point 1**, the $CO_2$ capture rate is very high due to the high L/G ratio but then drops quickly at **point 3** because at this time still hot water/steam is not being introduced to the reboiler which leads to a higher lean solvent loading because simply we are capturing a lot of $CO_2$ without regenerating the solvent properly. Thus, the absorption driving force i.e., the difference between the rich and lean loading decreases. Regarding the temperature profile in the absorber, at the beginning the peak temperature is close to the bottom and continues to migrate towards the top of the tower until the point where the solvent flowrate is increased to the full base load. At this point the peak temperature point starts shifting towards the bottom of the absorber at **point 2'** where most of the $CO_2$ is absorbed. As the time moves from **point 2' to 3**, the gas flowrate increases resulting in a decrease in the L/G ratio which forces the peak temperature to shift again towards the top of the absorber. from **point 3' to 4**, a decrease in the peak temperature magnitude can be seen but not the location because as mentioned before, the $CO_2$ capture efficiency drops due to increase in the lean loading. From point 5 and onwards, the capture efficiency starts to increase again and the lean loading drops as the reboiler temperature reaches the stripping value and thus temperature peak starts to increase again.

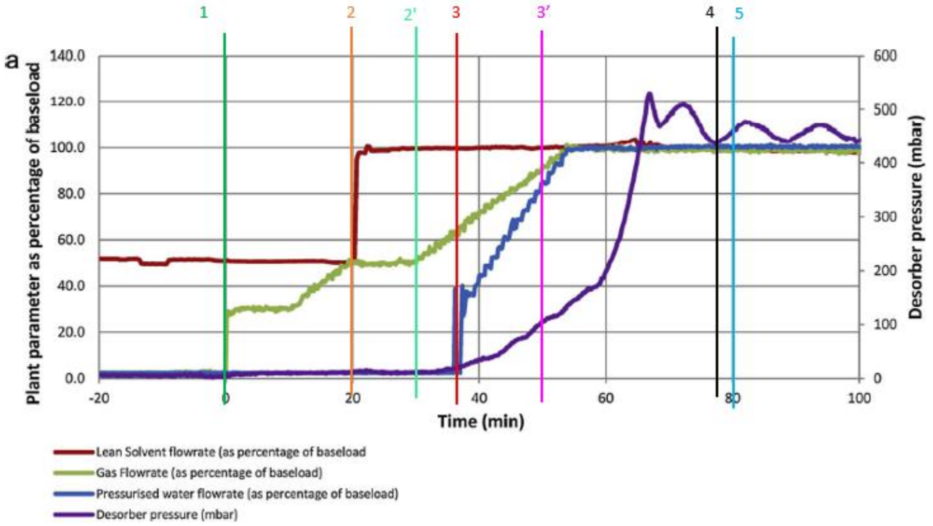

Figure 2.19 Start-up scenario 1 process key parameters

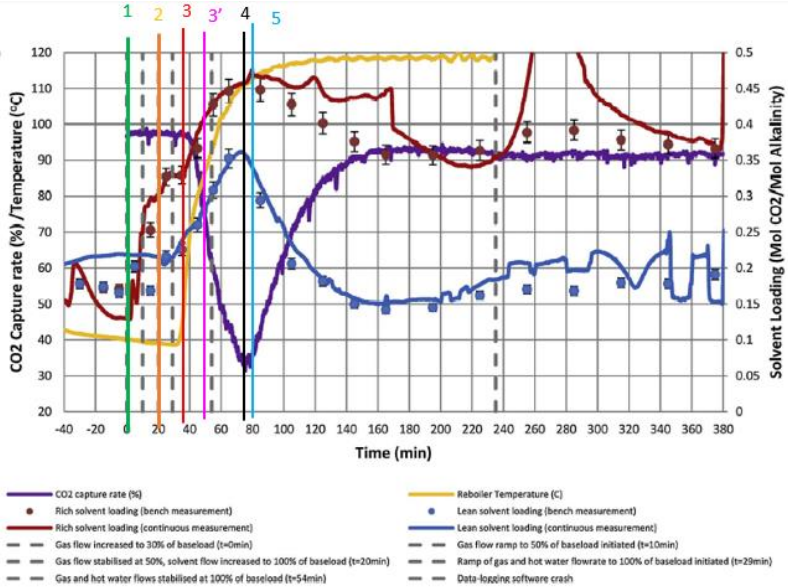

Figure 2.20 Start-up scenario 1 consequences to variation in parameters

**Scenario 2**

The second scenario instead implies the direct injection of steam to the reboiler as soon as it is generated and passes in the low-pressure turbine. In this scenario the plant takes less time to stabilize and reach high capture efficiency. Depending on the situation, it will be decided on the scenario also because different power plants have different scenarios for starting up such as WTE plants and refineries. This scenario is implemented when carbon emission price is very high. In Figure 2.21 and Figure 2.22 [12] we can see that from **point 1 to 2** the lean loading increases because we have a high L/G ratio while the reboiler temperature still didn't reach the stripping pressure. The same results can be seen between **point 2 and 3**. The rich solvent trend can be seen increasing from **point 1 to 3** because of the high L/G ratio during both periods.

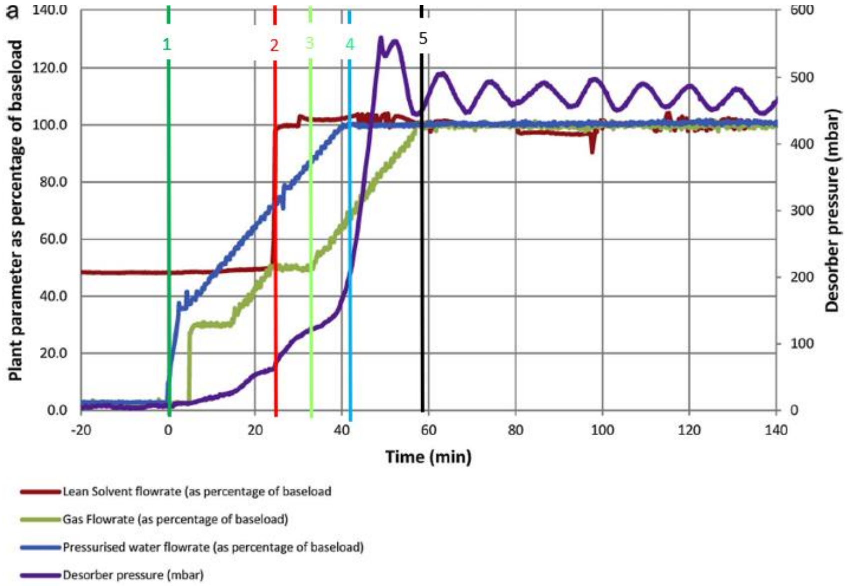

Figure 2.21 Start-up scenario 2 process key parameters

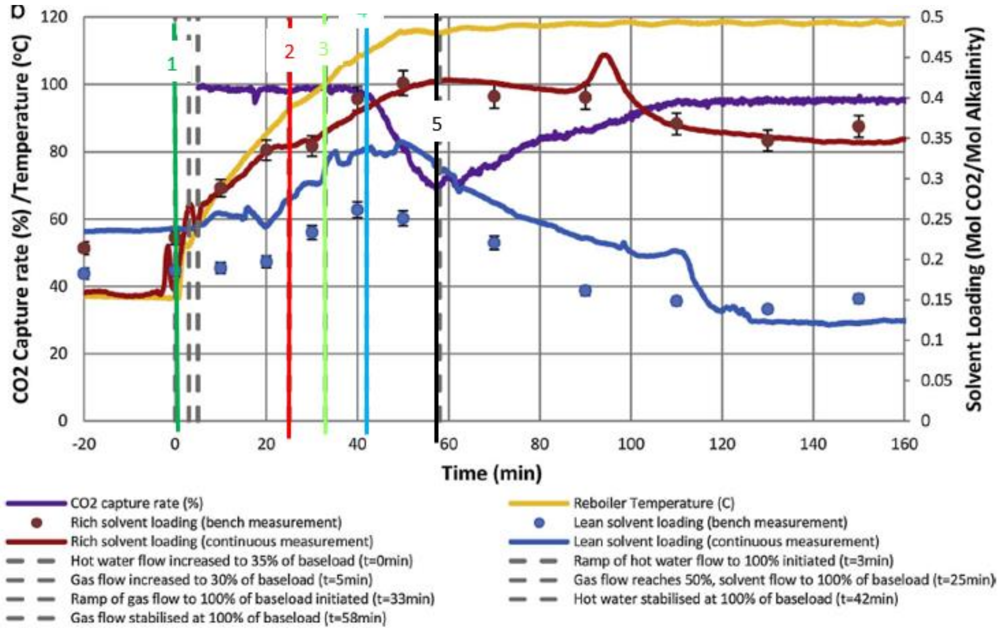

Figure 2.22 Start-up scenario 2 consequences to variation in parameters

## 2.8 Solvents

For many years MEA was the main solvent being used in post combustion carbon capture process. However, the main problem was the high regeneration energy required at the reboiler which results in a high penalty for the power plants. Moreover, degradation rates of MEA were very high due to its relatively low thermal stability and high reactivity with flue gas impurities. All this lead to high operating costs and pushed towards new solvents which are more robust, faster than MEA and by robust it is meant that it has a higher thermal and chemical stability and a larger cyclic capacity and by faster it is meant that these solvents are highly reactive with $CO_2$ and consequently require less mass transfer area and also easier to regenerate in the stripper and thus require lower regeneration energy in the reboiler. However, MEA solvent is still being used nowadays in running campaigns in new pilot plants as a reference to compare the performance of the new solvents to. Thus, in the following tables concerning the regeneration energy and emission rates, it was mentioned in some cases the results of the MEA campaigns and the new advanced solvents to understand how much these robust these new solvents can save in terms of energy and costs. Figure 2.3 gives an idea of how advanced solvents can enable smaller size pilots such as MTU or the JUST-CATCH to capture more $CO_2$ than a larger scale plant as TCM.

In this study, 14 innovative solvents have been tested and used in the pilot plant studied in this research and are listed in Table 2.5.

### 2.8.1 Solvent make-up

Solvent make-up is an essential aspect in large scale capture units to compensate for the solvent being lost in various forms such as entrainment and aerosols being emitted at the absorber's top as well as the solvent thermal and chemical degradation. Solvent Make up is an additional cost on the plant as it requires an additional pump as well as a solvent storage tank. However, on pilot scale level of capture plants, it was intentionally excluded in some projects or not brought in operations to better understand the effect of amine concentration on the solvent degradation rate (both thermal and oxidation) as well as amount of emissions. This could be beneficial to better understand the solvent degradation rate of new solvents being tested or already known solvents but being tested on flue gases from a new source. For instance, UK CAER University of Kentucky decided to exclude solvent make up during the first 800 hours to better understand the effect of coal fired flue gases on the H3-1 solvent. Unfortunately, solvent make up rates were not explicitly reported in this study due to the lack of information in the referenced papers being reviewed. However, it was mentioned in MEA Campaign [3] that the solvent losss in terms of pure MEA was 1.6 ± 0.1 kg per each ton of CO2 captured where the major loss was in the form of ammonia emissions (67%) while (16%) was lost in the form of identified degradation products.

| | |
|---|---|
| Gustav 200 | Used in **Niederaussem pilot plant** |
| Ludwig 540 | Used in **Niederaussem pilot plant** |
| DC-103 | Used in **Fagerlund Cansolv WTE Fortum** |
| S 21 & S 26 | Used in **Technology Centre Mongstad (TCM) & Aker's MTU in Mongstad** |
| CASTOR-1 & CASTOR-2 | Used in **Esbjerg plant** |
| CESAR-1 & CESAR-2 | Used in **Esbjerg plant, Niederaussem pilot plant and Uni. of Kaiserslautern** |
| OASE® blue solvent | Used in **Niederaussem pilot plant & NCCC** |
| Ionic solvents | Used in RECODEH2020 in Greece |
| KS-1™ | Mitsubishi Heavy industries &Kansai electric<br>• aqueous solution of a sterically hindered amine. SRD~ 3 GJ/$t_{CO2,}$ 20% less than MEA |
| Siemens AAS | Siemens & E.on<br>• Aqueous solution of an amino acid salt. Regeneration heat ~ 2.7 GJ/$t_{CO2}$ |
| H3-1 | Used in UK CAER University of Kentucky's pilot |

Table 2.5 Advanced solvents used in the studied pilot plants.

### 2.8.2 Solvent regeneration

Solvent regeneration is done through heating up the rich solvent in the reboiler through a heat source. Usually, the heat source is low pressure steam extracted from the steam turbine unless the pilot plant is equipped with an external steam generator or an electric reboiler. This is mainly the biggest energy penalty in power plants and especially in peak hours where the price of electricity is very high. Different attempts were made to reduce the regeneration energy through:

- Adopting new solvents which can be generated at a lower heat duty while guaranteeing similar cyclic capacity or better than MEA. This is achieved through lower L/G ratios offered by the new solvents.
- Adopting LVC configurations to extract additional $CO_2$ and vapor from the lean solvent and reintroduce them to the stripper and consequently reduce the amount of steam required for generating the stripping agent i.e., the reboiler.
- Adopting various dynamic scenarios that aim at storing $CO_2$ within the solvent during the peak hours by reducing the amount of steam extracted from the turbine while pumping more lean solvent that is available in additional reserve tanks as discussed in section 2.7. In this way the lean loading as well as the capture target can be kept to similar levels while the solvent is regenerated in the off-peak hours. This strategy maximizes the exporting of electricity to the grid. However, additional costs are needed for pumping and for the solvent reserve tanks.

### 2.8.3 Solvent filters

Solvents are subjected to high chemical and thermal stresses through their cycle in the capture unit and especially in the absorber and reboiler. Flue gas impurities such as $NO_x$ and $SO_x$ as well as high $O_2$ reacts with amine solvents and produce degradation products called heat stable salts which could precipitate in the pipes and equipment and causes clogging if not efficiently removed specially with solvents characterized by high degradability such as MEA. New solvents on the other hand have a much lower degradation rate compared to MEA. Nevertheless, it is considered a must in full scale capture units to have a solvent filter placed on the rich solvent line exiting the absorber as degradation is going to happen anyways. On pilot scale, different types of filters were used in cleaning the solvent from the solid particulates and salts such as:

- Mechanical filters
    - Physical barriers to trap the suspended solids in the solvents.
    - Effective at removing larger sizes rather than smaller ones.
- Carbon filters
    - Layers of activated carbon to adsorb impurities suspended in the solvents in addition to physically stopping particulates.
    - High efficiency of removing organic compounds but not suitable for high temperature applications.
- Organic filters
    - Also known as depth filters that consists of layers of fibrous organic materials.

    - Cheap and can handle high flowrates of solvents. However, they have a short lifetime and have to be changed at relatively shorter intervals.
- Cartilage filters
    - A combination of more than one filtration technology in one filter.
    - Expensive and requires special maintenance.

Carbon filters were the most common type of filter being used as seen in Table C.1 and the number of filters vary depending on the size of the pilot plant and consequently the amount of solvent circulating in the unit.

Solvent's purity is an important aspect in carbon capture process as any drop in purity can lead to a drop in the overall capture efficiency of the process. Solvent filters play a great role in maintaining this parameter as high as possible. However, solvent filters lead to a pressure drop on the solvent's side which should be compensated for by pumps. This leads to an increase in the energy consumed by those capture units and Differential pressure gauges are placed on both filter sides to measure the pressure drop on the solvent as it passes through the filters that shouldn't exceed a certain limit and if it does, the filters should be changed.

The choice of the filter should depend on many factors such as the type of flue gas being treated which depends mainly on the type of fuel being burned and the nature of the combustion process which will consequently control the level and the typo of impurities present in the solvent. Moreover, the maximum allowable pressure drop is another important factor as well as the lifetime of those filters i.e., the frequency of changing those filters.

### 2.8.4 Solvent Reclamation

Also known as solvent recovery or recycling, is a thermal process that aims at the reduction of the degradation products levels in the solvent which result from the thermal decomposition as well as the chemical oxidation of the solvent and its reactivity with other impurities in the flue gases such as Sox, Nox. Solvent reclamation is an additional penalty in the power plant because it requires heating the solvent with steam in a dedicated reboiler along with some acids.

Some advantages of solvent reclamation include:

1) Reducing operation expenses

    a) Reduces the purchase of new expenses solvent

    b) Reduces the solvent's shipping/disposal costs

2) Insures continuation of operations

3) Reduces the environmental impact of the whole process

4) Retaining the quality of solvent

i.e., preventing foreign contaminates from reaching the solvent in case of outsourcing the recovery process.

Results of Aker solutions' reclamation process at the MTU in Mongstad "S21&S26" [8]

- No fouling or precipitation were found.
- The total steam demand didn't change between reclaiming and normal operations.
- No increase in amine emissions.
- Color of the solvent changes.
- Amine concentration rises 2-3 wt%.
- 80% Removal of degradation products and impurities.
- HSS dropped from 0.1 mol/kg to 0.03 mol/kg.
- Solvent viscosity decreased.
- No significant increase in emissions. i.e., little or no degradation increase of solvent due to high temperature.

While solvent reclamation is a must in full scale capture units, not all the pilot plants adopted the solvent reclaimer in their configuration as seen in Table C.1, where for some of those pilots, new solvents were being tested and the degradation rate was still unknown and had to be determined for the specific flue gas. This will help in determining the makeup rate and how often should reclamation process take place.

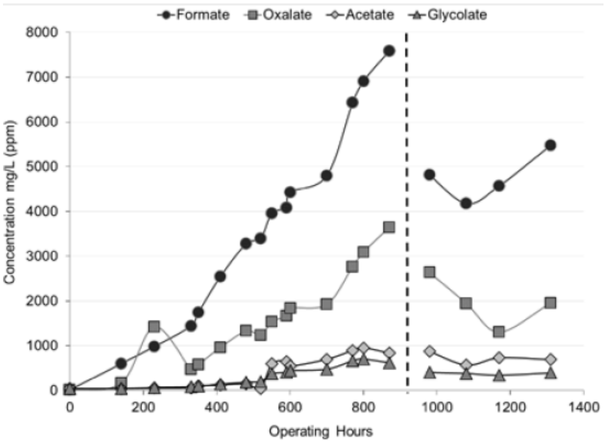

Figure 2.24 Oxidative degradation product formation during MEA solvent testing.

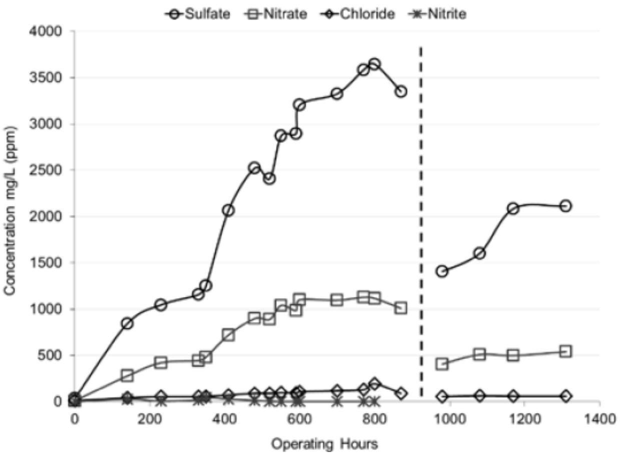

Figure 2.23 Flue gas HSS accumulation during MEA solvent testing.

In the University of Kentucky, MEA solvent reclamation was done after 880 hours as seen in Figure 2.24 and Figure 2.23 [10] where the dashed line represents the duration in which the thermal reclamation was done. HHS formed in the solvent is mainly because of the impurities (mainly Sox and NOx) present in the flue gases resulting from the combustion of coal. Another important reason for the importance of shifting towards new solvents is that $SO_2$ is highly soluble in MEA which can be seen in Figure 2.23 where the sulfate had the highest concentration among the other HSS before reclamation starts. The university of Kentucky reported a steady accumulation rate of sulfate of about 3.76 ppm/hr and a maximum of 3640 ppm before reclamation starts. Moreover, washing the flue gases with soda ashes in the DCC wasn’t so helpful with reducing the sulfates level.

### 2.8.5 Solvent degradation

Solvent is subjected to thermal stresses in the reboiler due to the high temperature needed for regeneration (120 °C) which increases with the increase of the stripper’s pressure forcing the regeneration temperature to exceed 140 °C. Moreover, flue gases from cement kilns, coal fired power plants and WTE plants have significant amount of impurities including NOx, SOx and heavy metals that lead to the formation of HSS as seen in Figure 2.25 [3]. Solvent degradation is considered a loss and leads to an increase in the operating cost, and it is required for the flue gases to pass through a high efficiency flue gas cleaning system to remove these contaminants. Nevertheless, degradation still occurs even with washing the flue gases with soda ash in the DCC. Consequently, moving towards more robust solvents that have very low reactivity with these impurities is very important not only to decrease the specific reboiler duty, but also to reduce the solvent loss and consequently the amine emissions resulting from this degradation. Less degradation means less make-up rates, less emissions, less reclaiming, less waste to be discharged and less corrosion and material consumption.

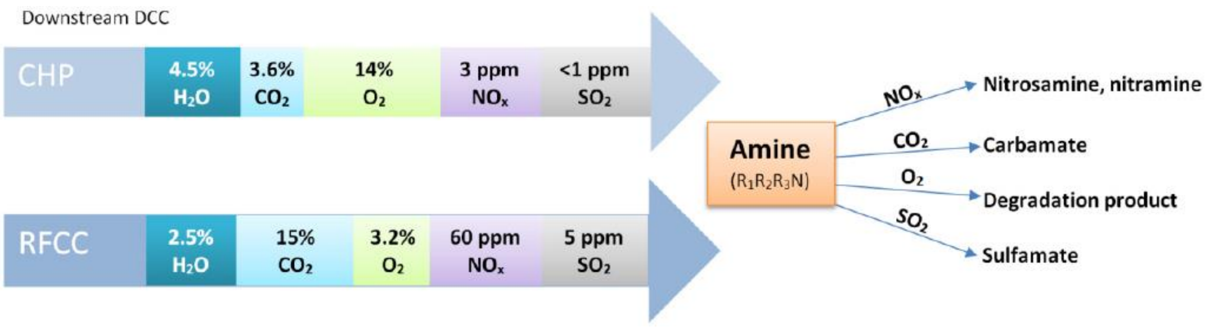

Figure 2.25 The effect of flue gas composition on reaction with MEA.

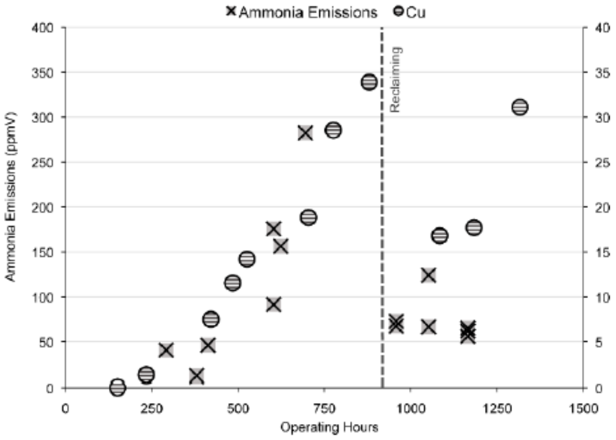

Figure 2.26 Absorber ammonia emissions (in PPMV) compared to the Cu concentration (ppm) in the solvent.

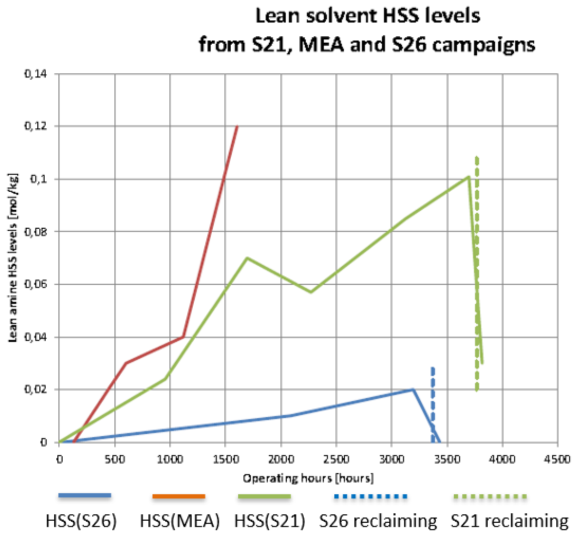

Figure 2.27 Lean solvent HSS levels from S21, MEA and S26 campaign.

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Figure 2.27 [8] reported by Aker Solutions, shows a comparison between 2 advanced solvents S21 and S26 in terms of the peak levels of HSS in the lean solvent as well as the time needed to reach that peak before reclaiming process could start. Table D.1 reports the results of Aker Solutions campaigns for MEA, S21 and S26 where it is clear that the MEA loss is 5 times more than the loss in S21 and 10 times more than S26 which proves that advanced solvents such as S21 and S26 can reduce the operating costs needed for reclaiming the solvent as well as compensating for the lost solvent due to its low reactivity with impurities. Figure 2.26 [10] shows a relation between the $NH_3$ emissions and the concentration of copper in the solvent which could be reduced by reclaiming. However, it is to be noted that copper and brass should be avoided in the equipment through which the solvent passes as these metals can speed up the degradation process of the solvents.

### 2.8.6 L/G ratio

Advanced solvents enable obtaining lower L/G ratios to capture the same amount of $CO_2$. This means that not only the power needed for circulating the solvent is reduced, but also the energy needed for regeneration i.e., the SRD is reduced. Table 2.6 summarizes the different L/G ratios for each pilot plant where it is seen in some campaigns such as in the CASTOR project and the University of Kentucky that used advanced solvents that the L/G ratio obtained by advanced solvents is much lower than the ones used for MEA. It is to be noted that the heat generated from absorption of $CO_2$ in the solvent is discharged into two main components: the sensible heat to raise the temperature of the solvent and the water evaporation. Increasing the L/G ratio will promote the portion of the sensible heat and will reduce the water evaporation.

| | **WTE Fortum Oslo Varme (FOV's pilot)** | **Technology Centre Mongstad (TCM)** | **CASTOR-Esbjerg Pilot Plant** | **UK CCSRC PACT facility** | **NCCC pilot plant** | **LTD pilot plant University of Kaiserslautern pilot** | | **UK CAER, University of Kentucky** |
|---|---|---|---|---|---|---|---|---|
| | | **CHP** | | | **PSTU** | **Gas-fired (Set I)** | **Coal-fired (Set II)** | |
| **L/G** | 2.4-3.1 L/m3 | 0.71–1.27 kg liquid/Sm3 | MEA 30% :- 2.5 , CASTOR-1 :- (2.5-3), CASTOR-2 :- 2 (kg solvent/kg flue gas) | 5 | 3 (unit not specified) | 2.7 kg/kg (0.45 L/G) | 3.5 kg/kg (0.94L/G) | *Average 2.5-3.8 wt/wt* **MEA30%** 3.5,4,5 kg/kg], [**MEA 40%** 3.2,3.5,4], [**H3-1** 3.1,3.7,4] |

Table 2.6 Comparison between various L/G ratios of different solvents for different pilot plants

## 2.9 Amine emissions control

Despite the benefits that post-combustion carbon capture brings to the market in terms of reducing the carbon footprint of many industries while enabling them to use fossil fuels. Yet using solvents can have a drawback in terms of emissions of degradation products such as $NH_3$, nitrosamines, nitramines, sulfates and many others which are very harmful to the environment and even carcinogenic. Amines are emitted to the atmosphere in 3 different phases which are gas phase emissions (volatile), liquid droplets entrainment and mist (Aerosol) formation. These emissions can be avoided by selecting solvents with no tendency to form stable nitrosamines and nitramines as well as using amine abatement technologies specific to each emission phase. Aerosol emission which is considered a major source of amine loss is considered another challenge for pilot plants where they are characterized by very tiny particle sizes that cannot be trapped by demisters or water wash beds. Aerosols were found to increase with the increased voltage of the wet ESP as well as in flue gases that are rich in $SO_3$ which produce sulfuric acid nuclei. As a result, new unconventional technologies were seen in some pilots such as dry beds and Brownian diffusion filter which will be discussed later in this section.

Adjusting some of the working parameters can also lead to the reduction of the aerosol emissions as it was reported by the NCCC [22]. In fact, it was found that amine losses in the form of aerosols can be reduced 5-10 times by:

- Increasing the lean solvent temperature at the absorber inlet.
- Increasing the absorber's pressure.
- Increase the cooling duty of the post-absorption washing section which results in much cooler $CO_2$ depleted flue gases.
- Higher absorption intermediate cooling temperature.

### 2.9.1 Post Absorption and stripping wash on gas-side.

The absorber top is considered the main emission point for amines where the $CO_2$ depleted flue gases leave the absorber carrying amine vapors as well as liquid fine droplets. Similar emissions are found at the stripper's top where the vapors carrying the $CO_2$ could also contain amines. For these vapor emissions, the presence of water wash sections or acid wash sections is crucial in reducing the rate of emission. In fact, cooling down the flue gases with water would lead to the dissolution of those amine vapors in water which would be reintroduced to the absorber or stripper in the form of reflux. Moreover, demisters are considered an important trap for liquid droplets carried with the huge flux of flue gases, especially in case of high superficial gas velocities adopted in the absorber and the stripper. High efficiency demisters could lead to a pressure drop on the flue gas side, but they are essential for reducing the amine emissions. Table G.1 lists down the different number and types of washing beds at the top of the absorber and the stripper where acid wash sections were mainly adopted for flue gases with high $SO_2$ levels.

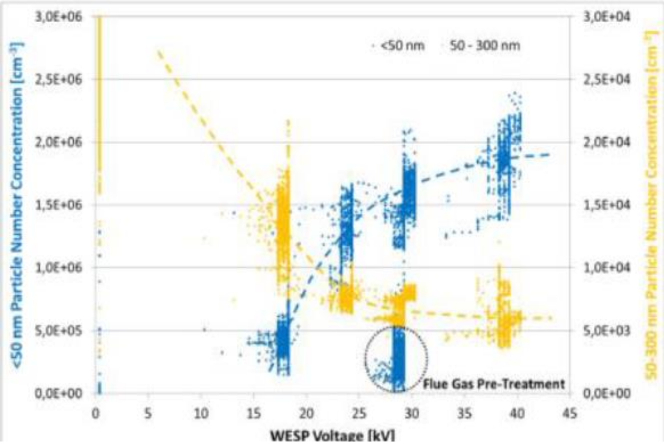


Figure 2.28 Effect of Wet ESP on the increase of ultrafine particulates.

### 2.9.2 Impact of ESP on amine emissions and adopting dry beds

Flue gases resulting from combustion of coal or waste as well as flue gases leaving cement kilns are characterized by high dust flowrates of different sizes. Several technologies are being used to trap and capture these particulates including cyclone, fabric filters and electrostatic precipitators ESP. Figure 2.30 [22] shows the campaign done by NCCC on the flue gases resulting from coal which are characterized by high concentration of fly ashes. The usage of high voltage wet ESP was so beneficial in reducing the concentrations of > 50 nanometer particles to below $10^4$ particles/cm$^3$ [22]. However, this led to the increase of the concentration of ultrafine particles of < 50 nanometer to above $10^6$ particles/cm$^3$ specially as the potential difference exceeds 15k volts as shown in Figure 2.28 [22]. These ultrafine particulates promote the formation of mist and increase the amine emissions in the form of aerosols.

Dry beds were patented and adopted by the NCCC on the absorber side where the absorber is equipped beds through which the $CO_2$ depleted flue gases pass. These dry beds proved their efficiency in decreasing the amine emissions in the form of aerosols while still adopting a high voltage on the wet ESP.

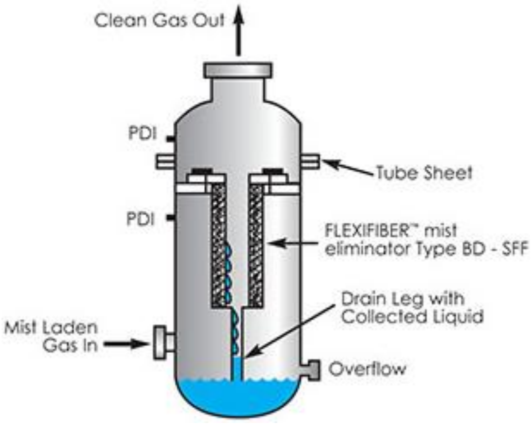


Figure 2.29 Brownian Diffusion filter.

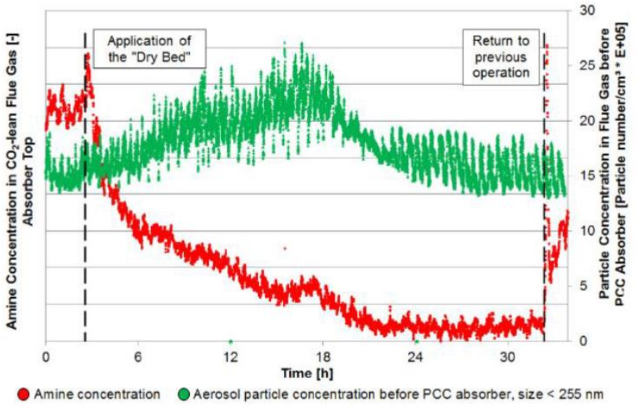


Figure 2.30 The Linde-BASF patented dry beds configuration for reducing amine emissions.

### 2.9.3 Brownian diffusion filters

Brownian diffusion filter is considered an effective way to capture aerosols entrained in the $CO_2$ depleted flue gas where it consists of a wetted rotating brush and a Brownian diffusion type candle filter as shown in Figure 2.29. This type of filter was tested by Aker Solutions in TCM where Aker's MTU is equipped with a special anti-mist unit and to compare its performance, a Brownian diffusion filter which is known for its ability to catch mist of the order of submicron particulates was installed upstream the capture unit. Results showed that by operating the Brownian filters, the mist nuclei were effectively eliminated especially $H_2SO_4$ and consequently the amine emission in the form of aerosols were reduced. In fact, Aker solutions reported in [23] that by using the Brownian diffusion filters, the amount of particulates collected went from 30 mg/Nm$^3$ to less than 1 mg/Nm$^3$. Nevertheless, the amine emission was still high (200pppm) when the Anti-Mist unit was off while it went down to 2 ppm when it was switched on. This can tell that the anti-mist technology designed by Aker solutions is very effective in reducing aerosol emissions.

## 2.10 Foaming

Foaming is considered a common issue in absorption processes that use solvents to capture $CO_2$ which is unfavored in processes as it negatively affects the overall performance of capturing units. Bubbles are created within the liquid solvent at very high rates and the disadvantages of foaming can include the reduction of the absorption efficiency as well as the increase of the pressure drop due to the work lost in compressing the gas bubbles in the solvent pumps which could lead to the damage of the equipment. This consequently will lead to a reduction in the circulation rate and could lead to flooding in the absorption. Absorber flooding basically means that liquids from lower mass transfer stages i.e., lower trays or lower packing comes in contact with upper stages causing a change in the equilibrium concentration of those stages and leads to a drop in the mass transfer efficiency. Common places in the carbon capture units where foaming could occur is:

- Absorption column
- Flash drum
- Stripping column

Foaming of solvents can occur due to different reasons such as high solvent flowrates or high $CO_2$ loading in solvents especially with MEA. In addition, the presence of accumulations of impurities in solvents can lead to foaming and that is why solvent filtration is an essential process. Finally, the presence of other gases in the solvent can lead to foaming and that is why the solvent selectivity to $CO_2$ should be a priority in selecting the solvent being used. Foaming severity on the other hand depends on the operating temperature and pressure as well as the concentration of $CO_2$ in the gas stream and the presence of impurities. There are various ways for foaming mitigation in chemical processes in general such as:

1. Use of anti-foaming agents
2. Process conditions modification such as P & T
3. Changing the absorber and stripper columns internals
4. Use of foam control devices
    - Foam sensors
    - Foam breakers
    - Foam suppression systems

Anti-foaming agents are designed to reduce surface tension and prevent bubbles from forming and they are added directly to solvents. The most common anti-foaming agents used in CCS units are Silicones, Polyglycols and Fatty alcohols. Despite the necessity of antifoaming agents, they could induce some disadvantages on the carbon capture process as they could lead to the increase of solvent degradation rate and reduce the capture ability of the solvent. To overcome this, it’s necessary to optimize the anti-foaming agent to guarantee the maximum benefit of it while not altering the efficiency of the solvents. Moreover, Innovative solvents have been developed to address foaming issues in CCS such as amino-methylated polyvinyl amine (AMP) which is characterized by a high foaming resistance. New technologies involve solvents that include ionic liquids, amino acid salts and switchable solvents where these solvents have lower volatility, lower viscosity, and higher thermal stability than MEA.

# 3. Enhancing Energy Performance

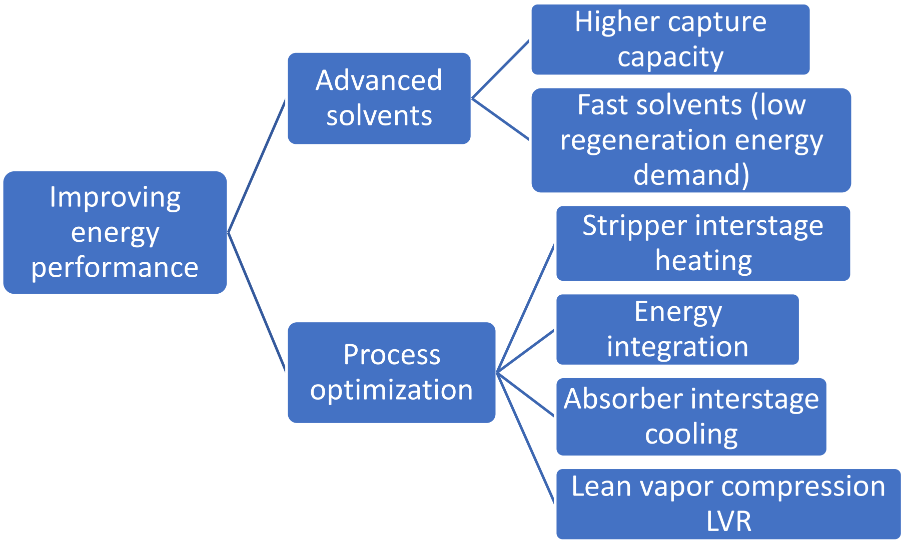


Figure 3.1 Different paths adopted by pilot plants to enhance energy performance for carbon capture.

In this chapter is dedicated to the efforts made to improve the energy performance of carbon capture technology and in particular post combustion technology by absorption with chemical solvents. Carbon capture and storage was initially done by using MEA 30% to absorb $CO_2$ present in the flue gases which results from the complete oxidation of fossil fuels. Despite its efficiency in capturing $CO_2$ that leads to 90-95%, it had a lot of drawbacks such as its high regeneration energy that ranges between 3400-3800 MJ/ton $CO_2$ and could reach up to 4490 MJ/ton $CO_2$ [2]. This energy is translated into low pressure steam being extracted from the steam turbine which is considered a great loss for power plants especially in peak hours where maximum expansion in the turbine is needed. Moreover, MEA solvent suffered a high reactivity rate with flue gas impurities such as $SO_x$, $NO_x$ and excess oxygen. Thermal stability of MEA was also a critical point which limited the temperature at which solvent can be generated in the reboiler and thus affects the levels of $CO_2$ available in the lean solvent (Lean loading) in addition to the generation of HHS. All this led to a higher degradation rate and consequently a higher operating cost needed for reclamation process, filtering and makeup of new solvent. Finally, amine emissions were a great disadvantage for MEA due to its relatively low stability as well as the lack of technologies to address aerosol emissions. Figure 3.1 summarizes various paths in which pilot plants have dedicated their enhancement in to reduce the cost of capturing while maximizing the efficiency. In the upcoming sections each one would be discussed separately while giving a summary of those campaigns dedicated to each key performance parameters.

First attempts to solve the problems arising from the MEA30% solvent was using a higher concentration of MEA which was 40%. This increase in concentration could solve the problem of the high regeneration energy by simply reducing the L/G ratio to as low as 3.2 kg/kg [10] thanks to the higher cyclic capacity of the 40% which allowed to achieve regeneration duty as low as 3024- 3489 MJ/ ton $CO_2$. However, the MEA 40% had lots of disadvantages regarding the increased viscosity compared to MEA 30% which increased the solvent circulating costs as well as the reduced heat conductivity which induced a higher heat transfer area and specially in the Lean-Rich HEX. In addition, the increased amine concentration led to the increase in corrosion rates in the main equipment and in the pipelines and especially at high temperatures and this led to the need for the use of corrosion inhibitors. Nevertheless, the degradation problem remained unchanged because simply the same amine is being used but just at a higher concentration. Consequently, conclusions were made that for the MEA solvent, lower concentrations i.e., diluted solvents are more desirable than higher concentrations for achieving a 90% capture efficiency due to the increased corrosion effect as well as the other disadvantages discussed previously. Diluted solvents have lower viscosity and a much better heat transfer performance and overall are desired in post combustion capture than high concentrated solvents.

## 3.1 Advanced solvents

Pilot plants have been testing and trying new solvents due to the drawbacks of the MEA solvents. As seen in Table 2.5 and Table C.1, 14 new solvents have been tested in various projects where their results were compared to results obtained from MEA 30%. Innovative solvents have shown better performance than MEA in terms of higher cyclic capacity, lower solvent specific regeneration energy, more stable solvents with less degradation rates, as well as being more environmentally friendly. Little information can be found about the composition of those new solvents due to confidentiality of some of those information. However, the most widely used solvent through this study was found to be CESAR-1 and CESAR-2 solvent as they were used in CESAR project in the Esbjerg pilot plant, Niederaussem pilot plant and Uni. of Kaiserslautern's pilot plant. Table 3.1 [17] lists the composition of those two solvents in comparison to the conventional MEA 30% which had much better results in terms of regeneration energy and lower L/G ratio which reached 2900 MJ/ ton CO2 [13] and 2.7 kg/kg for coal fired set up [17] respectively. This enhancement can be seen in Figure 3.2 [17] where the equilibrium curves of both solvents were plotted at high and low temperatures. The larger horizontal distance between the high and low temperature curves is strongly related to the solvent's flowrate and the stripping stream. In particular, the larger the distance, the larger the stripping enthalpy and consequently the lower the regeneration energy as well as the easier separation and the lower optimum solvent flowrate. It is important to know that the regeneration energy is divided into energy for $CO_2$ desorption ($ħ_{desorption}$), energy to heat-up solvent and the condenser reflux "Sensible heat" and the energy to supply the stripping stream. Moreover, the solvent $CO_2$ loading was represented as moles of $CO_2$ per Kg of solvent to give a sense of the solvent's flowrate.

| **Name** | **Composition** | **Note** |
|---|---|---|
| MEA | 0.3 g/g Monoethanolamine + 0.7 g/g Water | Reference solvent |
| CESAR1 | 0.28 g/g 2-Amino-2-methyl-1-propanol (AMP) +<br>0.17 g/g Piperazine (PIP) + 0.55 g/g Water | Mix of primary & secondary amines |
| CESAR2 | 0.32 g/g 1,2-Ethanediamine (EDA) + 0.68 g/g Water | Primary amine with 2 amine groups |

Table 3.1 Composition of CESAR-1 and CESAR-2 solvents.

The optimum flowrates can be seen in Figure 3.3 and Figure 3.4 [17] where the specific reboiler duty was plotted as function of the L/G ratio producing the famous U-shaped curve with a minimum point that represents the optimum operating point of the solvent. CESAR-1 achieved the best performance with a specific reboiler duty (SRD) as low as 3.3 GJ/ton $CO_2$ captured for coal fired setups and 3 GJ/ton $CO_2$ captured for gas fired setups.

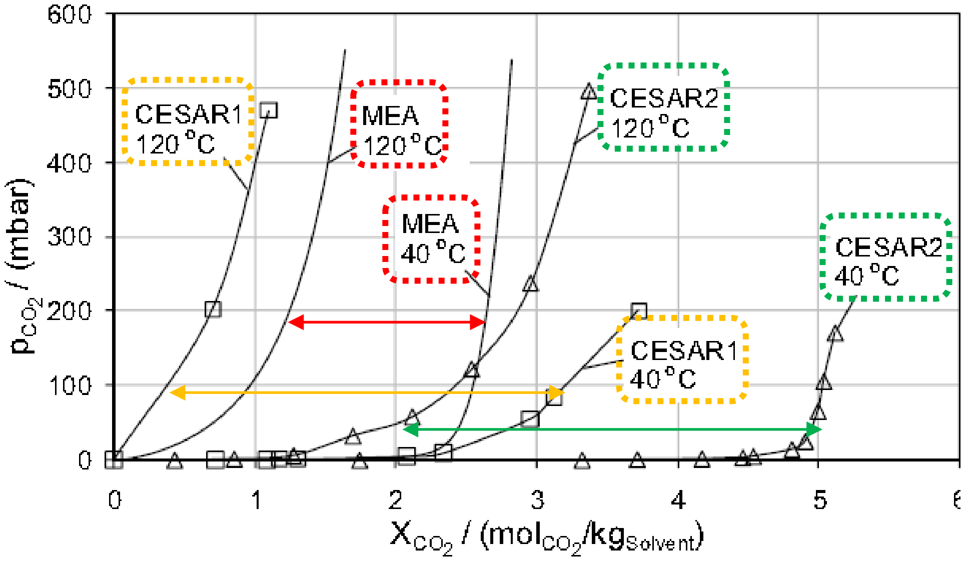


Figure 3.2 Calculated equilibrium data of CO2 solubility at 40 °C and 120 °C for MEA (30%) in comparison to experimental data for CESAR1 and CESAR2.

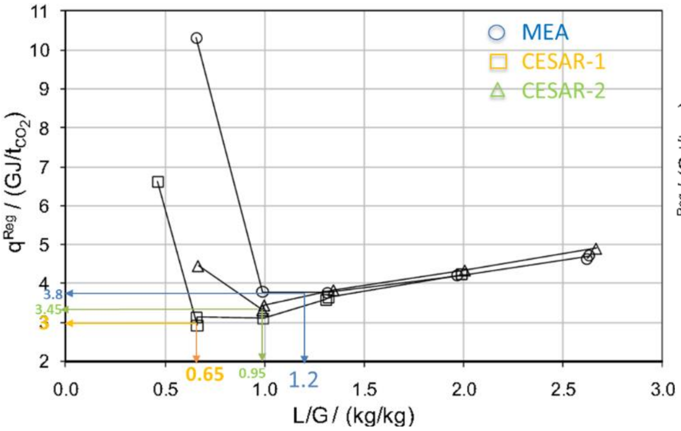


Figure 3.4 Optimum operating point at set I "Gas-fired."

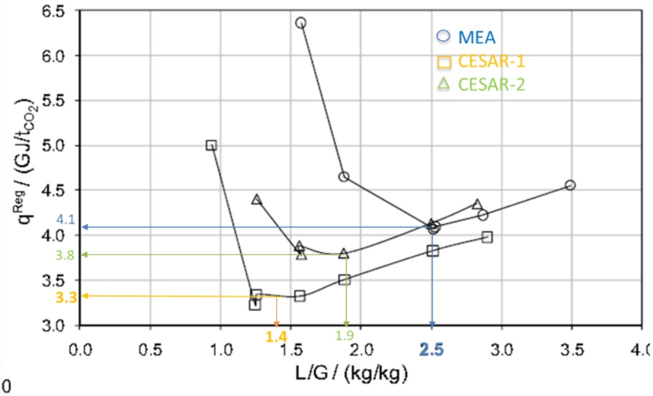


Figure 3.3 Optimum operating point at set II "Coal-fired"

### 3.1.1 Higher Capture Capacity

In compliance with the reduction in the size of pilot plants to shift toward more mobile units. It is important to adopt new solvents that can capture more quantities of $CO_2$. This was seen in the low L/G discussed before in the previous section but also can be seen in Table 2.6. Higher capture capacity could lead to not only reducing the specific energy needed for regeneration but also would result in decreasing the diameter of the absorber and stripper columns which would decrease the capital costs.

### 3.1.2 Fast solvents

MEA solvent's main disadvantages were the high regeneration energy requirement, which results in the high efficiency loss of the power plant as well as its relatively slow reactivity which implies a larger mass transfer area and thus a larger absorber. Trends are moving towards faster solvents which can react faster with $CO_2$, so for the same flowrate of solvent and flue gas, a lower number of transfer stages are required. Fast solvents are also easily regenerated in the stripper's reboiler which means that bonds between the solvent and the $CO_2$ are easily broken and consequently a lower SRD is achieved. Table F.1 lists down all the ranges of SRD achieved by various pilot plant for various innovative solvents where the lowest value was achieved by the H3-1 solvent developed by Mitsubishi Hitachi Power Systems which was (2093.4-3489) MJ/ton $CO_2$ while the average value was 2700 MJ/ton CO2 achieved by Ludwig 540 in Niederaussem and S21&S26 in Aker solution's MTU. In comparison to MEA, this enhancement can reduce the cost of capturing $CO_2$ and thus reduce the levelized cost of electricity.

### 3.1.3 Ionic solvents

Besides the efforts made to design and produce amine-based solvents that have better operating performance than MEA, new campaigns are being done on some plants to text capturing $CO_2$ from flue gases using ionic solvents. Ionic solvents are basically molten salts that melt below 100 $^{o}$C which is totally made of anions and cations. Those solvents are syrupy look-like because their viscosity $\mu$ is slightly higher. They have many benefits such as non-flammability, Negligible vapor pressure, chemical and thermal stability and variable miscibility with other solvents. Producing ionic solvents requires adding a complexing agent to a simple salt where the complexing agent helps in reducing the ionic attraction and thus becomes less solid.

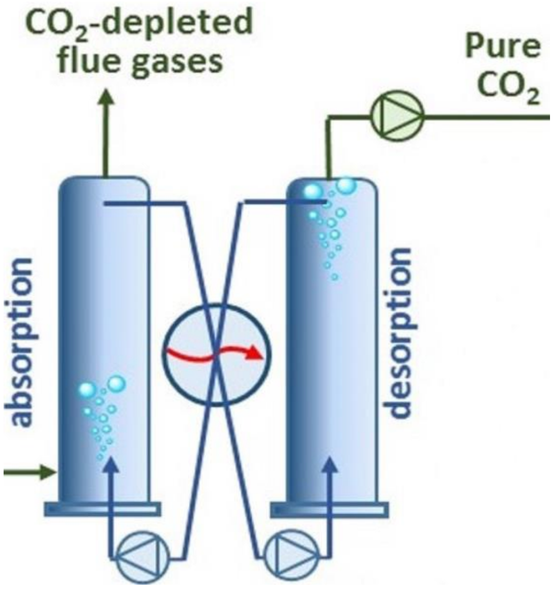


Figure 3.5 Absorber-stripper layout for ionic solvents

Kamari cement plant in Greece applied a test campaign to capture $CO_2$ using ionic solvents where the motive to the shift towards this kind of solvent is that simply they don't evaporate and thus, regeneration is done **by Vacuum** (20-100 mbar). This means that a simpler layout of the plant can be achieved as seen in Figure 3.5 [24] where the reboiler is no longer needed because there is no need for stripping steam and instead a vacuum pump is needed for regeneration. This advantage let to reducing the energy penalty by up to 50%. Moreover, the absorber and the stripper were operated at a temperature range between (60-80 $^oC$) thanks to ionic solvents which are also oxygen resistant and thus, very suitable for $O_2$ rich flue gas streams. Ionic solvents are also characterized by a lower degradation rate which means a long lifecycle. The RECODE2020 pilot plant is currently at TRL 6 [24] and is targeting a Capture efficiency 80% and $CO_2$ purity 99 vol-% while guaranteeing no VOC thanks to the environment friendly ionic solvent being used. Finally, the economizer between the lean and rich stream serves as a heat recovery to heat the rich solvent before being introduced to the stripper.

## 3.2 Process Optimization

Exploring new technologies for carbon capture is a very important aspect when it comes to increasing the performance of already existing units. These new technologies can help reduce the disadvantages of using MEA solvent which were discussed before. They can be listed as seen in Figure 3.1 and can be divided into two categories, the first one is adopting new configurations such as absorber inter-stage cooling, lean vapor compression (LVC) and stripper inter-stage heating while the other one is basically changing the operating conditions of some units such as increasing stripper pressure and throttling rich solvent at stripper inlet. The main goal of these new configurations is basically reducing the SRD which is the main source of the energy penalty in the pilot plants. This goal is achieved indirectly by either lowering the $CO_2$ loading of the lean solvent to increase its cyclic capacity or by lowering the L/G ratio which in the end will lead to reducing the amount of steam needed for regeneration.

### 3.2.1 Energy integration

In conventional pilot plants for carbon capture, the only heat recovery unit is the lean-rich heat exchanger. However, the University of Kentucky showed a great example of how energy can be integrated to minimize waste heat. As seen in Figure 2.12, heat integration was achieved through adopting a secondary air-stripper to further reduce the lean loading by bringing the lean solvent exiting the primary stripper with air which strips the $CO_2$ from the solvent and becomes rich in $CO_2$. This $CO_2$ laden air is then passed through a secondary heat recovery exchanger with the rich solvent leaving the absorber to pre-heat it before being introduced to the main boiler for combustion. In this way, the $CO_2$ loading is reduced to very low levels in the lean solvent and at the same time the concentration of $CO_2$ in the produced flue gases is increased which would increase the mass transfer driving force. After this secondary heat recovery, rich solvent is then passed through another heat exchanger where it gets heated up by low pressure steam and finally passed through the main lean-rich heat exchanger before being introduced to the primary stripper. On the other hand, heat is also recovered from the top vapor stream of the primary stripper where the water-cooled condenser is replaced by a heat exchanger that indirectly brings the top vapor stream in contact with a liquid coolant circulating in the so-called heat recovery loop. By doing so, the top vapor stream which consists mainly of $CO_2$ and water vapor is cooled and separated into a highly pure $CO_2$ stream and a liquid condensate where the captured $CO_2$ stream is directed to the stack for ejection (directed to the $CO_2$ compression train in case of full-scale unit) and the liquid condensate is redirected to the secondary air-stripper. This liquid coolant is then cooled down by chilled water before being directed to another heat exchanger to cool the extra-lean solvent leaving the bottom of the secondary stripper. On full scale application as seen in Figure 3.6, the configuration is slightly changed with respect to the pilot scale seen in Figure 2.12 where the design becomes more complicated due to the modification done on the main cooling tower in which it was divided in two sections. At the bottom part of the cooling tower, cooling ambient air is brought in contact with a liquid desiccant which absorbs the water from air to produce a dry air having a lower wet bulb temperature to provide further cooling for the cooling water that circulates in the turbine condenser. This will lead to an increase in the efficiency of the turbine because heat is rejected at a lower temperature. It can be seen also that additional heat exchangers are added for heat recovery which reflects the increased capital cost needed for such complicated and interconnected layouts that involves another stripper, modifying the main cooling tower and adding a desiccant loop. Moreover, the operating costs needed to overcome pressure drops in those heat exchangers and pipes. Nevertheless, this configuration helped to achieve SRD as low as (2326 - 3721.6) MJ/ton CO2 for MEA 30%, (2093.4- 3489) MJ/ton CO2 for H3-1 and (2900-3300) MJ/ton CO2 for CDRmax.

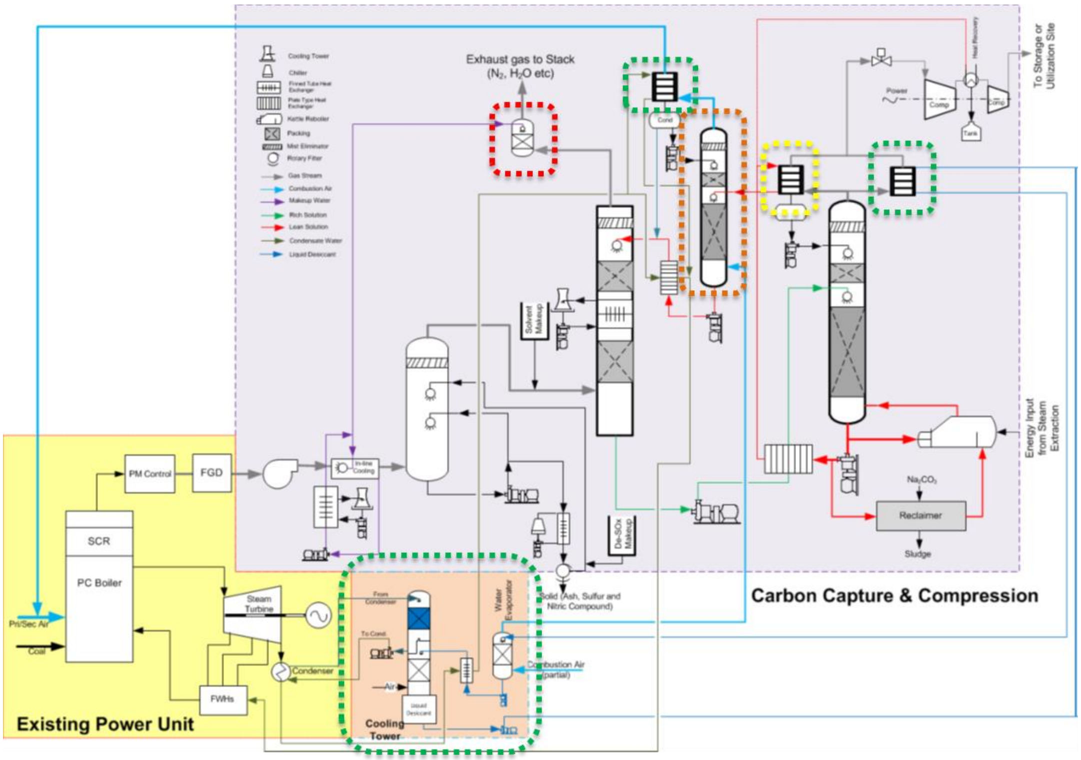


Figure 3.6 UK CAER, University of Kentucky full-scale unit P&ID

## 3.2.2 Absorber inter-stage cooling

$CO_2$ capture by amines is an exothermic process that produces heat along the path of solvent from the top of the absorber all the way down to the bottom. This would lead to an increase in the temperature of the solvent and consequently would lead to the decrease in the rate of reactions as exothermic reactions are favored by low temperatures. Solvent interstage coolers helps in reducing this effect by interrupting the continuous flow of solvent from the top at an intermediate stage where solvent is directed outside the absorber to a water cooler where it is cooled down and redirected back to the absorber to continue its absorption through the remaining part of the packing. Solvent interstage cooler can reduce the area needed for mass transfer and result in a smaller size of the absorber. Moreover, it helps in operating at a lower L/G ratio because the same amount of $CO_2$ can be captured with less amount of solvent.

Nevertheless, absorber interstage cooling has its own disadvantages such as the need to have an additional pump for circulating the solvent out and through the cooler and back to the absorber which adds extra operating costs for pumping. Moreover, the cost of the additional pumps and heat exchanger which would also need maintenance from time to time and finally the need to connect to the main cooling system.  lists the pilot plants that adopted the absorber interstage cooling where 5 pilot plants decided to exclude such configuration from its layout at least on pilot scale level.

The absorber interstage cooling didn't show much reduction in the SRD as expected. However, it is very useful when it comes to dynamic operations as seen in Figure 3.7 [25] where adopting interstage cooling can lead to increase the range at which optimum L/G ratios can be adopted while guaranteeing minimum SRD. This advantage can be useful in peak hours where the price of electricity is very high, and steam is needed to expand in the turbine instead of being bled out to be fed in the reboiler. In this case the solvent flowrate can be increased to store $CO_2$ within the solvent while reducing the amount of steam flowing to the reboiler without increasing the SRD. Such scenario was tested in TCM [2] and proven its success.

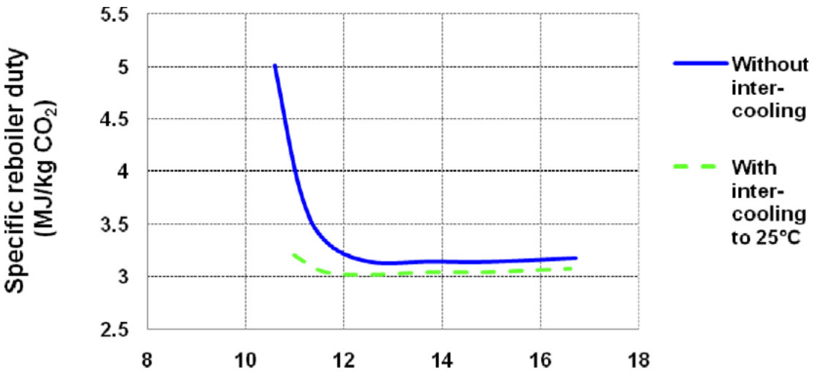
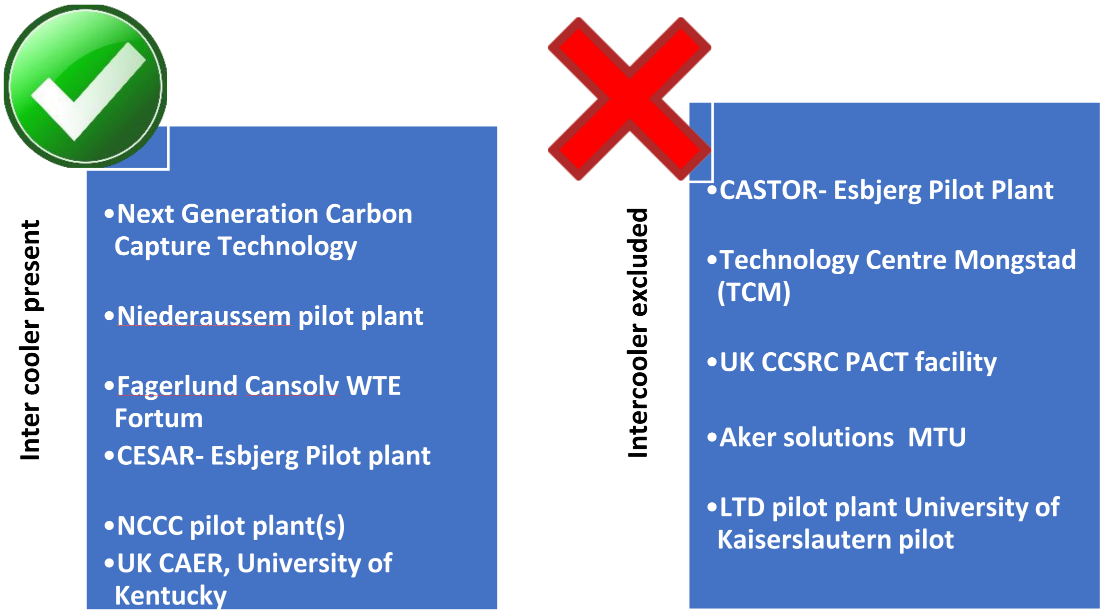


Figure 3.7 Specific heat reboiler duty VS. solvent flowrate.

The NCCC has adopted a unique design for the interstage cooler with a gravity driven mechanism to eliminate the need of adding a solvent circulating pump [21] [26] as seen in its P&ID in Figure 3.9 [18]where it could be a good solution to reducing the capital and operating costs. Solvent precipitation upon cooling was another problem that was addressed and solved by NCCC where it was found that if the solvent temperature dropped below 40°C. For this case a temperature switch was placed to turn off the coolers if the temperature dropped below 40°C in case of changing the ambient temperature of the water and air that is used for cooling.



**Inter cooler present**

- Next Generation Carbon Capture Technology
- Niederaussem pilot plant
- Fagerlund Cansolv WTE Fortum
- CESAR- Esbjerg Pilot plant
- NCCC pilot plant(s)
- UK CAER, University of Kentucky

**Intercooler excluded**

- CASTOR- Esbjerg Pilot Plant
- Technology Centre Mongstad (TCM)
- UK CCSRC PACT facility
- Aker solutions MTU
- LTD pilot plant University of Kaiserslautern pilot

Figure 3.8 Classification of pilot plants adopting or excluding the absorber interstage cooling.

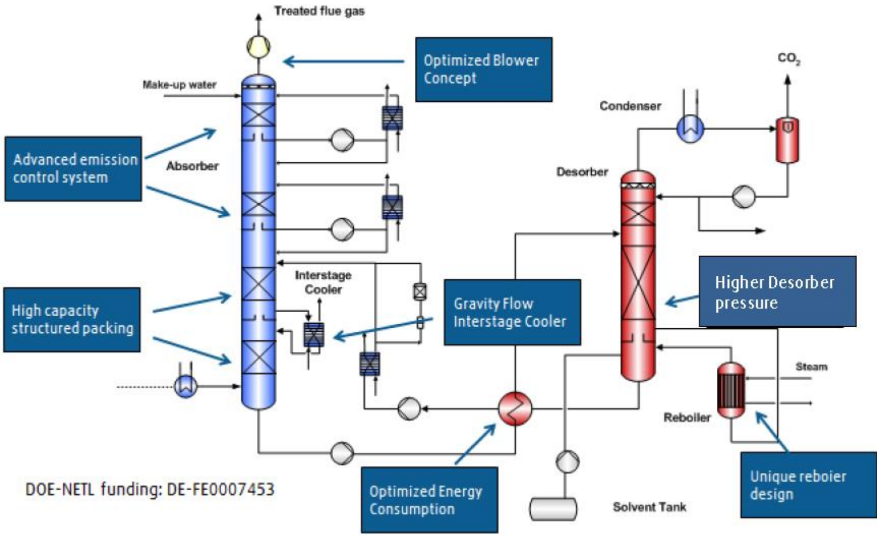


Figure 3.9 Linde- BASF NCCC pilot plant **Configuration-1 "LB1"**

### 3.2.3 Lean Vapor Compression (LVC)

The lean stream leaving the sump of the stripper is still carrying a quite large amount of $CO_2$ and vapor that could be separated from the solvent if pressure of the stream is dropped. Once the stream is flashed, the bottom liquid solvent is pumped back to the lean-rich heat exchanger while the top vapor product is then compressed at a high pressure and reintroduced back to the stripper. In this way, less stripping agent(vapors) is needed in the stripper which corresponds to less steam available at the reboiler and consequently less energy penalty. Despite the benefits of this configuration, it was only adopted by TCM Figure 1.3 and the CESAR project in Esbjerg pilot plant Figure 2.14. This could reflect the lack of interest in such technology.

## Components and different configurations

The LVC consists basically of a throttling valve, flash drum, vapor compressor "Usually Turbo blower with $\beta = 2$" [27], amine pump and an anti-surge tank which was found only in TCM [4]. The anti-surge tank is mainly found in TCM because TCM had a large compressor which must always be operating at an optimum flowrate range to protect it. Moreover, turbo blowers are usually made for large flower rates and thus, it is not suitable for pilot plant scales. It is to be noticed that TCM units is not a full-scale capture unit, but it cannot be fully considered as a pilot plant due to its large size compared to other 13 pilots that were studied in this work. The additional anti-surge tank in TCM changed and affected the power consumption of the compressor and thus it can be difficult to compare results with the ones obtained in CESAR project.

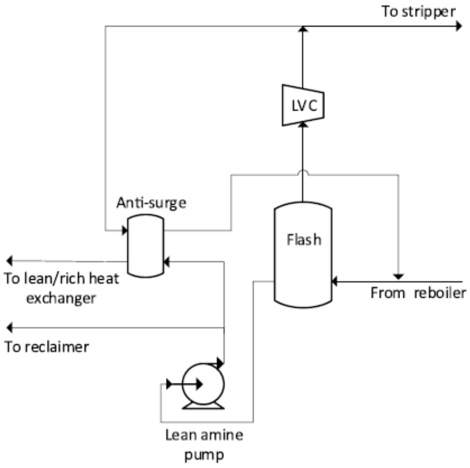


Figure 3.10 TCM lean vapor compression configuration with anti-surge tank.

## Effect on cost and overall energy performance

There are 4 main operating parameters in the LVC which affect the SRD which can be listed as follows:

1. Stripper's pressure.
2. Compressor pressure.
3. Inlet flue gas CO2 concentration.
4. Flashing pressure.

The stripper's pressure is a very important operating parameter that will be addressed in more detail in section 3.2.5 where its increase has huge benefits on the stripping process. Besides pressurizing the stripper will lead to the reduction of the volumetric flowrate of the vapor stream leaving the top of the stripper to the condenser. This can lead to the elimination of the first compression stage in the $CO_2$ compression unit which is the biggest stage and thus reducing the capital costs of the $CO_2$ compressor.

In fact, according to the campaign done in TCM [4]as stripper pressure increase, a decreasing trend in SRD is seen [0.16 GJ/ton] "excluding compressor's power". However, this increased pressure will cause back pressure on the compressor which will experiences a higher ΔP thus Power of the compressor increases by 0.04 $GJ_{electric}$/ton.

The adoption of the LVC configuration leads to the reduction of the SRD by about 23% according to TCM's campaign [4] in addition to the flattening of the U-shaped SRD curve against the lean solvent flowrate or the L/G ratio as shown in Figure 3.14 [4] which can make it not easy to identify the optimum operating point i.e., the solvent flowrate or the L/G ratio at which the SRD is minimum.

The thermal power in SRD & elec. Power used by compressor can't be directly subtracted and an $\alpha$ term is needed which can be obtained from the graph in Figure 3.13 obtained by Olav Bolland [28]. This $\alpha$ represents the loss in the power output of the steam turbine compared to the heat of the steam. It is expressed in the following equation where its value for low pressure steam extracted at 4 bar absolute is found to be 0.23. In other words, the LVC will only be effective if it's able to reduce the heat input to the reboiler by 4.3 times the electric work produced if the steam at 4 bara was allowed to expand in the LP turbine where 4.3 is the reciprocal of 0.23. This can be explained in the 2nd equation to better understand how, and at which point the LVC starts to be effective.

$$\alpha = \frac{incremental\ power\ reduction}{incremental\ heat\ output}$$

$$Q_{input_{Reboiler_{LVC}}} = Q_{input_{Reboiler_{without\ LVC}}} - 4.3 * \mathrm{Work_{elec}}$$

There are 2 scenarios for LVC configuration adoption:

- Capture plant designed with LVC & its dimensions are adapted to it.
    - Stripper diameter is larger to handle more vapor.
    - Heat transfer area of LR HEX & Condenser ↓
- LVC is retrofitted to a basic capture plant.
    1. Stripper can't be altered.

**TCM** which is using Sundyne compressors → $\eta_{compressor} = 80\%$ and an anti-surge valve to control the steady state flow, reported that net energy saving is 3% when adopting LVC for $\eta_{capture}$ 80 & 90% 30%MEA solvent [4] where it is seen as a very little reduction because results are affected by anti-surge which could increase the compressor's energy consumption (25-50% of flow recycled back to compressor) which means that up to 50% of LVC's increase in power consumption comes from recycling. Anti-surge makes it difficult to generalize the concept because it becomes configuration dependent and consequently, LVC's impact should be studied without anti-surge to have a clearer picture. In the same study[4], TCM suggested coupling the pilot plant's LVC with hydro or wind turbine [green energy] to avoid extracting power from the steam turbine.

Figure 3.16 [4]represents the effect of the $CO_2$ concentration on the SRD in the presence and absence of LVC at 90% capture efficiency where the graph shows that LVC is more suitable for high $CO_2$ conc. Operations as WTE, Cement and RFCC. The Sundyne compressor design specifications were reported in Table 3.2 [4].

| | Unit | Design | Low inlet | High inlet | Campaign |
|---|---|---|---|---|---|
| **Polytropic efficiency** | % | 78.1 | 77.7 | 77.8 | |
| **Inlet conditions** | | | | | |
| **Mass flow** | Kg/h | 7025 | 5677 | 11,105 | 6800-7400 |
| **Pressure** | Bara | 0.95 | 0.7 | 2.1 | 0.87-1. 1 |
| **Temperature** | C | 102 | 94,19 | 123.7 | 97-103 |
| **Outlet conditions** | | | | | |
| **Pressure** | Bara | 1,9 | 1.5 | 3.5 | 1.9-21 |
| **Temperature** | C | 189.4 | 190.2 | 189 | 171-198 |
| **This flow includes anti-surge, The flow in/out of the LVC is 3600—5400kg** | | | | | |

Table 3.2 TCM's Sundyne Compressor design specification.

**Esbjerg plant** on the other hand reported "9% net reboiler duty reduction at 115 kPa flashing pressure "CESAR-1 solvent" [25] which works better when combined with absorber interstage cooling & in absence of anti-surge.

## Optimizing vapor flashing pressure.

The flashing pressure at which the flash tank is set is considered a very important factor in determining the overall performance of the LVC configuration. The lower the pressure at which the lean solvent is introduced, the more $CO_2$ and water will be separated from the lean stream and thus the better the efficiency of this technology. But it is to note that the lower this pressure, the more the compressor must work to raise that low pressure up to the stripper's pressure. So, the flashing point is a parameter that must be optimized to maximize the benefits while reducing the costs.

In fact, the SRD and the specific power of the compressor are plotted against the flashing pressure as seen in Figure 3.12 and Figure 3.11 [4] which were plotted using a MEA 30% solvent with flow rate of 200 000 kg/hr. in which linear tends were found for both the SRD and the compressor's power. Figure 3.15 results from [25] were plotted to optimize the pressure at which the lean solvent is flashed with respect to the reduced SRD and the increased compressor work. It is to be noted that the campaign from which results were taken and plotted was done at fixed lean and rich loading, solvent flowrate and $CO_2$ capture rate and it was reported also that reboiler duty was reduced by 124 kW.

For the anti-surge tank in TCM, the gas recycled to the compressor was plotted against the anti-surge valve opening as shown in Figure 3.18 where it showed linear relation. In addition, Figure 3.17 shows that the more solvent circulating, the more $CO_2$ & $H_2O$ will be vaporizing & the less opening of anti-surge valve is needed which makes the anti-surge tank a good compromise for large scale capture units.

In a summary, as $P_{flash}\downarrow$, Cost of compressor and pump ↑ because $\beta\uparrow$. Moreover, the cost of flashing vessel ↑ but it is compensated by ↓ cost of LR-HEX, condenser and reboiler.

## Effect of flashing on lean solvent temperature

Flashing amine causes a large drop in amine temperature with a linear dependency as seen in Figure 3.20 [4]where lower $T_{lean\ amine}$ means lower $T_{rich\ amine}$ of solvent leaving the Lean-Rich H.EX and going to stripper. Consequently, this will correspond to a lower $T_{stripper\ gas\ out}$ as seen in Figure 3.19 [4] which will need less cooling water needed in the over-head condenser and by this it leads to a lower energy consumption. It is to be noted that those two graphs were plotted at a MEA30% solvent flowrate of 200 tons/hr.

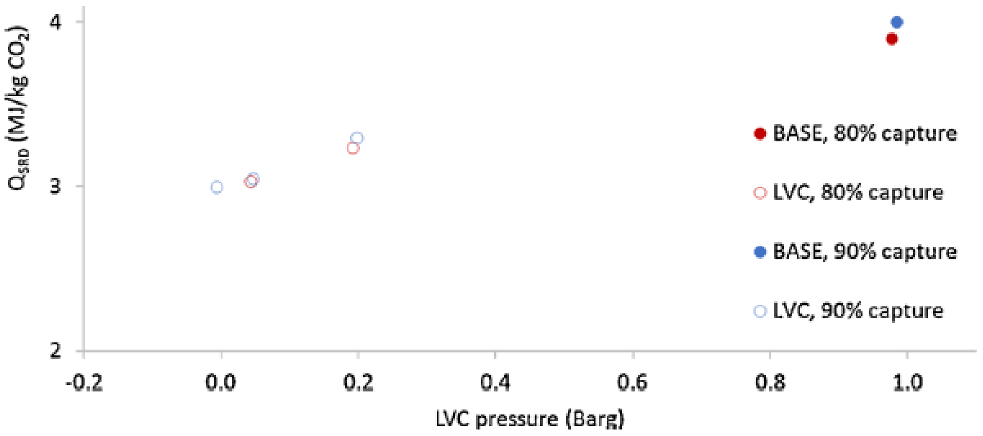


Figure 3.11 SRD VS Flashing pressure

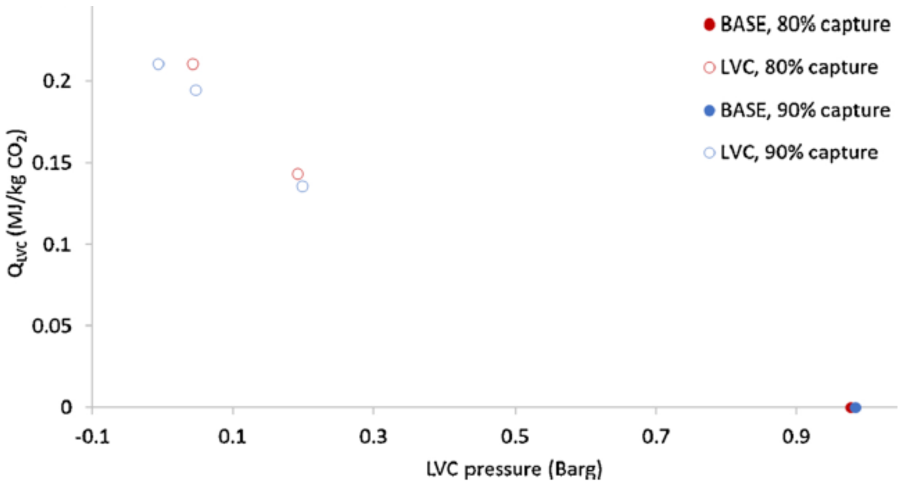


Figure 3.12 $Q_{LVC}$ VS Flashing pressure

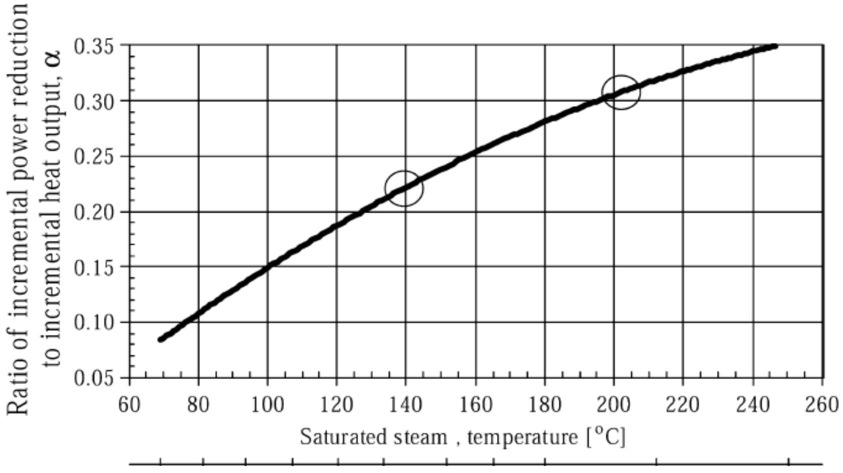


Figure 3.13 The ratio ($\alpha$) of incremental power reduction to incremental heat output when extracting steam at given pressures from a steam turbine.

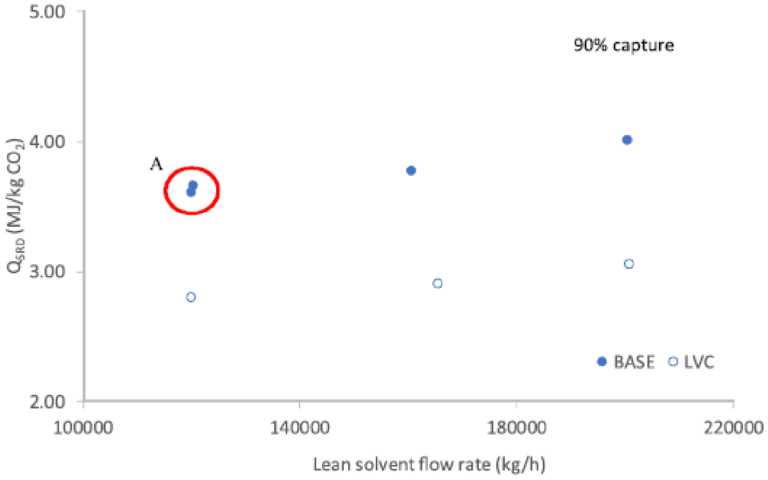


Figure 3.14 SRD as a function of solvent flow rate.

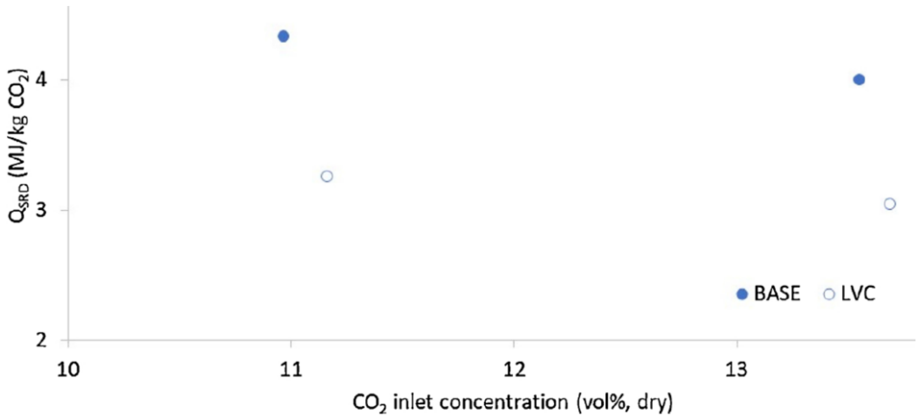


Figure 3.16 SRD VS inlet flue-gas CO2 concentration (dry basis).

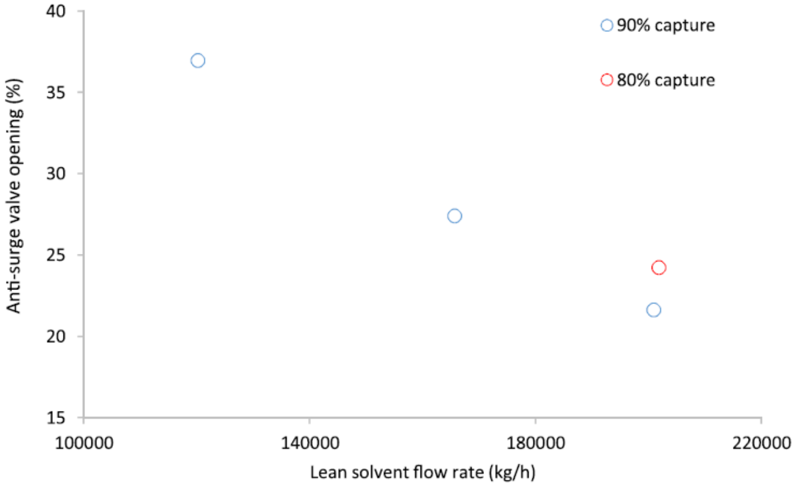


Figure 3.17 Anti-surge valve opening VS solvent flow rate.

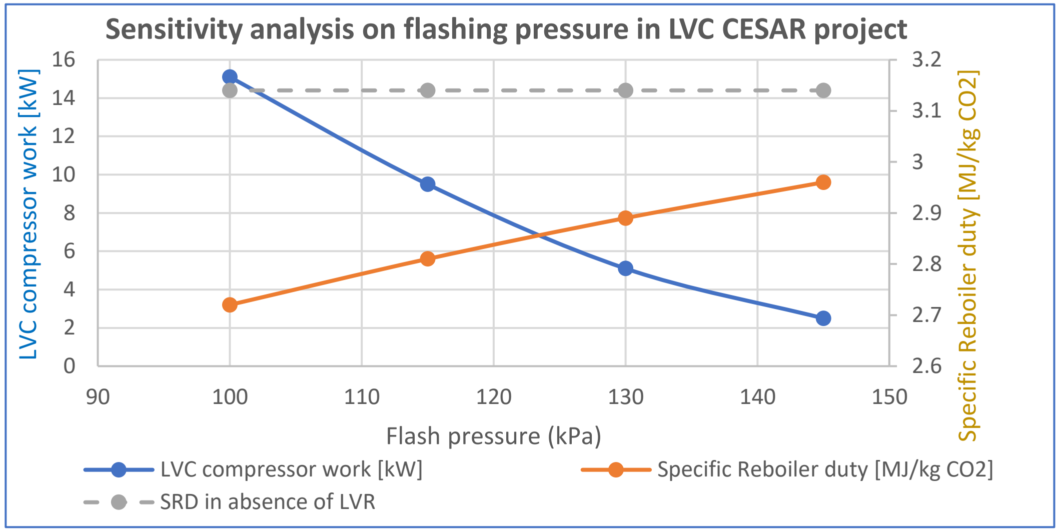


Figure 3.15 Sensitivity analysis on flashing pressure in LVC CESAR project

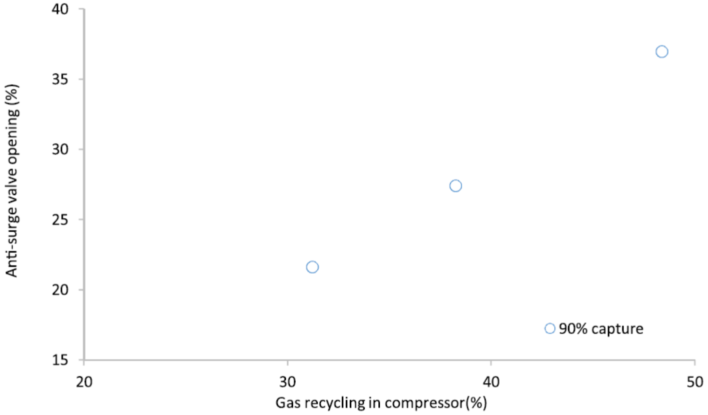


Figure 3.18 Anti-surge valve opening VS gas recycling in compressor.

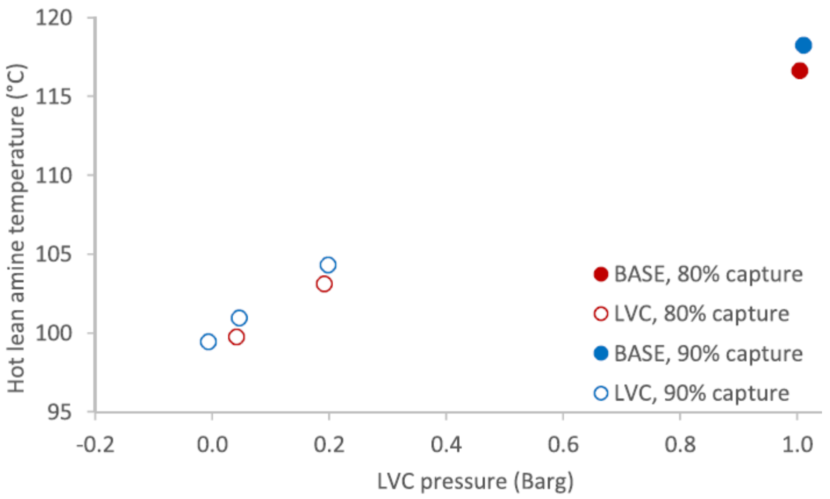


Figure 3.20 Hot lean amine temperature after flashing VS flashing pressure.

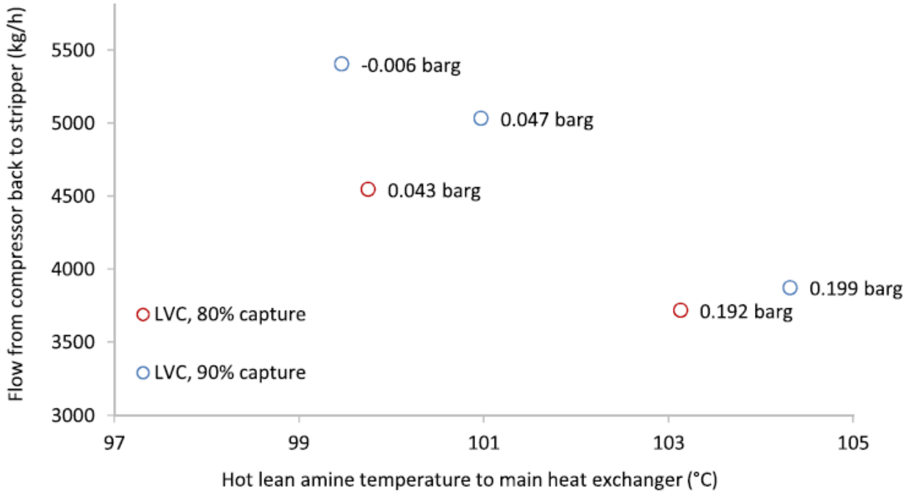


Figure 3.22 Flow from compressor to stripper as a function of hot lean amine

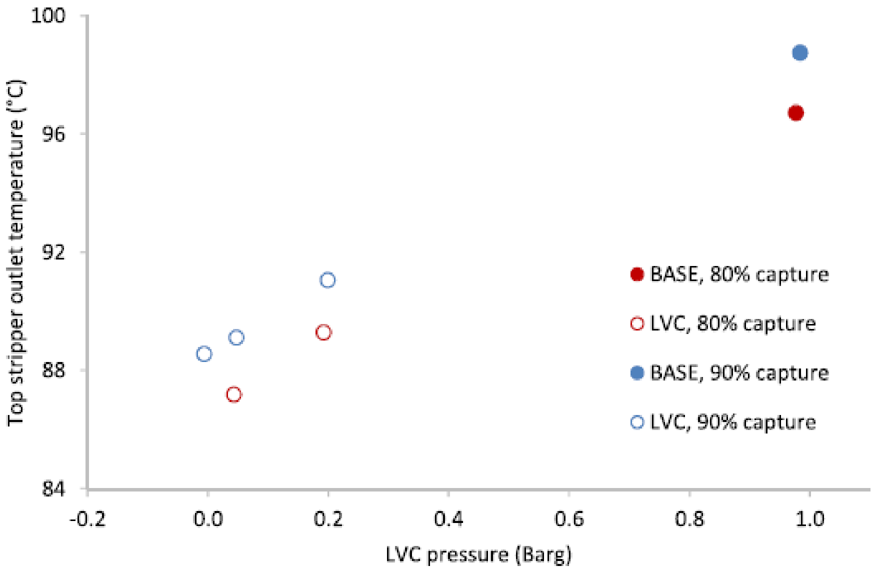


Figure 3.19 Top stripper outlet temperature VS LVC pressure.

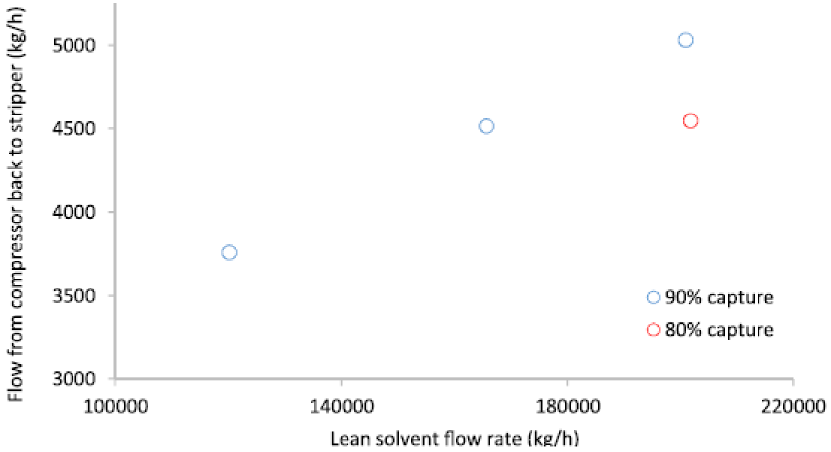


Figure 3.21 Flow from compressor back to stripper (equivalent to flow into the LVC

## Capturing 80% VS 90% CO2 with LVC

More flashing means higher vaporization which means more flow from compressor to stripper and as said before, lower lean amine temperature which can be seen in Figure 3.22 [4]. However, the degree of regeneration in the stripper led to an unexpected result. The capture efficiency depends on the quantity of steam introduced in the reboiler where at 90% more steam is extracted from the turbine and thus the lean stream leaving the stripper's sump has a lower $CO_2$ loading i.e., lower amount of $CO_2$ in the lean stream. So, by flashing the lean solvent, it was expected to have less vaporization. However, what was found that more vaporization occurred and that the recycling anti-surge valve opening was reduced. On the other hand, 80% capture efficiency means that less steam was introduced to the reboiler so the lean stream leaving the stripper's sump has relatively higher amount of $CO_2$ with respect to the 90% case. Consequently, on flashing this stream it was expected to have more vaporization because simply there is more $CO_2$ available, but it was found that the vaporization was less and the anti-surge valve opening was increased. Figure 3.23 summarizes those different paths with color codes to simplify the results.

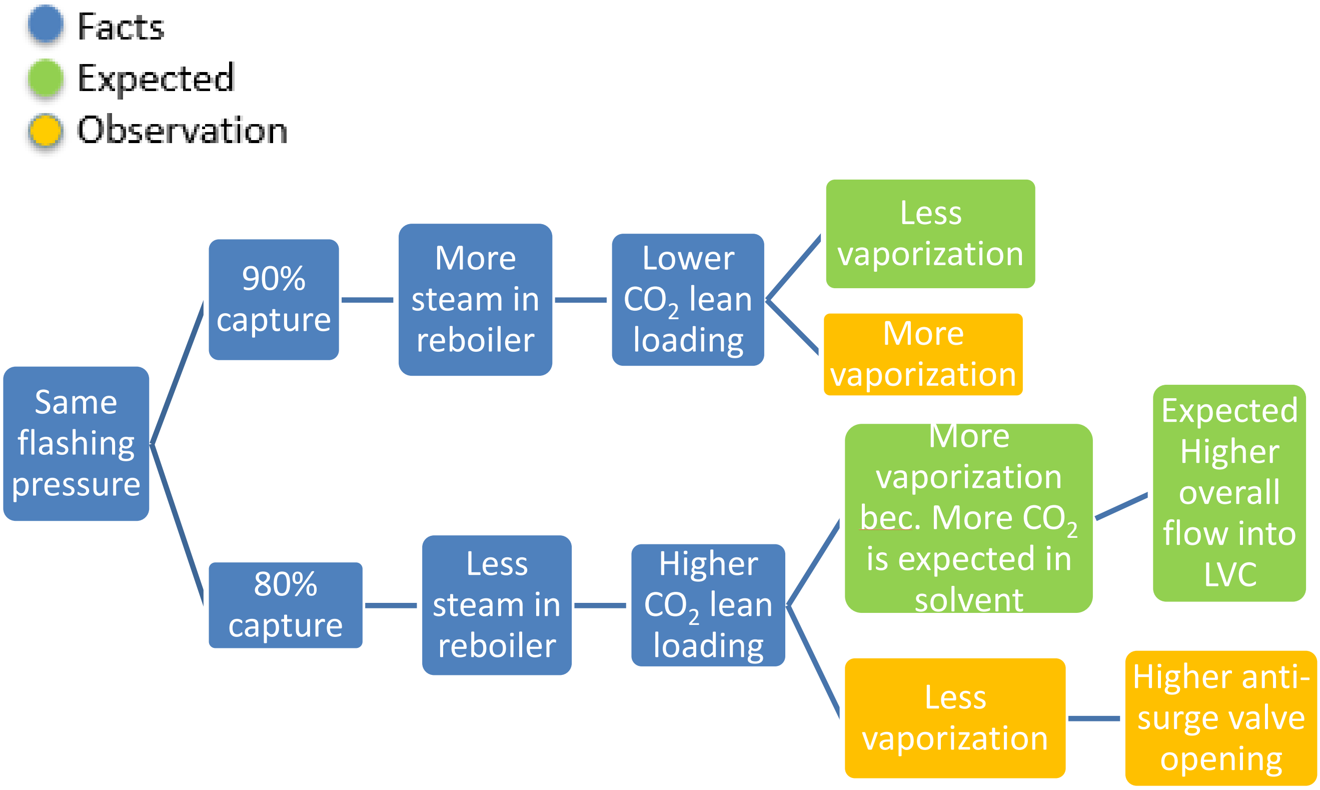


Figure 3.23 Effect of degree of regeneration on the anti-surge valve opening.

This could be explained because at 80% we have higher $CO_2$ **but lower Temperature** as seen in Figure 3.22 [4] which leads to vaporize more $CO_2$ but less $H_2O$. Vaporization has 85%$_{wt}$ $H_2O$, 15%$_{wt}$ $CO_2$, 0.5 %wt. MEA so, water reduction is higher than $CO_2$ increase and the overall LVC vaporization is lower which leads to a higher anti-surge valve opening. So, going from 90% to 80% $\eta_{capture}$ , we get 35% more $CO_2$, 15% less $H_2O$ and 30% less MEA

A personal opinion on that would be that:

- 80% capture efficiency is a better option for LVC configuration because it:
    - ❑ will reduce $Q_{SRD}$, → Lower energy penalty.
    - ❑ Decrease overall flow to stripper → lower gas flow at stripper top → lower condensation duty.
    - ❑ lower amine evaporation→ lower amine emissions → more environmentally friendly
    - ❑ Higher consumption of LVC compressor because anti-surge valve is opened more.

More information about lean vapor compression was obtained from [29][30] and [31].

### 3.2.4 Stripper Inter-stage heating "SIH"

This technology was adopted only by Lind- BASF pilot in NCCC as seen in Figure 3.24 [18] which had a positive impact on the energy performance of the capture unit. In this configuration the rich solvent's flow is interrupted in the stripper where it is extracted from a middle stage, directed to a heat exchanger where the rich solvent is heated up by the lean solvent leaving the reboiler. Therefore, the energy demand for solvent regeneration is reduced i.e., a lower amount of steam is needed in the reboiler. Stripper Inter-stage Heating (SIH) also improves heat recovery from CO2-lean solution leaving stripper and thus reduces the amount of heat wasted in the lean solvent cooler and consequently, the net efficiency of the power plant increases. Figure 3.26 and Figure 3.25 [18] show that adopting stripper interstage heating could increase the plant's overall efficiency by almost 1% through a simple configuration that requires only an additional heat exchanger without complications of the LVC.

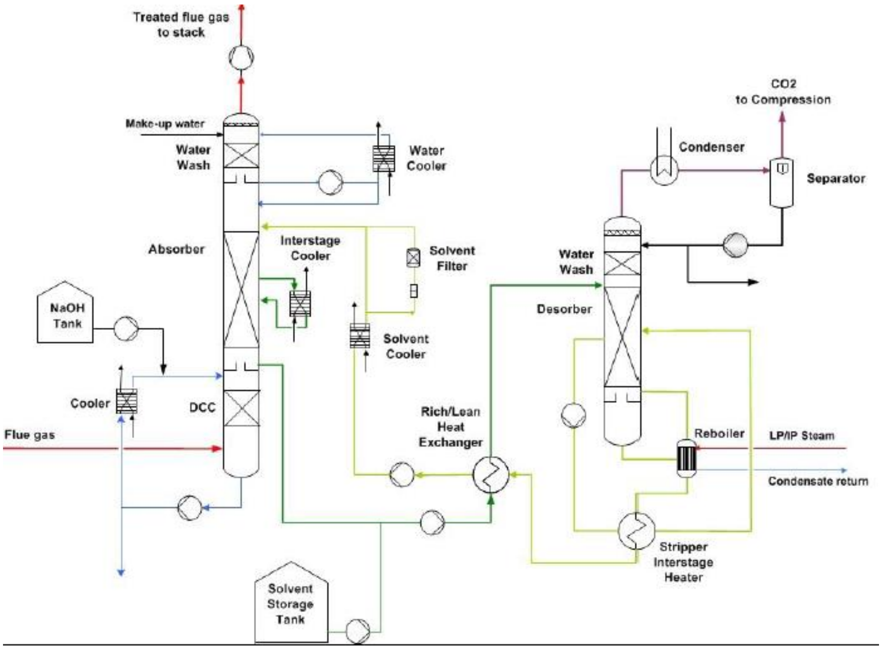


Figure 3.24 Linde-BASF NCCC pilot plant **Configuration-2 "SIH"**

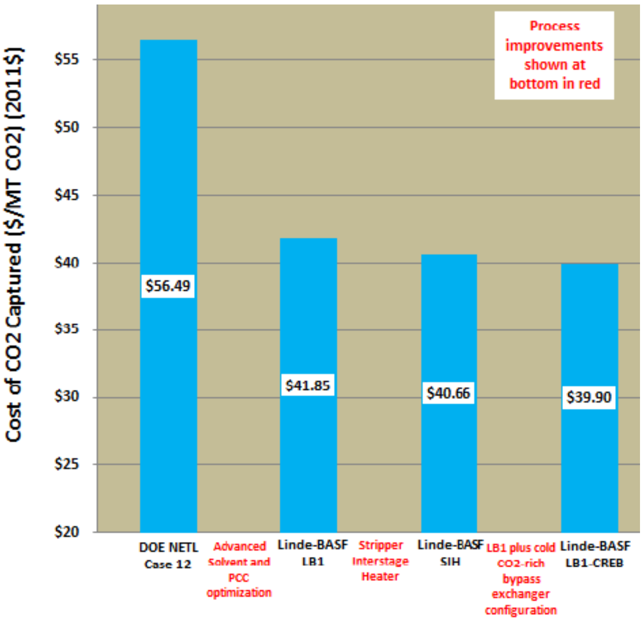


Figure 3.25 Cost of CO2 captured ($/MT CO2) 2011$

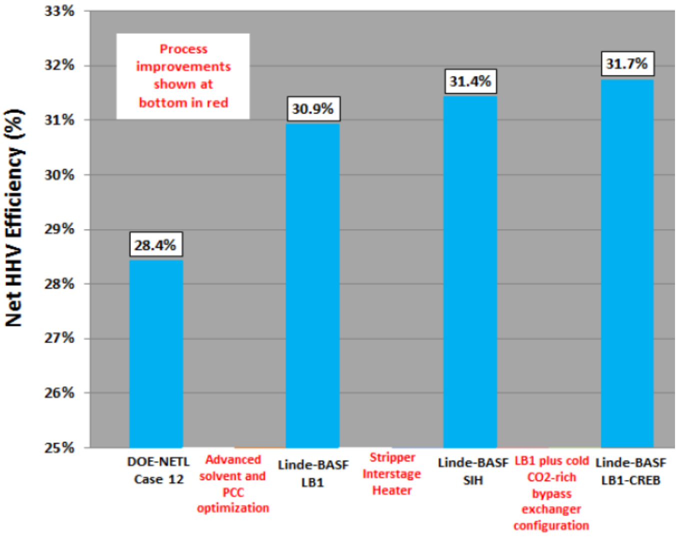


Figure 3.26 Net HHV efficiency

### 3.2.5 Increasing stripper pressure

Trends are going towards higher stripper pressures as seen in Figure 3.27 where many advantages can be obtained specially in terms of cost savings. Pressurizing vessels is usually done by controlling the vapor outlet valve at the top. By doing so, the vapor stream leaving the top of the stripper which mainly consists of $CO_2$ and water is at a higher pressure and consequently a lower volume. This is very beneficial for eliminating the first stage compression in the $CO_2$ compression train which is considered the biggest and the most expensive stage. Moreover, increasing the pressure of the stripper can allow us to design new pilot plants with reduced diameter compared to the ones with lower pressures. The high pressure in stripper will produce a high-pressure stream of lean solvent leaving the stripper and entering the reboiler which will require a higher energy duty to vaporize the $CO_2$ and water dissolved in the solvent. Thus, the SRD is increased with such configurations which increases the energy penalty resulting from the increased flowrate of steam extracted from the turbine. However, this increase is eliminated by the reduced specific work of the compressor which would require less energy to increase the pressure of the vapor stream since it is already at a high pressure.

Stripping solvents at a high pressure can be beneficial from the energy performance point of view for solvents whose enthalpy of vaporization is higher than the vaporization enthalpy of water ($\Delta H_{vap,H2O}$ = ~40 kJ/mol) as this will lead to the increase of the partial pressure of $CO_2$ which will lead to the reduction of the quantity of water vaporized from the solvent. The greater the vaporization enthalpy difference, the lower the amount of water vaporized (Oexmann, 2011). However, higher pressure solvent stream would require a higher amount of energy for regeneration which means that regeneration must be done at a higher temperature which can lead to solvent degradation specially for MEA which has a high thermal degradation rate specially at temperatures above 120 °C. This problem can be solved by adopting new solvents that have higher thermal stability compared to MEA.

UK CAER, University of Kentucky pilot plant which used 4 different solvents in its campaigns reported multiple results of those different solvents tested at different stripper pressures. In addition, they reported the highest pressure which was 4.51 bara in its primary stripper. It is to be noted that some other pilot plants went up to 10 bar but they were not reported in this study.

Finally, adopting a LVC configuration with an increased stripper pressure will lead to a back pressure on the compressor and thus the compressor must work more.

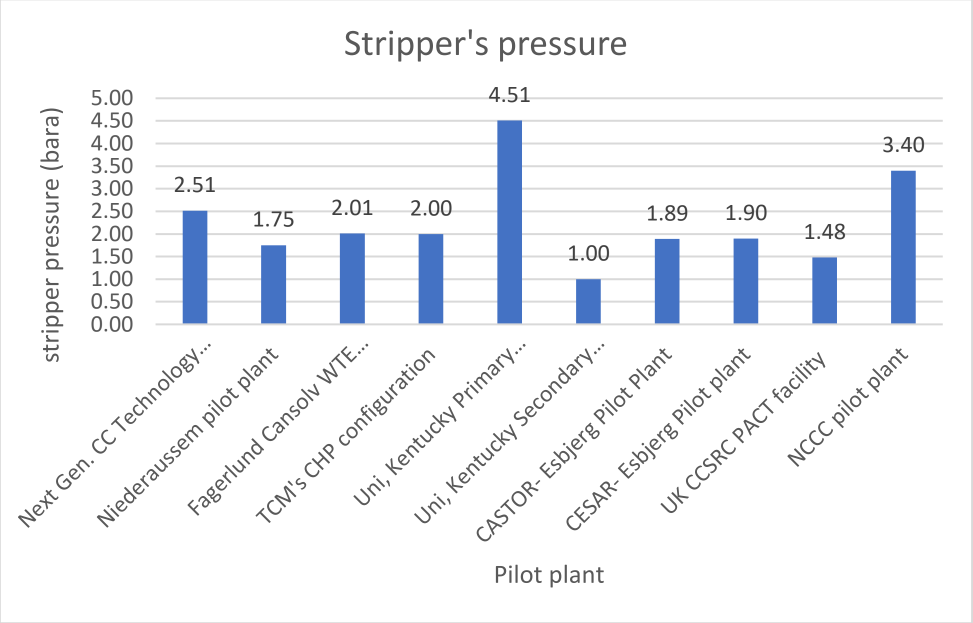


Figure 3.27 Stripper pressure of the studied pilots

### 3.2.6 Throttling rich solvent at stripper inlet

This process was tested in the NCCC BASF-Linde pilot plant where its results were seen on the $CO_2$ recovery, stripper’s pressure, the mass flow rate of pure $CO_2$ gas stream and the stripper’s liquid level as seen in Figure 3.28, Figure 3.29, Figure 3.30 and Figure 3.31 [18]. In fact, this led to the stability of these terms and reduced the fluctuation. The pressure of the $CO_2$ rich solvent inside the lean-rich H.EX should be high to suppress vaporization of $CO_2$. Throttling is done directly before stripper solvent inlet to flash the rich solvent stream to release $CO_2$ and excess water vapor. However, Excessive pressure reduction in pipe leading to stripper can lead to $CO_2$ buildups which will lead to large and irregular bursts of liquid and vapor and consequently, fluctuation in stripper pressure and CO2 recovery rate.

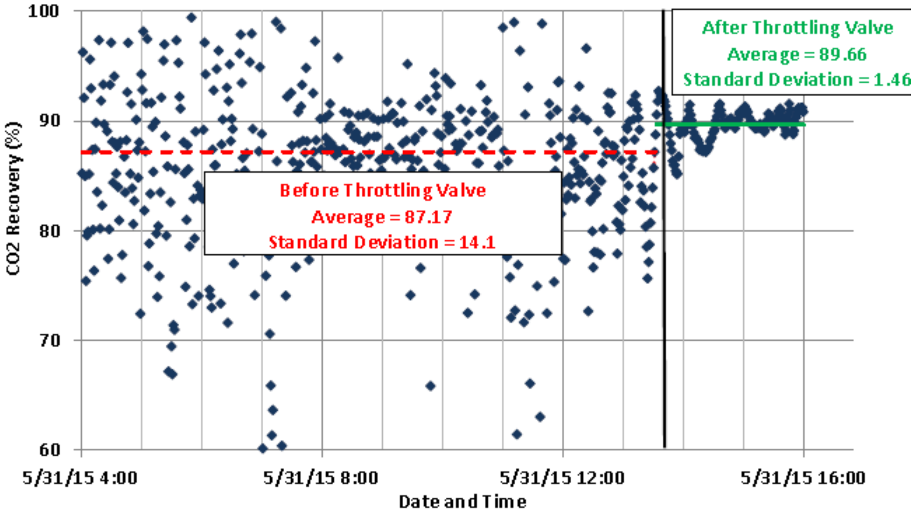


Figure 3.29 Effect of throttling on $CO_2$ recovery

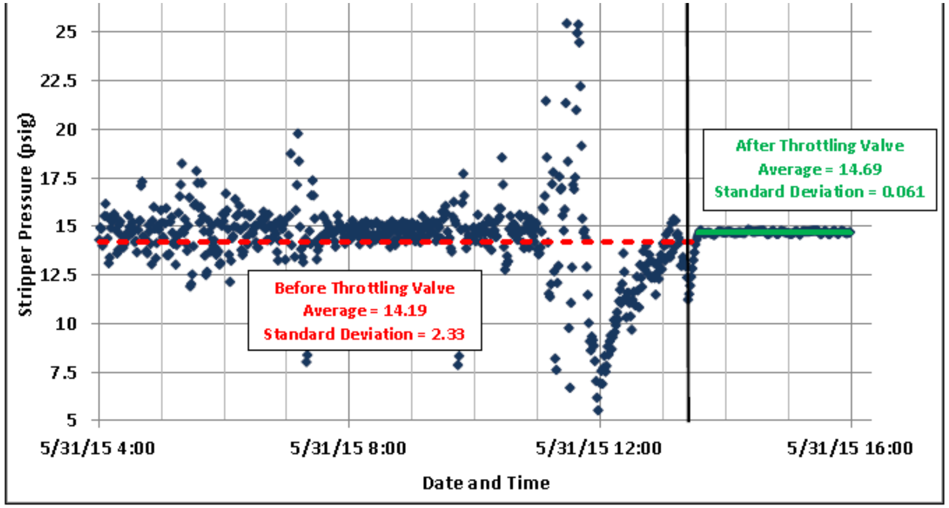


Figure 3.28 Effect of throttling on Stripper's pressure

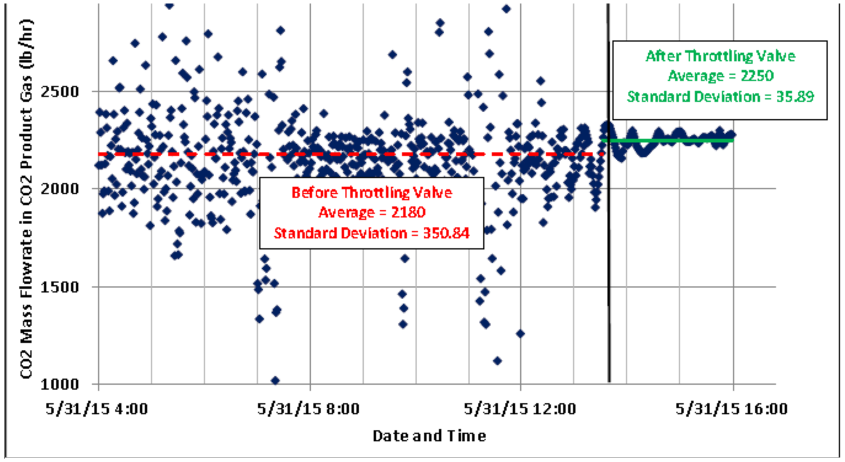


Figure 3.30 Effect of throttling on mass flowrate of $CO_2$

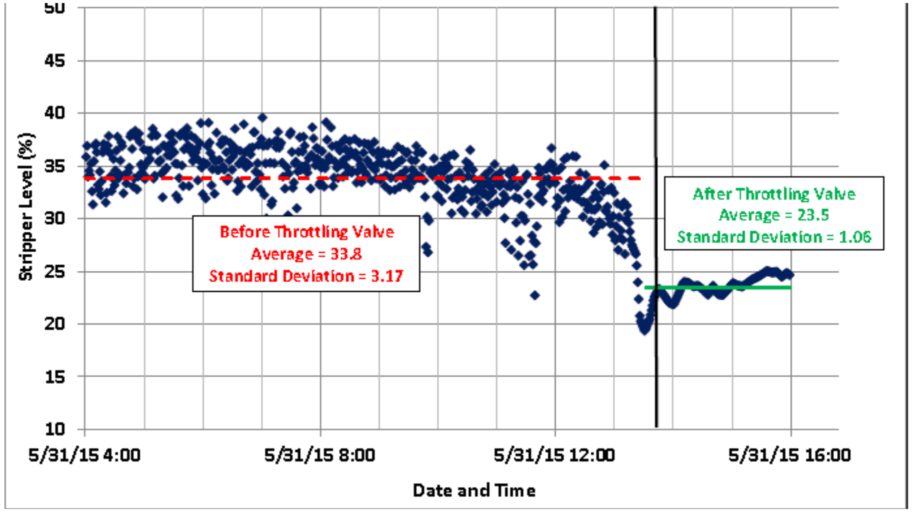


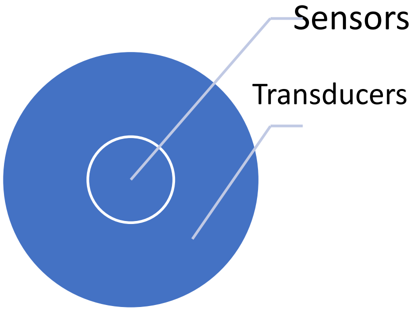
Figure 3.31 Effect of throttling on stripper's level

# 4. Instrumentation

## 4.1 Introduction

Carbon capture units and in particular pilot plants are very complicated, and they are designed to test new solvents and new technologies aimed at stabilizing the process, reducing the specific energy required for capturing and reducing the emission levels. Consequently, a large amount of instrumentation must be placed to verify the mass and energy balance and reduce the errors in their closure. In the following chapter, a brief introduction about sensors, transducers and transmitters is given as they represent the basis upon which most of the instrumentation works. Furthermore, instrumentation for pressure, temperature, level and flow measurements will be discussed separately in the following sections in addition to liquid and a gas analyzer. Finally, a final section will be dedicated to a proposal for new pilot plants.

A sensor is the element that makes physical contact and detects change in physical behavior while the transducer is the device that provides an output quantity in specific relation to the input of the sensor. On the other hand, a transmitter is a device that transmits a standard instrumentation signal representing a physical measured variable. Briefly, all sensors are transducers while not all transducers are sensors. Sensors create signals of an order of 0-3 milli Volts while the transducer tells the transmitter what type of physical quantity is being measured. Through the transmitter, the signal is amplified and standardized to an electrical signal of the order of 1-5 volts or 4-20 mA in what is called signal conditioning.



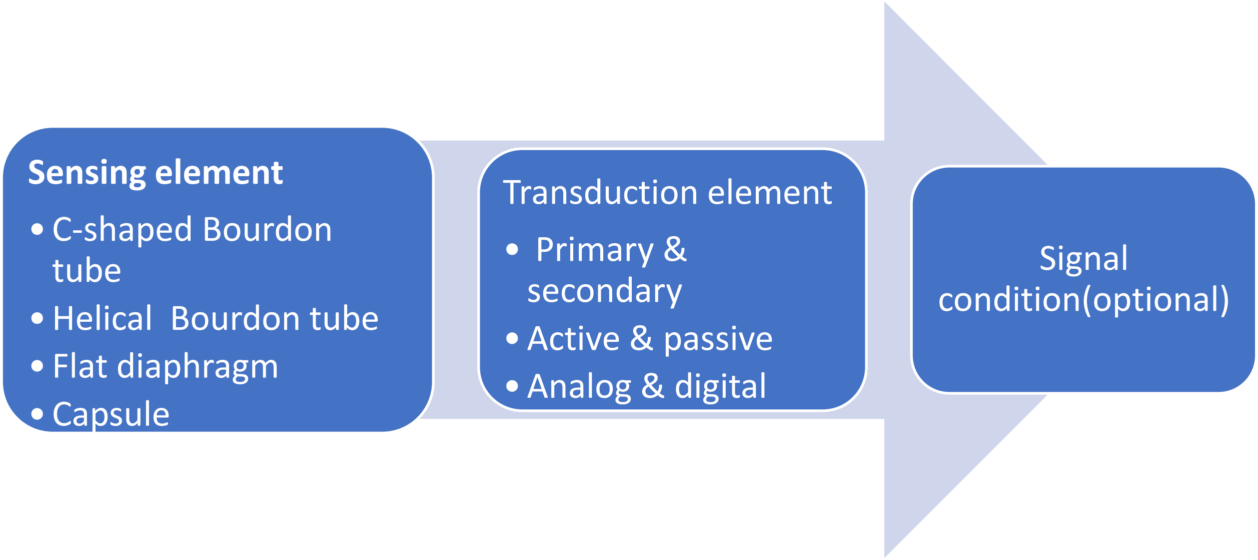


Figure 4.1 Sensor functional blocks

Figure 4.1 summarizes the functional block diagram of sensors where it is to be noted that Primary transducer is the mechanical device that changes the physical quantity into a mechanical signal while secondary transducer converts the mechanical signal into an electrical signal depending on the magnitude of the mechanical one. In addition, active transducers don’t need an external power supply while passive ones need an external power supply.

## 4.2 Pressure measurement and instrumentation

Pressure sensors are essential in pilot plants specially in pressurized equipment where it is important to monitor the pressure to avoid any excessive pressure build up that could lead to equipment failure and could lead to injuries in case of operators nearby. Moreover, process performance depends on the operating pressure of the absorber and the stripper as discussed before in section 3.2.5. In addition, pressured lines must always be monitored to avoid failure and damage.

Pressure sensors Works on Piezoelectric effect i.e. materials create electric charge when subjected to stress (pressure) as seen in Figure 4.2 and they require calibration from time to time.

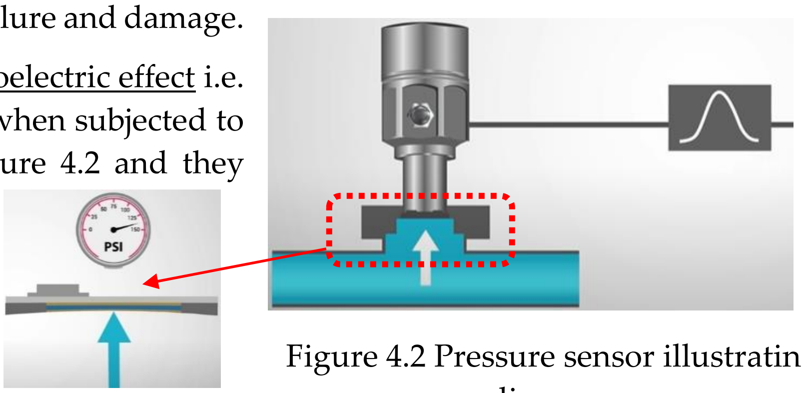


Figure 4.2 Pressure sensor illustrating diagram.

Pressure transducers can measure static pressure, dynamic pressure and stagnation or total pressure while based on the measuring mechanism, they can read absolute, gauge and differential pressure. Pressure sensors play an important role in steam applications and in carbon capture units, steam is introduced in the reboiler to heat up the solvent. Thus, a pressure sensor can determine when steam can flow to avoid any buildup inside the tubes by connecting the sensor to a control valve to keep the flowrate and pressure of steam within the desired limit.

Filters are found in pilot plants on the lean solvent side to clean the solvent of its solid deposits of heat stable salts and degradation products. A differential pressure sensor is placed against those filters to detect the maximum allowable pressure drop after which the filter must be changed due to clogging. In addition, in closed tanks such as solvent makeup tanks and chemical tanks, differential pressure can be a cheaper way to determine the liquid level inside those tanks. On the other hand, gauge pressure sensors can be used in open tanks "atmospheric" to determine the liquid level through the hydrostatic pressure measured which can be an alternative in the absorber's sump in case of failure of the dedicated level instrumentation.

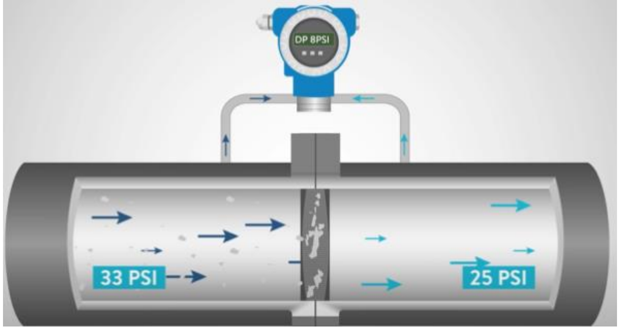


Figure 4.3 Differential gauge pressure on a solvent filter illustrating diagram.

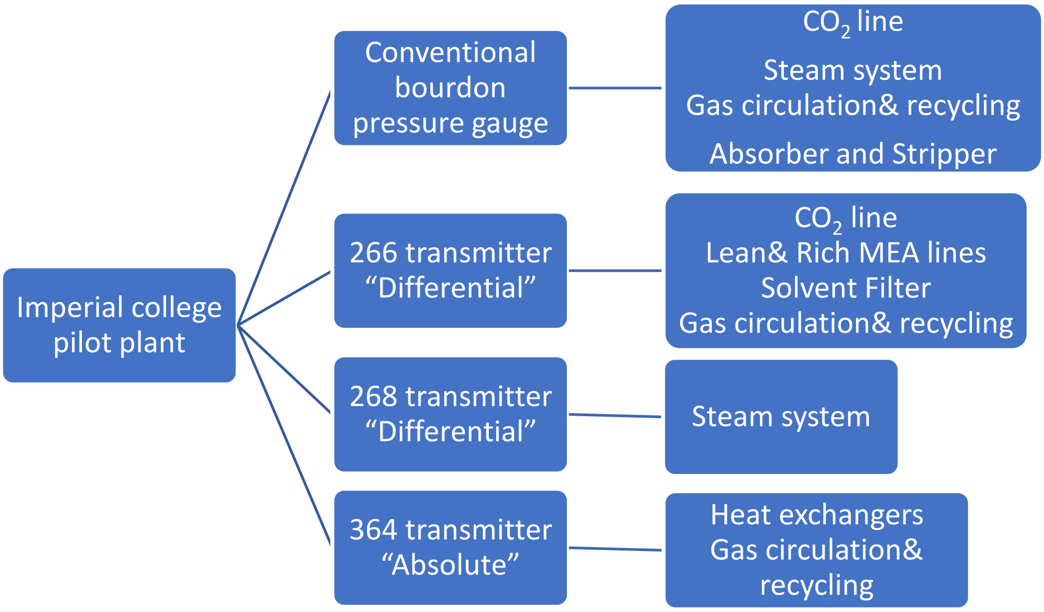


Figure 4.4 Imperial College pressure instrumentation

## 4.3 Temperature measurement and instrumentation

Temperature sensors and transmitters are widely used in industrial processes and especially in the field of power production and carbon capture. In carbon capture and storage, temperature instrumentation is found in a huge number distributed all over the equipment and especially in the absorber and the stripper. As seen in Figure 1.4 and Figure 1.5, TCM had 96 temperature probes distributed along the absorber and 28 probes along the stripper as discussed previously. TCM highlighted the importance of having multiple probes placed at the same horizontal level at each stage in the absorber as it can tell a lot about process performance and optimization where the difference in readings between those probes reflects the poor and uneven distribution of gases and the solvent on the packing. The most used types of temperature sensors are Resistance temperature detectors (RTD) and thermocouples where a comparison between those two types can bs seen in Table 4.1.

| Resistance temperature detectors (RTD) | Thermocouples |
|---|---|
| • Produces a change in resistance with temperature change.<br>• (2,3,4 wired)<br>• Passive device "needs an external electric current or voltage source.<br>• Voltage drop across the RTD is an indication of temperature.<br>• PT-100 is the most common type.<br>• 10 times more accurate than thermocouples | • Produces a change in voltage when temperature changes.<br>• (2-wired)<br>• Works on the Thermo-electric effect<br>• Self-powered i.e., they require no external power.<br>• Mainly for furnaces, GT- combustion chambers, high temperature exhaust ducts,..etc..<br>• Accuracy is a limitation |

Table 4.1 Comparison between Resistance temperature detectors and thermocouples.

## 4.4 Flow measurement and instrumentation

Flow measurements are useful in the closure of the mass and energy balance of the carbon capture unit where it's usually important to control the flow of the solvent through the absorber to control the capture rate of $CO_2$. In addition, the presence of multiple water coolers requires accurate flow measurements to control the temperature at which the absorption process is carried out especially that multiple unsteady state campaigns are being carried out with pilot plants to test different operating scenarios. Unlike temperature measurement units, flow measurements devices are classified into different types as seen in Figure 4.6 where in each category there are multiple technologies that work on different principles. The choice of the type of flow measurement device depends on multiple factors which are summarized in Figure 4.5.

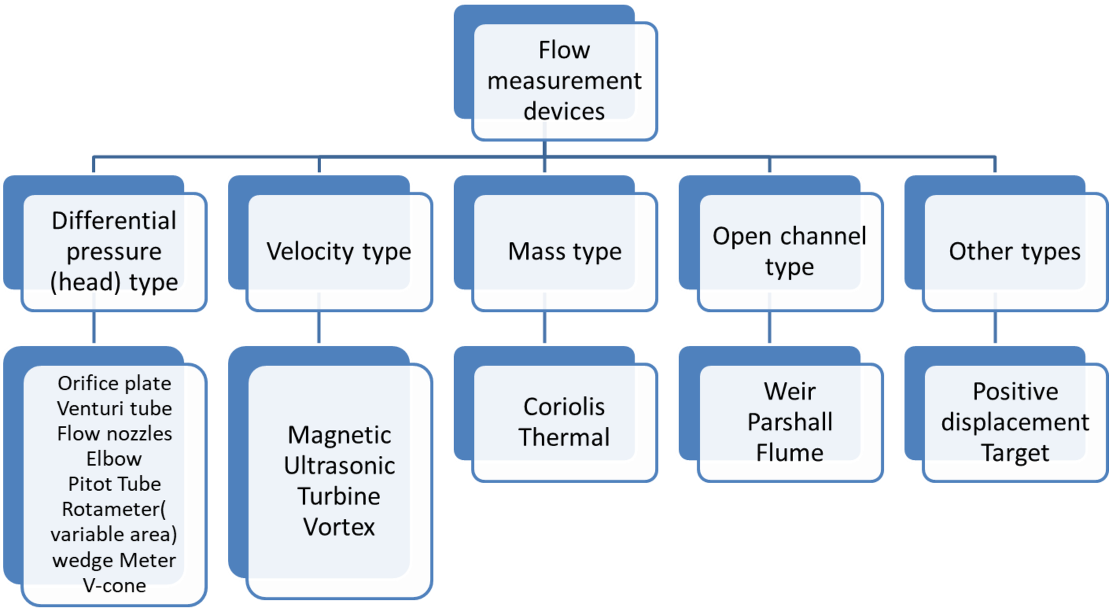


Figure 4.6 Classification of flow measurement devices.

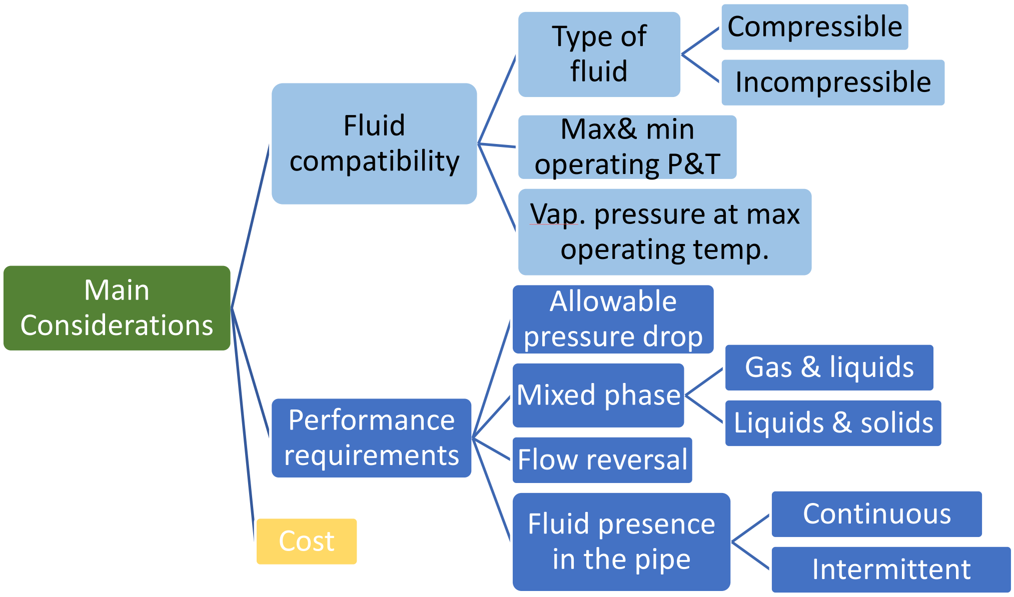


Figure 4.5 Main considerations for selecting the flow measurement instrumentation.

The most common types of flow measurements used in pilot plants are the orifice plate flowmeter, the rotameter, magnetic flowmeters, vortex flowmeters, turbine flowmeters and swirl flow meters.

**Orifice plate flowmeters** measure the fluid static pressure before and after the orifice to determine the flowrate. The mass flowrate is obtained by measuring the viscosity of the fluid in case incompressible fluids or calculating it by knowing temperature and pressure for compressible flow.

**Rotameters** which are also known as variable area flowmeter uses the force of the moving fluid to move the float upwards as seen in Figure 4.7. Higher flowrate means higher equilibrium point of the float. Despite the advantages of rotameters such as low cost, simplicity, low pressure drop, no power needed and the wide range of applications where it can be used, rotameters must be vertically oriented. Moreover, rotameter's graduations are specific to fluid at a given temperature (ϱ, μ) so it's not suitable for the solvent side applications specially that the CO2 loading can change from time to time depending on the operating regime of the power plant such as peak and off peak scenarios where the degree of regeneration of the solvent depends on the price of electricity and consequently the amount of steam extracted from the turbine.

**Magnetic flow meters** works only with conductive liquids where the motion of conductive fluid across the magnetic field generates a voltage ∝ to the velocity of the fluid. Those devices induce no flow restriction i.e., (no pressure drop) and are mainly for harsh liquids such as (sewer, sludge,..etc..). This device requires that the pipe must always be full for the emf to drive voltage & current to the electrodes. In addition, it should be placed within straight pipe before and after which makes it challenging for small pilot plants due to the limited space available horizontally. Finally, it is not suitable for high temperature measurements.

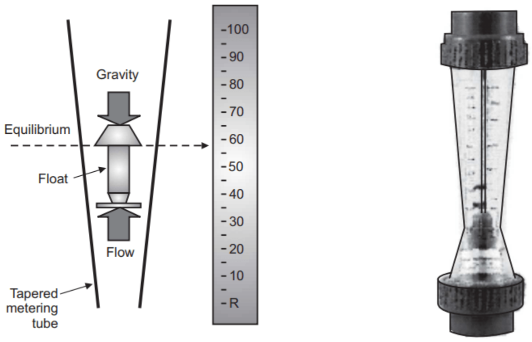


Figure 4.7 Rotameter

**Vortex flow meters** have a shredder bar placed to obstruct the flow as seen in Figure 4.8 where a pressure sensor (working on piezoelectric effect) measures the frequency of vortices generated around the obstacle ∝ to $V_{fluid}$. These devices need turbulent flow so zero reading doesn't mean there is no flow in the pipe, but flow could be linear.

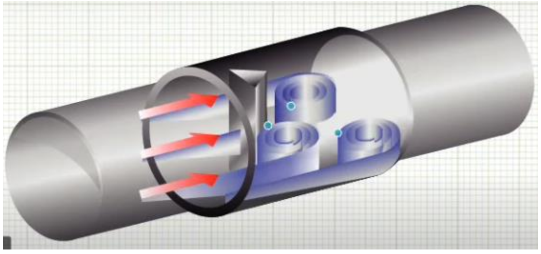


Figure 4.8 Vortex flowmeters.

**Turbine flow meters** contain a turbine rotor placed in the fluid with a magnetic sensor placed on top as seen in Figure 4.9. The rotor's rotational speed depends on the fluid velocity (i.e., flowrate). The presence of the turbine requires a clear fluid without solids which means that in carbon capture units, it's better to place it after solvent filters to guarantee the minimum amount of solids present. Moreover, it needs a straight pipe before and after like the case of Vortex devices. Turbine flow meters are calibrated based on µ fluid (thinner or thicker fluid will change the speed of rotation) so it is not recommended for steam.

**Swirl flow meters** measure pressure variation when a flow is interrupted by an obstacle "swirler" fixed spiral vanes as seen in Figure 4.10 where the frequency of fluid rotation ∝ to Vfluid. Sensors are equipped with piezo elements that sense only vibrations and noise, to subtract it from the total signal measured to get the net flow signal "isolated". Specific flow velocity is required to start measurement (i.e., can't start from 0). Swirl flowmeters are very useful in industrial processes as they measure a variety of liquids, gases and steam as well as being applied to a wide range of liquid viscosities. In addition, it is tolerant to sediments entrained in liquids and resistant to vibrations & shock waves. Finally, it is easy and inexpensive to install because it contains no moving parts.

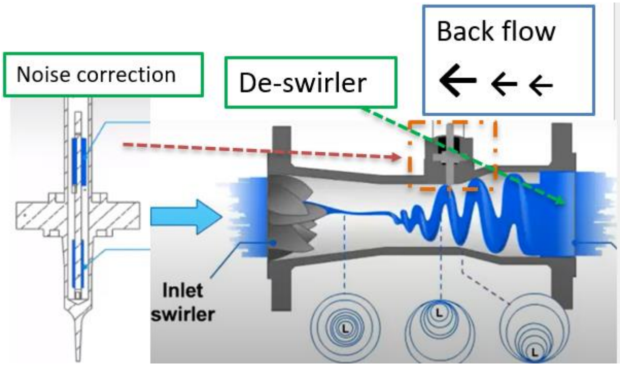


Figure 4.10 Swirl flowmeters.

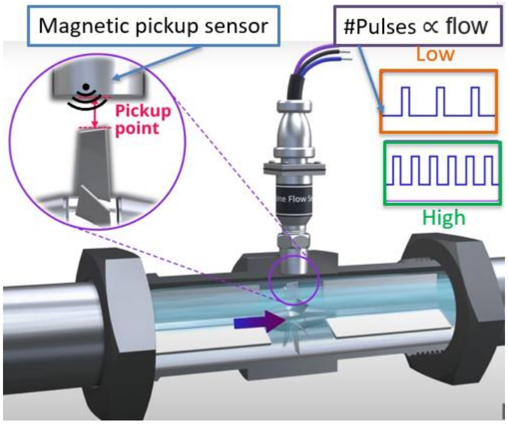


Figure 4.9 Turbine flowmeters.

## 4.5 Level measurement and instrumentation

Liquid level is a very important parameter in industrial processes and has to always be controlled inside tanks and columns' sumps. An increase in liquid level can indicate a buildup due to clogging somewhere which is undesired, especially in absorbers and strippers as it can lead to flooding of the towers and consequently the reduction of the capture efficiency. A drop in the liquid level can indicate a leakage or a loss in liquid somewhere in the system which can potentially lead to cavitation, especially in tanks placed upstream a pump. In carbon capture, liquid level can indicate the amount of solvent that was lost due to emissions and degradation which can be compensated by pumping new solvent from the makeup tank.

Level instrumentation can be divided into two main categories which are point level measurements and continuous measurements. Point level instrumentations are devices that can indicate a high or low level only such as capacitance, optical, conductivity, vibrating (tuning fork) and float switch. On the other hand, continuous level instrumentation can continuously measure and indicate the current level of liquid at any time such as ultrasonic and radar (Microwave).

**Capacitance level sensors** detect the effect of the level on the electrical field and they are best used in liquid storage tanks. They are small, less expensive, accurate and have no moving parts. However, they are invasive i.e., they touch the liquid, they need calibration and they only detect certain liquids.

**Optical level sensors** work by converting light rays into electrical signals where it measures a physical quantity of light and translate it to measurement. Usually, they are used as low-level indicators to prevent run-dry conditions. Those sensors are small, have no moving parts and are not affected by high Pressure or temperature. However, the lens gets dirty/coated and requires cleaning.

**Conductivity (resistance) level sensors** use a probe to read conductivity where a circuit is closed when liquid covers the probe and current flows which will signal a high or low level. These sensors are easy to use, have no moving parts and are available at low costs. However, it is invasive and can only sense conductive liquids. Over time, the probes suffer erosion and have to be changed.

**Vibrating (tuning fork) Level sensors** consist of a fork which vibrates at its natural frequency. When liquid covers the fork the frequency changes as seen in Figure 4.11. It is used in Oil & Gas applications, chemical industries, food and beverage. This type of sensor is an interesting application for pilot plants for carbon capture as they are small, easy to install and maintenance-free.

**Float switch Level sensors** work on a simple mechanism whereas the level increases, the float rises and a circuit is closed while as the level decreases, the float drops and the circuit opens. This means that they will only give high/low indication i.e., not for variable levels. Despite being inexpensive, the non-dependency on a power source and the direct indications they give, yet they are invasive, have moving parts and above all they are relatively large so won't be a good choice for small absorber diameters.

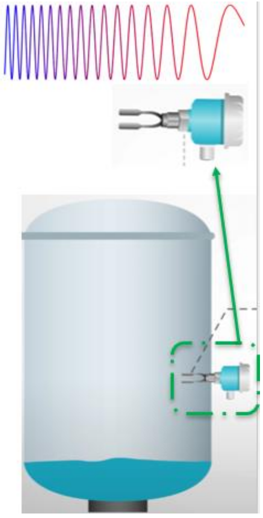


Figure 4.11 Tuning fork level sensors.

**Ultrasonic sensors** emit waves in which the time taken for waves to get detected back reflects the height of liquid. They have no moving parts, compact, Non-invasive, Self-cleaned due to the vibrations they produce. However, they are expensive and are negatively affected by the environment they are measuring.

**Radar (Microwave) level sensors** include an antenna which transmits microwaves on radar sensor. The product being sensed reflects the waves back to antenna and the time taken for waves to get detected back indicates the height which makes it ideal for hot liquids storage tanks. These sensors are not affected by pressure, temperature or dust. In addition, they measure liquids, pastes, powder and solids as well as being Non-invasive, accurate and requires no calibration. The disadvantages of radar sensors are found in their high cost as well as in their limited detection range.

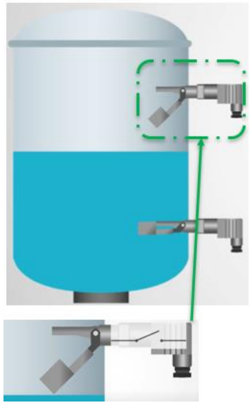


Figure 4.12 Float switch Level sensor.

Figure 4.13 shows the absorber and stripper's liquid continuous level measurements where the absorber's level is more stable because it is a direct level control "Fast response". On the other hand, the stripper's liquid level is connected to water wash cooling water flowrate in which as the stripper level drop, an increase in cooling water flowrate in absorber wash section is done so, more water is condensed from flue gas and the liquid level increases in stripper. This is an indirect level control i.e., more fluctuations "slow response."

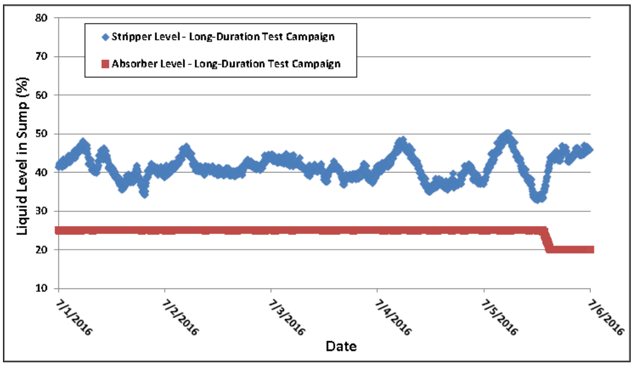


Figure 4.13 Level control NCCC Linde-BASF plant

## 4.6 Gas and liquid analyzers

Gas and liquid analysis are very important in determining the most important parameters of the carbon capture process such as the loading of solvent as well as the composition of flue gases leaving the absorber to determine the capture efficiency. Thus, investing in advanced analyzer with high accuracy can help reduce the mass and heat balance closure error. In gas analysis the nature of gases being sampled is important and it is divided into condensing gases with high water content and noncondensing gases. Both categories require heating of the sample to guarantee complete evaporation (~180°C) where it is to be noted that high water content is a challenge to analyzers.

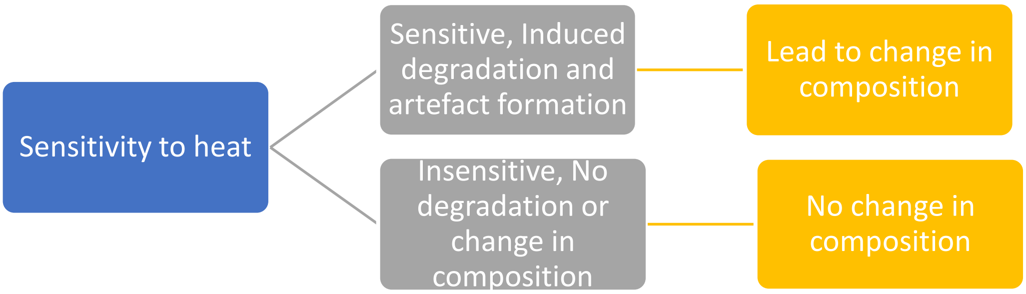


Figure 4.14 Sensitivity of samples to heat.

Main challenges of online sampling and analysis

- **Representative flue gas sample**
    - In-situ → (no transfer required)
    - Extractive sampling "Isokinetic" → (transfer required)
- **Sample transfer** which has the risk of altering the sample composition through:
    - Degradation
    - Artefact formation
    - Condensation "$H_2O$ vapor removes soluble from gas & cause slugging."

Flue gas leaving the absorber contain high water content (negative effect on analysis results) as well as Organic compounds "solvents and their degradation products such as N-Nitrosamines, Alkyl amines, Amines and Aldehydes which have different thermal stability and boiling points so as temperature is increased, they decompose to $NH_3$, $CO_2$, HCN, $NO_x$. Moreover, flue gases contain $NO_x$ and secondary amines, $SO_2$, $NH_3$ and $O_2$ which lead to artefact formation. Analyzers are divided into **extractive gas analyzers** which involves heating sample to avoid condensation or drying the sample to remove water, **In-situ probe analyzers** where sensors are placed directly in flue gas stream to measure a single compound and **Across-stream in-situ analyzers** which is an optical analysis methodology. However, it has problems with liquid droplets and mist.

**Gas chromatography (GC)** analyzes and separates complex mixtures of gases. It consists of a stationary phase (solid-liquid) {Wax, silicon, grease} and a mobile phase (inert gas gas {He, $H_2$ or $N_2$) as seen in Figure 4.15 where separation occurs based on the interaction of molecules between mobile & stationary phase. The column placed in a chamber for maintaining temperature while detectors could be Thermal conductivity detector (TCD), Flame–ionization detector (FID), Photo-ionization detector (PID) “UV lamps” or Flame–photometric detector (FPD).

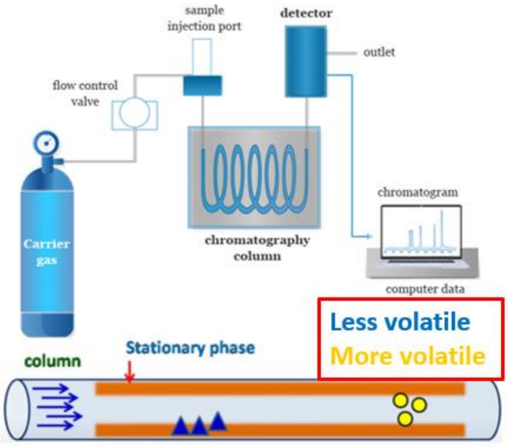


Figure 4.15 Gas chromatographer.

**Spectroscopy “Optical methods”** which is the study of interaction between light and matter and works on the principles of observing the electromagnetic radiation spectrum. They include different methods such as:

**i) Infrared Spectrometry (IR):** include different absorption instruments which work on Near, Middle and Far Infrared regions such as

1- Dispersive grating spectrophotometers

2- multiplex instruments (FT)

3-non-dispersive photometers

A summary of detection mechanism is illustrated in Figure 4.16.

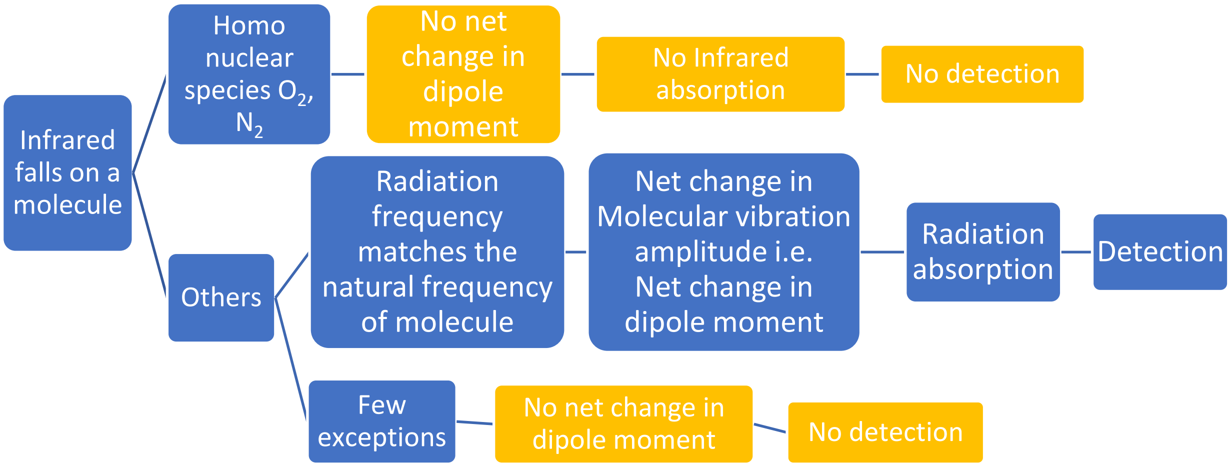


Figure 4.16 Infrared Spectroscopy detection mechanism.

**ii) Fourier Transform Infrared spectroscopy (FTIR):** measures all IR frequencies simultaneously where it converts signals measured in time domain to frequency domain. FTIRs are cheaper to build than monochromators as well as being fast, high resolution and sensitive. In most of the pilot plants studied in this work, it was used in detecting $H_2O$, CO, $CO_2$, $SO_2$, $NO_x$, $NH_3$, $N_2O$, $O_2$. FTIR is a good match for monitoring MEA emissions. However, high water content will affect the analysis result. Another disadvantage is that complex organic compounds show a broader band of absorption which overlap because these compounds have similar molecular weights and structure.

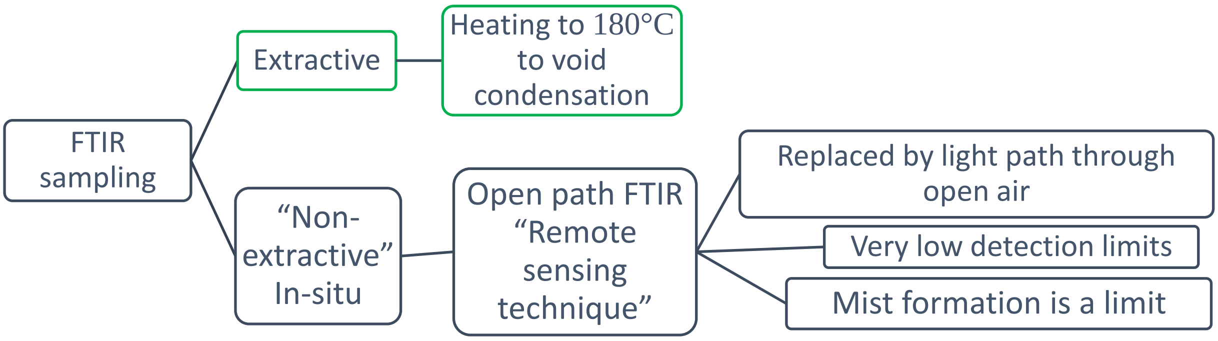


Figure 4.17 FTIR sampling techniques.

**iii) Non-dispersive Infrared spectroscopy (NDIR)**: is a simple device used as gas detectors for air pollution monitoring where no contact with the gas occurs and thus, more reliable. Gas concentration $\propto$ light absorbed [Difference between emitted and detected IR light] in a specific $\lambda$. They are constructed for specific gases and consequently, not affected by other gases. They are not affected by oxidizing compounds, so they are highly durable.

**iv) Ultra-violet and visible spectroscopy (UV-vis):** For multiple bond molecules where a strong UV absorption occurs in chromophores {aromatics, conjugated system of bonds and carbonyl groups}. UV can detect $SO_2$, NO, $NO_2$, $Cl_2$, $NH_3$ and $CS_2$.

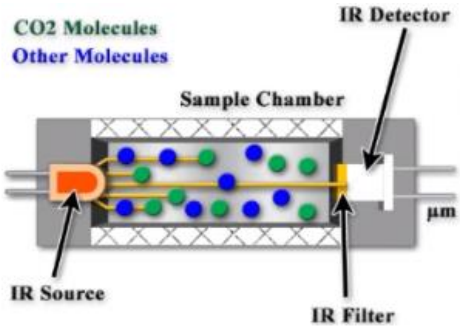


Figure 4.18 NDIR

**v) Tunable diode laser absorption spectroscopy (TDLAS):** Uses absorption bands instead of spectra. New ones provide in-situ measurements so no need to sample transfer. Measured gases includes {$O_2$, $CH_4$, CO, $NH_3$, HCl, $H_2O$, $CO_2$, NO, $NO_2$, HF, $H_2S$}. TDLAS can detect low concentrations up to 1 mg/Nm3 and can be used for detecting gas T, P, velocity, mass flux.

**vi) Differential Optical Absorption Spectroscopy (DOAS):** Suitable for observing atmospheric trace gases such as $O_3$ & $NO_2$ as it works with individual absorption characteristics of molecules. It is mainly used for gas leak detection. It works on the Lambert-beer's absorption law required a long measurement path "Difficult to implement in a stack". It requires that the flue gas stream needs to be free from droplets and aerosols.

**Mass spectroscopy is used to** identify organic molecules based on the relation between molecular weight and net charge. Organic compounds need to be ionized before analysis in the mass spectrometer. Most common devices are Quadrupole, Time of Flight (TOF) and Magnetic Sector (MS). It can be combined with liq/gas chromatography for analyzing complex gas mixtures. Requires sample heating (120-180 °C) "degradation problems. Ionization is divided into two techniques, first is called Electron impact "bombarding molecules with electrons" where organic molecules lose an electron and become +ve charged. The second is called chemical ionization "soft" also known as (PTR) proton transfer in which it Utilizes already charged molecules such as $H_3O+$ to ionize molecules of interest.

**GC-MS and LC-MS** combine liquid or gas chromatography with mass spectrometry which leads to a higher accuracy and cleaner mass spectra because of separation.

- LC-MS is more suitable for water soluble compounds or high boiling points compounds.
- GC-MS is more suitable for volatile compounds which are thermally stable.

**Proton-Transfer-Reaction Mass Spectrometry (PTR-MS)** is a highly sensitive device for detecting VOC in real time as it combines between soft ionization mass spectrometry $H_3O^+$ (chemical, non-fragmenting) and highly sensitive product ion formation in an ion drift tube. Sampling is done directly without sample pre-treatment where measurements are done online with ~ 10 PPTV detection limit. This technique is suitable for amines, amides, nitrosamines and nitramines.

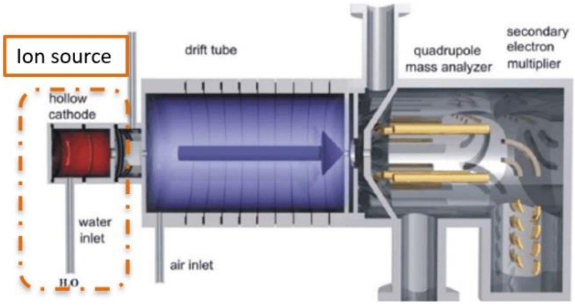


Figure 4.19 PTR-MS

**Proton-Transfer - Time of flight - Reaction Mass Spectrometry (PTR-TOF-MS)** combines a PTR source with time-of-flight mass spectrometer where it can identify the exact atomic composition of C, H, N & O ions. VOCs are measured in complex gas mixtures which makes this technique suitable for car engine emissions, fire emissions, waste incinerator gas, gasified wood and fermentation gas. This device is suitable for detecting {amines, amides, nitrosamines, nitramines} to as low as 10 PPTV. However, sample should be heated to avoid condensation.

**Ion mobility Spectrometry (IMS):** measures the velocity of ionized substances in an electric field. Main components of this device are an Ion source, a drift tube "where ions are separated" that contains drift/buffer gas which slows down the ions and a detector. It uses the same ionization techniques as in LC-MS where the ions' velocity reduction depends on the size and arrangement of ions, i.e., Isomers can be separated with IMS. This device is mainly applied for {Acids and corrosive gases, VOC, NH3 [in water and air] and it is to be noted that 2 phase systems require an evaporator (heat the sample).

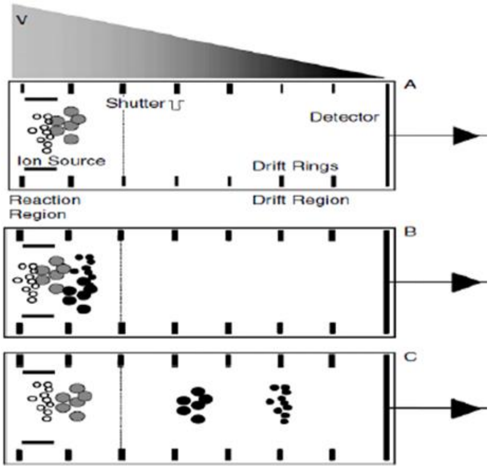


Figure 4.20 Ion mobility Spectrometry (IMS)

## 4.7 Instrumentation proposal

Instrumentation is a very important aspect in designing carbon capture and storage plants as it requires advanced technologies for monitoring process performance as well as pollutants which sometimes have to be measured at very low concentrations. This would require advanced analyzers which are very expensive and require careful use depending on the objective of the pilot plant and the type of flue gas being treated as well as the type of solvent being used.

In this section, two different scenarios are proposed for instrumentation of a pilot plant for carbon capture as seen in Table 4.2. The first scenario assumes a limited budget of 250,000 euros while the second one assumes an unlimited budget. Those two scenarios are based on the data collected from the previously studied pilots in addition two other papers and reference that were mainly focused on instrumentation such as [32], [33] and [34].

Rough estimations for gas and liquid analyzers pricing are listed below.

- Gas chromatography (GC)→$10,000 to over $100,000 USD
- FTIR→ $15,000 to over $100,000 USD
- ATR-FTIR→ $25,000 to over $50,000 USD
- PTR-TOF-MS→ $200,000 to over $500,000 USD
- LC-MS → $100,000 to over $500,000 USD.
- GC-MS → $50,000 to over $300,000 USD

| Comparison point | Location | limited budget € 250k | Unlimited budget | Comments | Reference |
|---|---|---|---|---|---|
| **Temperature sensors** | Absorber & Stripper | 1 per each height step | 3-4 per each height step | Monitor absorption and stripping performance by monitoring liquid and gas distribution as seen in TCM | TCM [4] |
| **Continuous Level sensors** | • DCC sump<br>• Absorber sump<br>• Stripper sump<br>• LVC Flash tank | Ultrasonic | Ultrasonic | • Cheaper than Radar (Microwave)<br>• More effective in small tanks (sumps) because radar beam can become dispersed and result in inaccurate readings<br>• Minimal maintenance requirements.<br>• Can be placed outside the tank. (non-contact)<br>• Foam can interfere with ultrasonic level sensors. | |
| **Point Level sensors** | • DCC sump<br>• Absorber sump<br>• Stripper sump<br>• LVC Flash tank<br>• Solvent make-up tank<br>• Reboiler<br>• Stripper's top Condenser | Tuning fork | 2 float switches (high and low) case of errors in ultrasonic or foam | • Back-up in case of failure of Ultrasonic<br>• Also helps in calibration of Ultrasonic level instrument.<br>• Cheapest, less susceptible to erosion (unlike capacitance and conductivity instruments)<br>• No need for continuous measurements. | |

| Comparison point | Location | limited budget € 250k | Unlimited budget | Comments | Reference |
|---|---|---|---|---|---|
| **Gas analyzers** | Absorber Inlet | FTIR (extractive sampling) + oxygen detectors | Gas chromatographer | **FTIR**:<br>• Less expensive than Gas chromatographer<br>• FTIR is selective for the functional group i.e., "can identify a wider range of VOCs<br>• Difficulty in detecting low amine conc. (Max 1ppmv)<br>• It isn't a good match with new solvents because they already have very low amine emissions.<br>• Requires several seconds to minutes (slow)<br>• Not a perfect match with high conc $SO_3$ [NCCC]<br>• Needs oxygen detector because it can't detect diatomic or noble gases<br>**Gas chromatographer:**<br>• Very expensive<br>• Require sample preparation.<br>• Requires a constant supply of high-purity gases | Gasmet FTIR→ TCM & Aker solution's MTU<br>AIT "applied instrumentation technology" (FTIR)→ TCM<br>FTIR→ Niederaussem & Fortum & NCCC |

| Comparison point | Location | limited budget € 250k | Unlimited budget | Comments | Reference |
|---|---|---|---|---|---|
| **Gas analyzers** | Absorber Exit | ATR- FTIR | PTR-TOF-MS | **PTR-TOF-MS:**<br>• More sensitive than FTIR → detects VOC at PPTV (part per trillions)<br>• Highly selective for protonated VOC i.e., "provide more detailed information on the specific VOCs" (M.wt & chemical structure) isomers & can be used for new solvents since not all amine group are known<br>• sampling rates of up to 10 Hz or more (very fast)<br>• More expensive than FTIR & ATR-FTIR in capital& maintenance cost.<br>**ATR-FTIR:**<br>• Higher sensitivity than FTIR but lower than PTR-TOF-MS<br>• selective for the functional group i.e., "can identify a wider range of VOCs<br>• If cost is a limit, ATR-FTIR with longer pathlength can be used.<br>• Solid or liquid samples can be analyzed directly, without complex sample preparation for solvent analysis | PTR-TOF-MS→ TCM & Fortum |

| Comparison point | Location | limited budget € 250k | Unlimited budget | Comments | Reference |
|---|---|---|---|---|---|
| **Liquid analyzers** | Lean and Rich Solvent, Water wash blowout | ATR- FTIR | LC-MS | • If the goal is to identify and quantify specific functional groups in the solvent, ATR-FTIR is better, Also ATR-FTIR is much cheaper than LC-MS.<br>• If the goal is to obtain a detailed analysis of the composition of the solvent, including impurities and degradation products, LC-MS would be more suitable. | TCM |
| **Gas Flow measurements** | Absorber Flue gas inlet & exit | Turbine flowmeters | Coriolis flowmeters | **Turbine flowmeters:**<br>• Turbine flowmeters are relatively cheap and don't require a long straight pipe before and after.<br>• They need a lot of maintenance because of the rotating parts | Imperial college |
| **Gas Flow measurements** | CO2 product flow | V-cone, Orifice | Coriolis flowmeters | • V-cone flowmeters don’t require straight pipes and is a good match for tight fits and retrofits (especially mobile pilot plants that should be compacted and small). | NCCC |
| **Liquid flow measurements** | Lean and Rich Solvent, Water and acid wash, water coolers, | Magnetic flowmeters or Swirl flow meters | Coriolis flowmeters | **Magnetic flowmeters:**<br>• They do not need straight pipes.<br>• Can provide accurate measurements for a relatively low cost | Imperial college |

| Comparison point | Location | limited budget € 250k | Unlimited budget | Comments | Reference |
|---|---|---|---|---|---|
| **Pressure measurements** | Stripper top, absorber top, flowlines, LVC flash tank | 268 pressure transmitter + Bourdon tube pressure gauges | 364 pressure transmitter or Pressure switches + Bourdon tube pressure gauges | suitable for measuring gauge and absolute pressure | Imperial college |

Table 4.2 Instrumentation proposal with 2 scenarios.

# 5. Absorber modelling

## 5.1 Introduction

In this study, a model verification and fitting of an absorber column for post combustion capture with MEA 30% solvent has been done in Aspen Plus. The absorber was modelled using the rate-based model where it is found to be more realistic than equilibrium model because the latter model assumes that liquid and vapor phases leaving each stage are in thermodynamic equilibrium with each other. Unfortunately, this assumption is only valid at the interface between liquid and gas (films) when gas and liquid are brought in contact on trays or in packing sections and this is why the equilibrium model overestimates the capture rate and efficiency. On the other hand, the rate-based model uses thermodynamic, mass transfer, kinetic and hydrodynamic correlations to simulate and predict the performance of packed and tray columns. Nevertheless, there are some parameters that can be empirically adjusted such as the transfer condition factor, the reaction condition factor, film discretization ratio and the flow model condition factor at the top and bottom to match the model predictions with the experimental data. In addition, there is also the interfacial area, heat transfer factor and finally the liquid and vapor mass transfer condition factor. The model predictions are influenced by these parameters to a great extent and multiple iterations must be done independently to understand the effect of each parameter on the overall performance of the model in way that the error between simulation results and real experimental data should be minimized.

## 5.2 Objectives

Data was taken from Faramarzi et al. (2017) [35] for a baseline test in TCM in 2015 to verify the absorber modeling performance with the Aspen plus Simulation. In this model only the absorber is modeled excluding the water wash sections at the top part of the absorber. Operating parameters and results in Table 5.1 and in particular for the test run C3-4 were taken from [35] and plugged in the Aspen Plus model. The absorber in Mongstad is quite big and is made of concrete with a rectangular shape and an equivalent diameter of the circle that has an equal cross section area had to be calculated since it is impossible to model rectangular columns in Aspen Plus.

| **CHP flue gas supply rate** | **Sm3/h** | **59 430** |
|---|---|---:|
| **CHP flue gas supply temperature** | °C | 29.8 |
| **CHP flue gas supply pressure** | barg | 0.01 |
| **CHP flue gas supply CO2 concentration (dry)** | vol% | 3.7 |
| **CHP flue gas supply O2 concentration (wet)** | vol% | 14.6 |
| **CHP flue gas supply water content** | vol% | 3.7 |
| **Lean MEA concentration (CO2 free)** | wt% | 31 |
| **Lean CO2 loading** | mol CO2/mol MEA | 0.2 |
| **Lean amine supply flow rate** | kg/h | 57 434 |
| **Lean amine supply temperature** | °C | 37 |
| **Rich solution return temperature** | °C | 33.2 |
| **Temperature above upper absorber packing** | °C | 39.7 |
| **CO2 capture** | (%) | 83.4 |
| **Equivalent absorber diameter** | (m) | 3.006 |
| **Packing height** | (m) | 24 |
| **Flue gas supply temperature** | (°C) | 30 |
| **packing type** | | Flexipac 2X |

Table 5.1 Averaged process data for the test period C3-4 of baseline testing in September 2015

By running the model after inserting the TCM baseline test data, results of the simulation showed a deviation from the reported TCM results and in particular the rich solvent temperature at the absorber exit as well as carbon capture efficiency and the temperature of the flue gases after leaving the last packing section and upstream the water wash sections. In addition, the temperature profile along the absorber's 24 m height of packing Table D.2 [35] was plotted against the liquid and vapor temperature at each of the stages along the absorber Figure 5.1. It is good to mention that the absorber was discretized into 50 stages in the Aspen Plus file for increasing the accuracy and to eliminate the effect of various types of flow modeling on the final results.

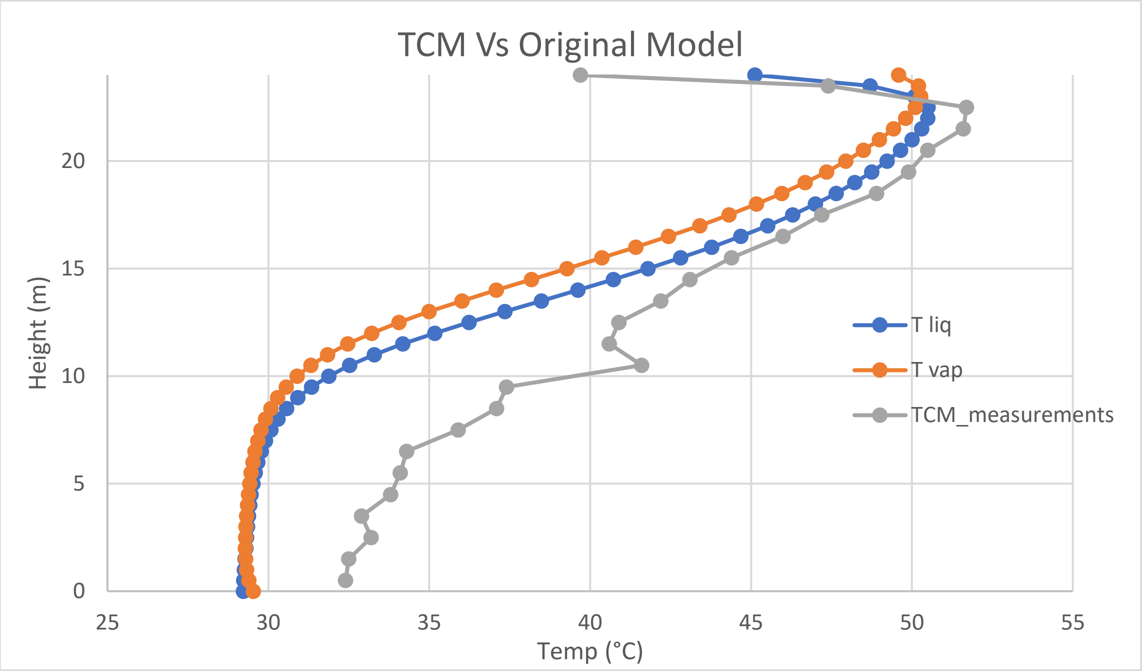


Figure 5.1 Temperature profile of TCM average readings Vs the Aspen Plus model's initial results

To reduce this average temperature profile error along with the other three errors mentioned in , iterations had to be done on different parameters in the global set up of the Aspen plus file and based on the direction of the error reduction, each parameter was set to the new value and iterations started on the next parameters

| | **TCM Real case results** | **Initial Model results** | **error (%)** |
|---|---|---|---|
| **CC efficiency %** | 83.4 | 87.3 | 4.71% |
| **T rich solv (°C)** | 33.2 | 29.2 | 12.04% |
| **Flue gas Temp above packing height** | 39.7 | 47.7 | 20.26% |
| **Temp profile Average relative deviation** | - | - | **10.61%** |

Table 5.2 TCM real results compared to the initial model results and the error percentage.

### 5.2.1 Iteration on the Global setup

#### Transfer condition factor

The mass transfer condition factor ∅ is a factor used for weighting and in particular for the calculations of the average temperature and compositions in the liquid film in the rate-based model. It's initially set at 0.5 and can vary between 0 and 1. At 0.5 the temperature profile as well as the mole fractions in the film are linear and consequently any deviation from this value will induce nonlinearity in those terms. In particular, any change in this value will affect the:-

- $\Gamma_j^{VF}$ &$\Gamma_j^{LF}$ the matrices of the thermodynamic factors for vapor and liquid film-non-ideality corrections.

- $R_j^{LF}$ & $R_j^{VF}$ film resistance terms across the films.

- Mass transfer coefficients (K) in Liquid and vapor film.

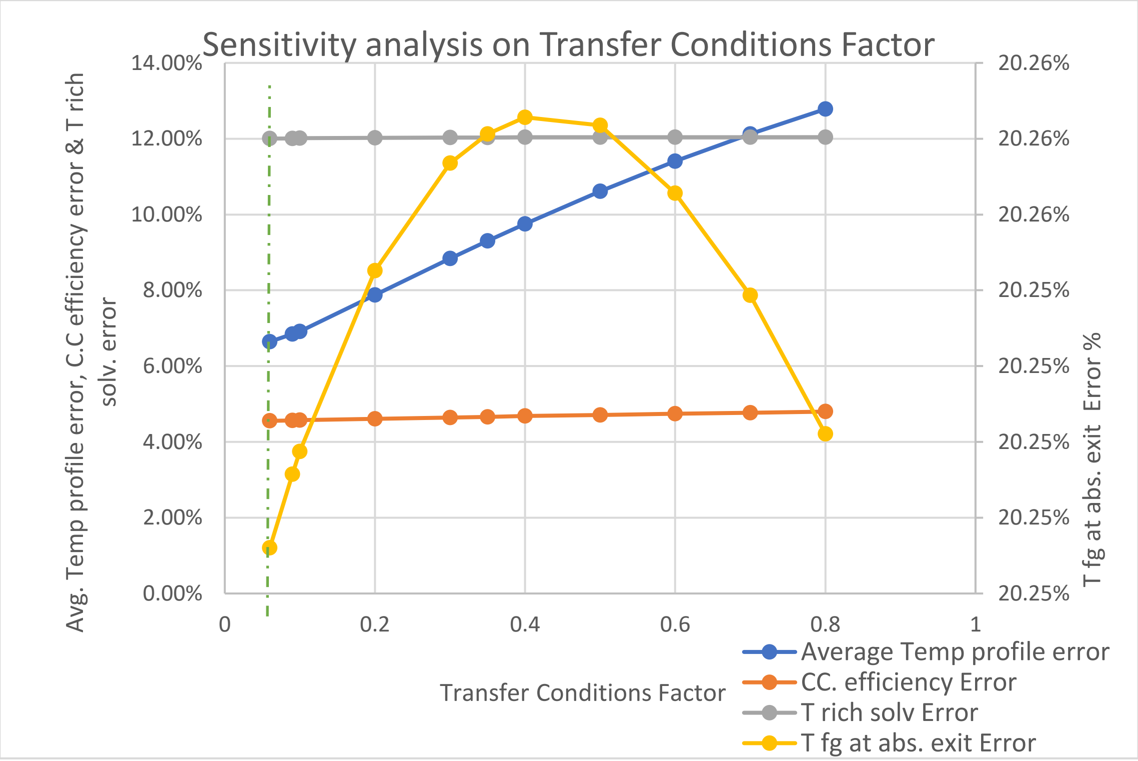


Figure 5.2 Sensitivity analysis on Transfer Conditions Factor

From Figure 5.2 it is clear that the direction of decreasing that factor reduced the error in both the temperature profile and the flue gas at the exit of the last packing stage in the absorber. Figure 5.3 shows the effect of increasing the value up to 0.8 [left graph] which is undesired and decreasing it to 0.06 [right graph] which is desired and consequently the final value was set to 0.06.

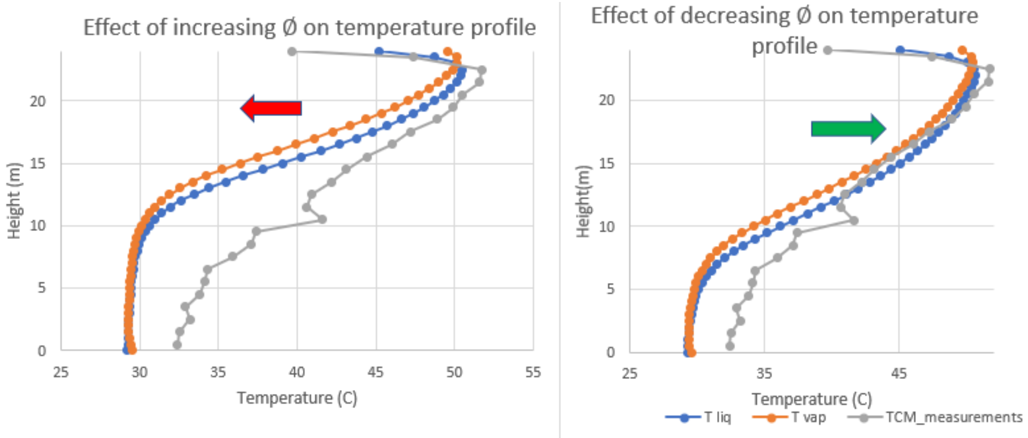


Figure 5.3 Effect of increasing and decreasing the transfer condition factor on the temperature profile.

## Reaction condition factor

The reaction condition factor $\eta$ is another weighting factor used for calculating the reaction rate in the film. Like the transfer condition factor, this term is set by default to 0.5 and can vary between 0 and 1. Changing this term will affect the reaction terms and in particular in the liquid film and obviously induce nonlinearity in the liquid film.

Figure 5.4 shows the iterations done on the reaction condition factor and its effect on the 4 errors. Figure 5.5 on the other hand shows the effect of increasing the $\eta$ value to 0.9 which will push the temperature profile from the middle and the lower part to the right. It is to note that further increasing of this value beyond 0.9 will increase the temperature profile error again even though the other three errors are decreased. Thus, 0.9 was selected to be the new value instead of 0.5.

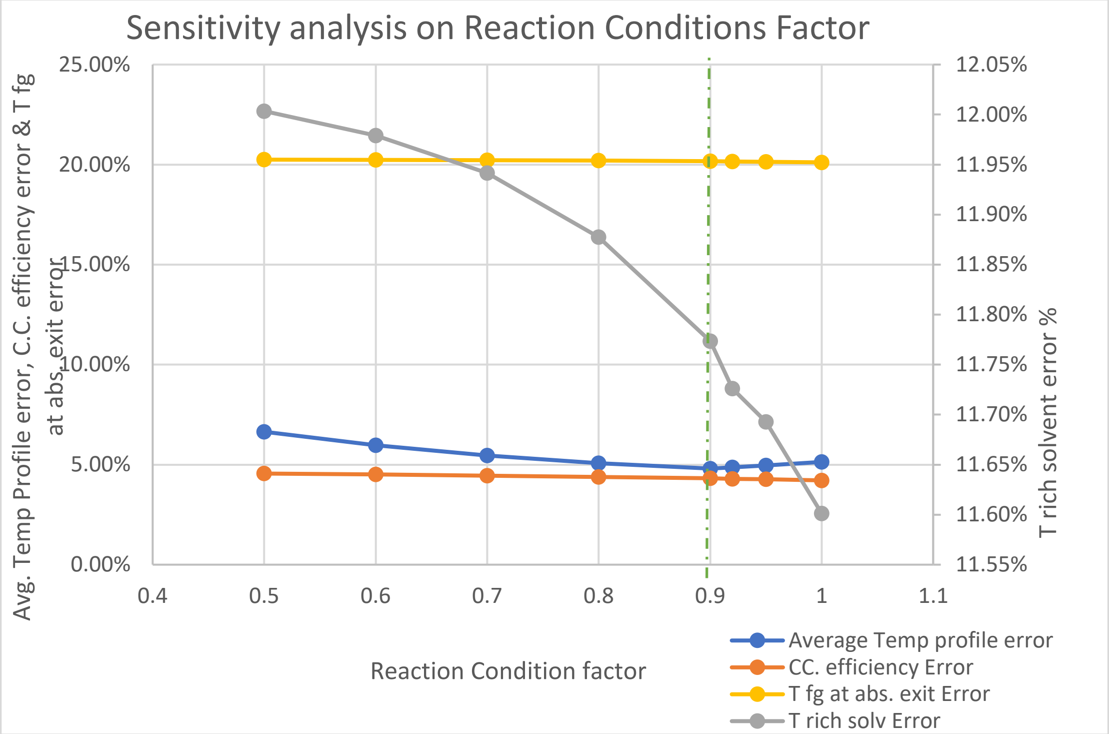


Figure 5.4 Sensitivity analysis on Reaction Conditions Factor

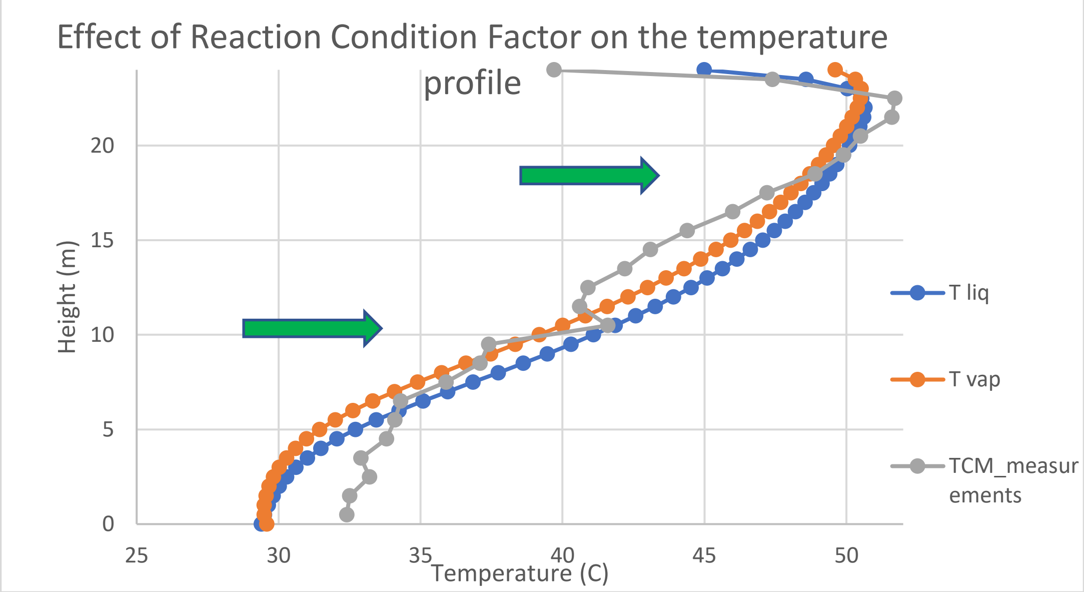


Figure 5.5 Effect of increasing the Reaction condition factor on the temperature profile.

### Flow model condition factor at the Top & Bottom

In calculating the temperature driving forces as well as the liquid and vapor film driving force in the j$^{th}$ stage in the rate-based model, a flow model must be selected because this flow model is used to determine the average of these driving forces as well as the temperature, pressure and the bulk composition. Modeling packed columns in Aspen plus is usually done by selecting one of the available flow models where each flow model represents a scheme of numerical integration along the height of the packing. The number of stages refers to the finite difference which is used in this integration. The absorber in our model was divided into 50 stages and as seen in Figure 5.6 [36], as the number of stages reach a certain value, all the flow models lead to similar results and that explains why changing the flow model at the top and bottom had no effect on none of the 4 errors.

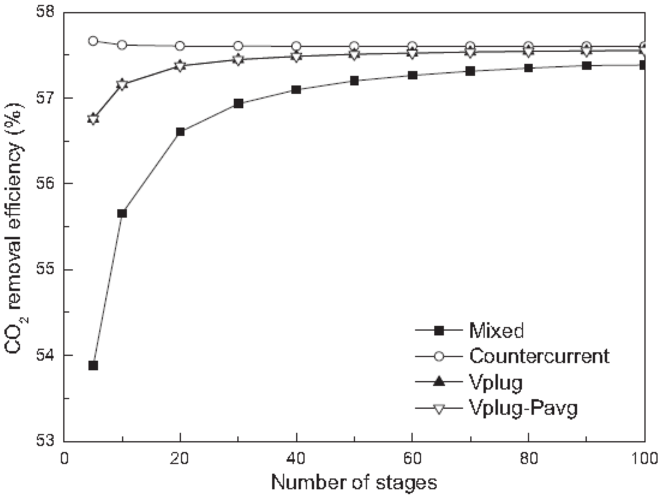


Figure 5.6 Effect of flow model selection on simulated CO2removal efficiency.

## 5.2.2 Iteration on the tuning factors.

### Interfacial area $a_j$

Heat transfer rates consist of a combination of conductive and convective heat transfer which is a function of the interfacial area at each stage j in the rate-based model. Thus, changing this factor will affect the rates of heat transfer. Starting from the initial value of 0.7, iterations were made by varying this value from 0.8 to 0.6 as shown in Figure 5.7 and it's clear that increasing that value will result in a higher carbon capture efficiency and consequently a higher error because our goal is to decrease this error. Moreover, the temperature profile will be shifted to the left as seen in Figure 5.8 [left graph] which will induce a higher temperature profile error. On the other hand, decreasing this value will shift the graph to the right and again increase the temperature profile error as well but will decrease the carbon capture efficiency error. Therefore, it was set to 0.69 instead of 0.7.

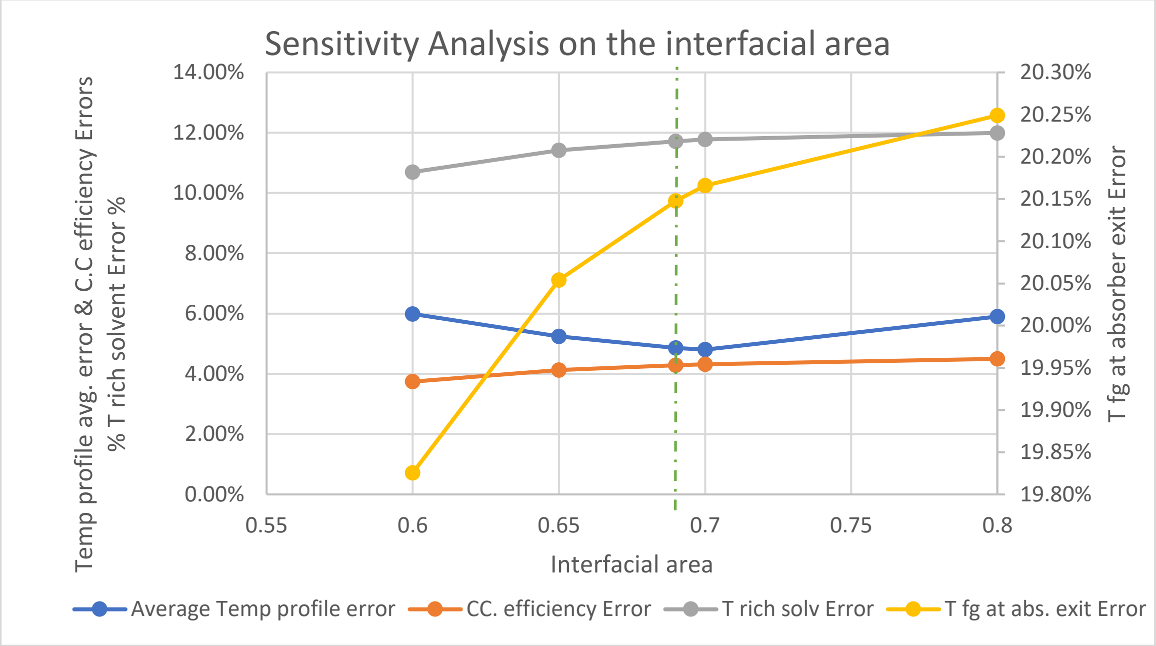


Figure 5.7 Sensitivity Analysis on the interfacial area

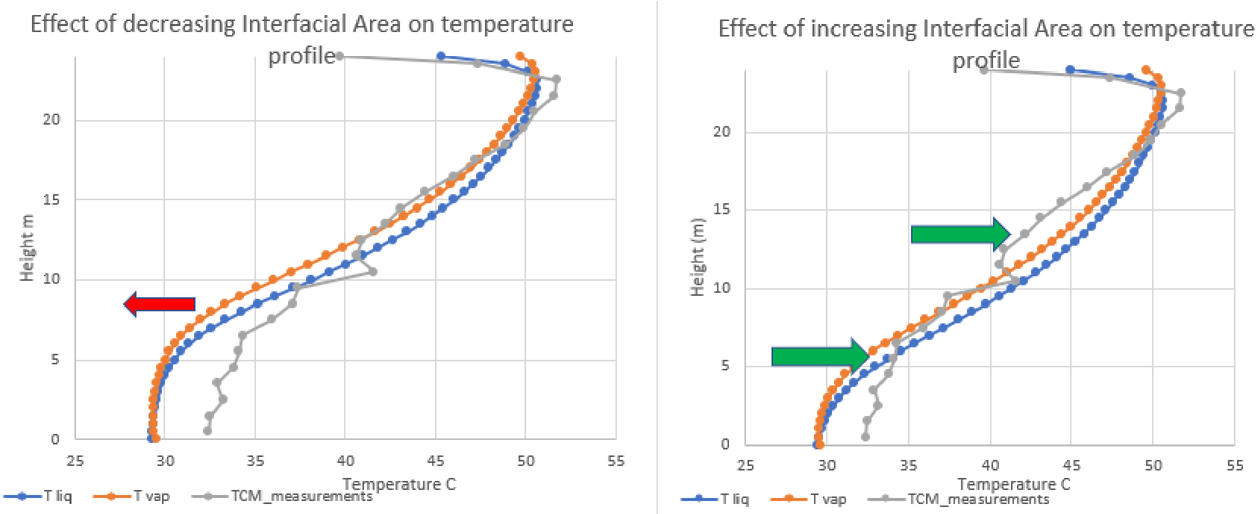


Figure 5.8 Effect of increasing and decreasing the interfacial area on the temperature profile.

## Heat transfer factor

The heat transfer factor was initially set at 1 and iterations were done in a decreasing way up to 0.33 as seen in Figure 5.9 where this decrease forced the liquid temperature to and vapor temperature lines generated by the Aspen Plus model to move away from each other as seen in Figure 5.10. The more the gap between the liquid and the vapor lines increase the TCM measurement temperature profile line becomes more contained within those two lines and thus the error decreases. However, this had a negative effect on the temperature of the flue gases leaving the absorber's last packing stage. Finally, it was selected to be set at 0.33 and it's good to know that below this value, computation becomes lengthy, and the model doesn't converge.

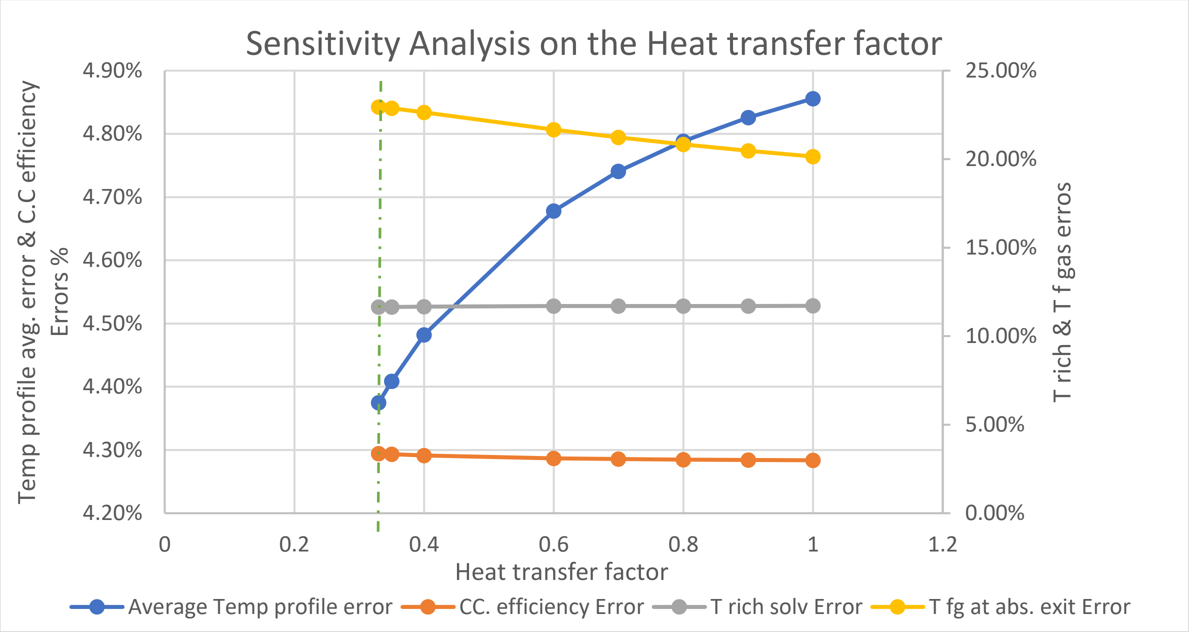


Figure 5.9 Sensitivity Analysis on the Heat transfer factor

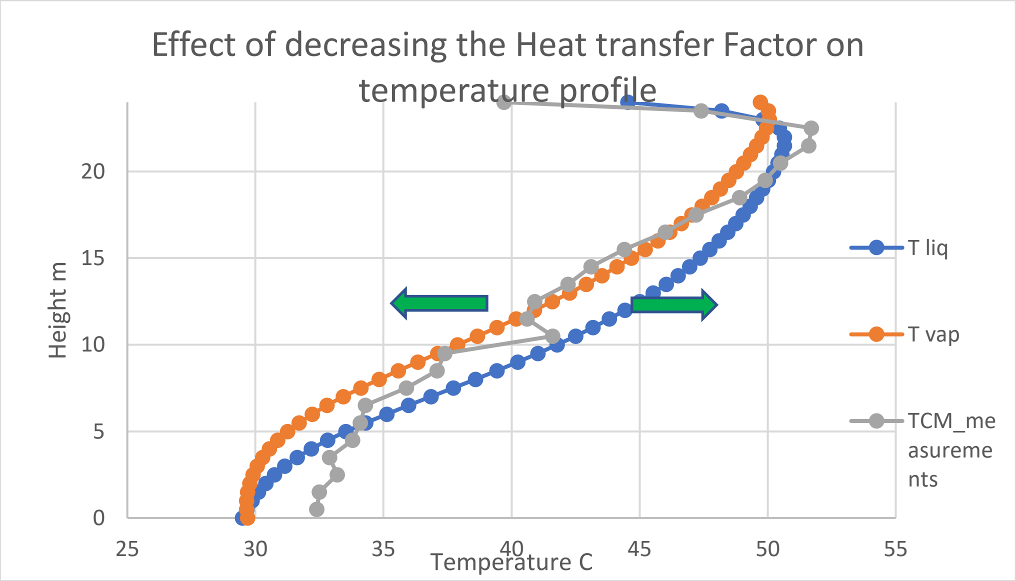


Figure 5.10 Effect of decreasing the Heat transfer Factor on temperature profile.

## Liquid mass transfer coefficient factor

The liquid mass transfer coefficient factor is a parameter that controls how fast the MEA 30% solvent can absorb $CO_2$ from the flue gas stream. It was initially set to 1 and iterations were done by increasing to 1.1 and decreasing to 0.9 as seen in Figure 5.11. This factor represents the mass transfer resistance between the liquid and gas films where the higher this coefficient, the lower is this resistance and consequently the higher the $CO_2$ capture efficiency. Unfortunately, this is not in favor of our model as our goal was to decrease the capture efficiency to match TCM results. On the other hand, reducing this coefficient indicates a higher mass transfer resistance and consequently a slower absorption of $CO_2$. This direction will lead to a decrease in the C.C error but will force the temperature curves to shift to the right Figure 5.12 and thus the temperature profile's average error will increase again. Consequently, it was chosen to be kept at 1 as it was initially.

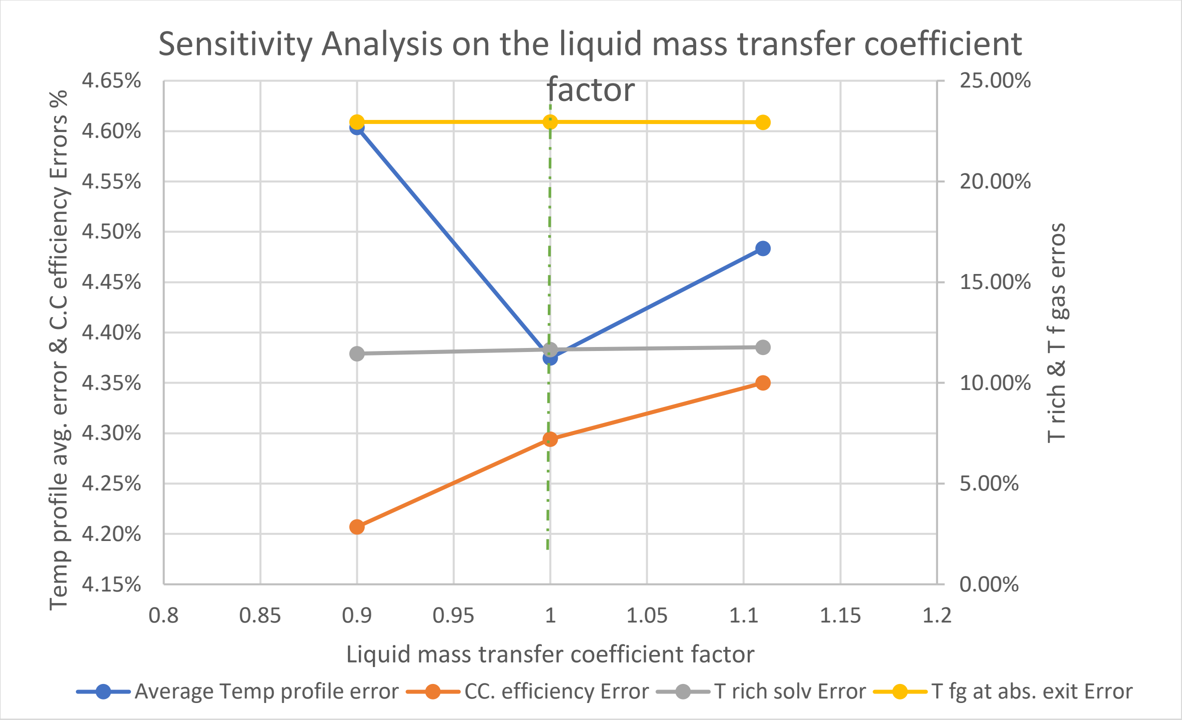


Figure 5.11 Sensitivity Analysis on the liquid mass transfer coefficient factor

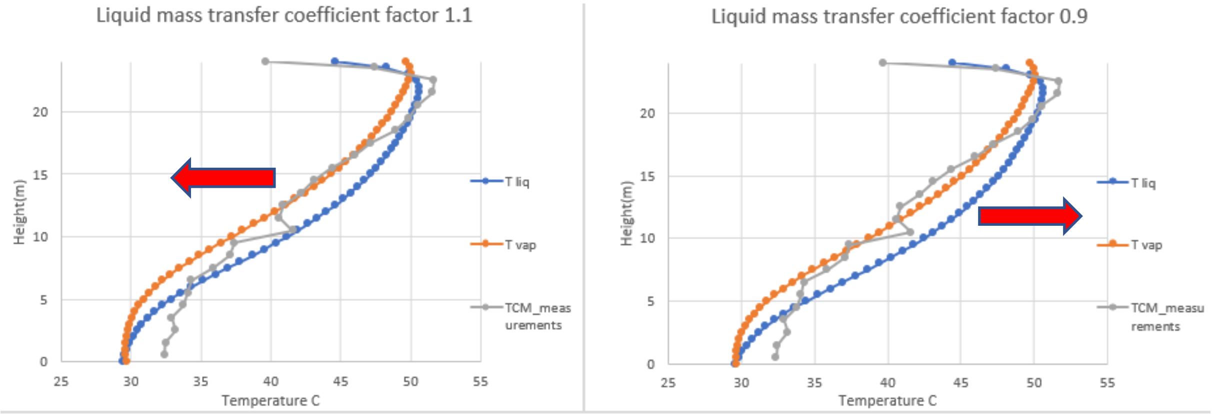


Figure 5.12 Effect of Liquid mass transfer coefficient factor on the temperature profile

## Vapor mass transfer coefficient factor

This factor is an indication of how fast solvents can release the captured CO2 in the absorber if subjected to a reduced temperature or pressure where a higher value means that the solvent can easily release $CO_2$ in the absorber which is un favored in the absorber. Initially, this term was set to 1 and iterations were made in the direction of lowering this value up to 0.6 as seen in Figure 5.13. a value of 0.7 was chosen to be a better point than that one as it resulted in decreasing the capture efficiency's error as well as the temperature profile's average error.

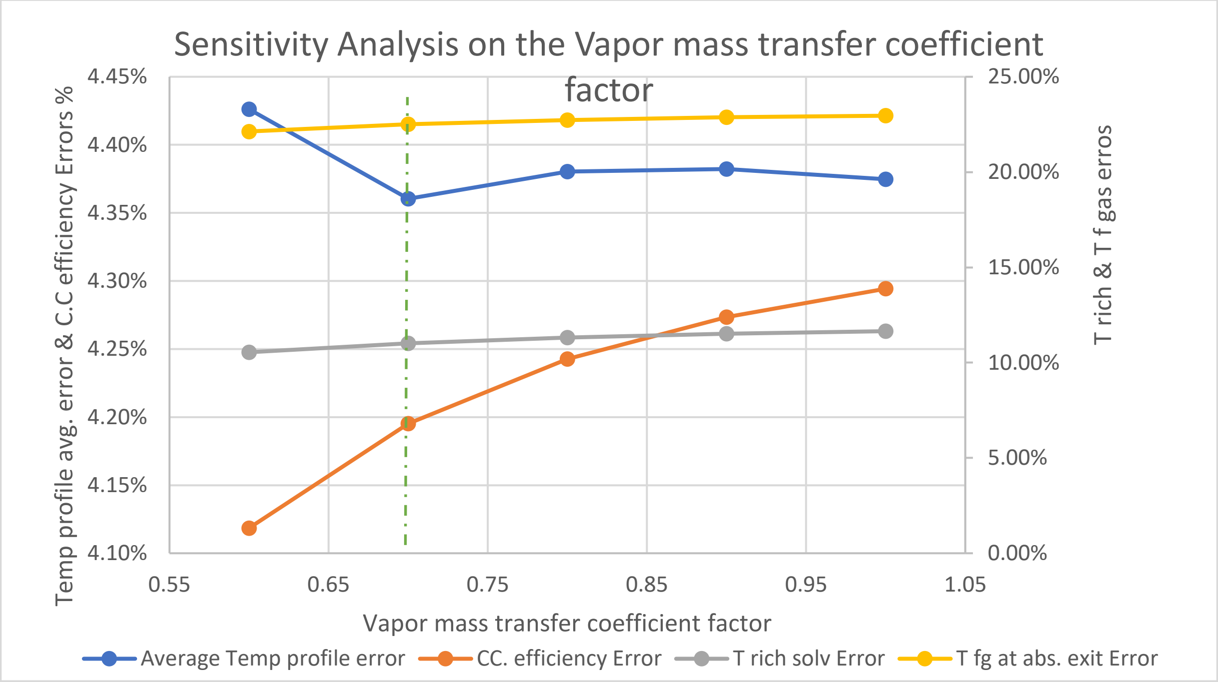


Figure 5.13 Sensitivity Analysis on the Vapor mass transfer coefficient factor

### 5.2.3 Results and discussion

By performing such iterations on both global set up and tuning factors independently, a better point was achieved for a TCM absorber model. Initially, the model had a CC efficiency error of 4.71%, rich solvent temperature's error of 12.04%, an error of flue gas temperature leaving the top absorber packing of 20.26% and a temperature profile average error of 10.61%. By changing those factors, a much better point was achieved that has much lower error in terms of the temperature profile as the model results are aligning with the measured data from TCM's probes as seen in Figure 5.14. A comparison between the initial and the final results can be seen in Table 5.3 where a slightly lower carbon capture efficiency error was achieved as well as a lower temperature of the rich solvent leaving the absorber. Unfortunately, the temperature of the flue gas leaving the top packing section of the absorber before entering the water wash section was slightly increased which caused the error to increase from 20.26% to 22.5%.

This iteration work was done manually by seeing the effect of the change of each parameter independently and basing the decision on personal opinion. However, similar results were found by having a different combination of different values for the tuning factors and the global set up parameters which means that even though this point has a better result compared to the initial setup values, it is not the optimum point and an optimization problem can be written with an objective function to reduce the carbon capture efficiency error while keeping the temperature profile's average error within acceptable limits. By doing so, an optimum point can be found for this model while saving time consumed in doing iterations manually. Moreover, this model has to be tested with different data produced from different pilot plants such as NCCC or Niederaussem by changing the absorber's diameter, type of packing and its height, as well as the solvent and the flue gas working parameters. A percentage of error will always be present when trying to model such a complicated equipment as the absorber. However, this will help in finding better values for those parameters that better fit the absorption modeling results.

| | Initial Model results | error (%) | Final Model results | Final error (%) |
|---|---|---|---|---|
| **CC efficiency %** | 87.3 | 4.71% | 86.89% | 4.2 % |
| **T rich solvent (°C)** | 29.2 | 12.04% | 29.5 | 11.02% |
| **Flue gas Temp above packing height** | 47.7 | 20.26% | 48.6 | 22.5% |
| **Temp profile Average relative deviation** | - | 10.61% | - | 4.36% |

Table 5.3 Comparison between the initial model results and the new results after changing the global set up parameters and tuning factors.

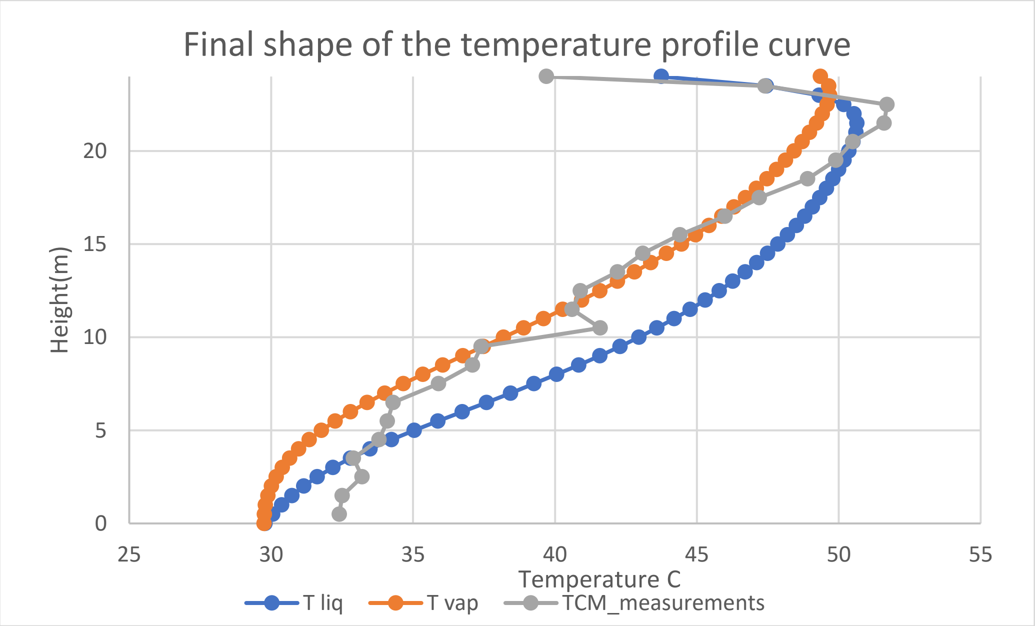


Figure 5.14 Final shape of the temperature profile

# 6. Conclusion and future development

This study involved a qualitative and a quantitative comparison between 13 different pilot plants dedicated to capture $CO_2$ from flue gases for different types of industries such as power plants, waste to energy power plants, cement kilns and refineries. These plants use fossil fuels or nonrenewable sources of energy such as coal, natural gas and waste where the higher the $CO_2$ concentration in flue gases the easier it is to capture it with less energy. The main reference here was Technology Center Mongstad which is not considered fully a pilot plant given its large size compared to the other pilots. In fact, TCM holds the largest absorber equivalent diameter among the others (3 meter) [the absorber is 3.55 m × 2 m (Rectangular)] while the others were ranging between 0.4m and 1.1 m while the smallest diameter was found in LTD pilot plant University of Kaiserslautern with 0.125 m. It can also be seen in its highest packing height of 24m as this unit treats about 60000 Sm3/hr which is a huge flow compared to the flow rate of flue gases in RECODEH2020 pilot (50 $Nm^3/hr$) which is testing ionic solvents to capture $CO_2$. TCM also has the privilege of having two different flue gas types with 2 different compositions and characteristics where the first is resulting from combusting natural gas in the CHP combined cycle which has a $CO_2$ concentration of 3.6-4.1 vol% while the other one is flue gases leaving the RFCC which is characterized by a high concentration of $CO_2$ to as high as 13-14.5 % mol.

Through the study, a detailed comparison was made between those pilot capture units in terms of flue gas characteristics where the concentration of $O_2$, $CO_2$ were reported to show the effect of the increased $CO_2$ levels on the reduction of the SRD. This suggestes that carbon capture is more interesting for waste to energy, coal-fired power plants as well as cement kilns and refineries. However, specific configurations were adopted in the University of Kentucky using secondary air strippers to further reduce the levels of $CO_2$ in the lean solvent to increase its cyclic capacity. The air used in stripping (which is highly rich in $CO_2$ is then directed to the main boiler to be used in combustion which will reduce the flame temperature to eliminate the thermal $NO_x$ as well as increase the concentration of $CO_2$ in flue gases which could be an interesting configuration for natural gas fired power plants. Moreover, a summary for all the 14 solvents being used shows the importance of shifting from MEA to more robust solvents that are fast in their reactivity as well as in their regeneration. Thus, a lower L/G can be adopted while keeping the same capture efficiency thus a lower SRD is guaranteed. The H3-1 advanced solvent which was produced by Mitsubishi Hitachi Power Systems held the lowest SRD with (2093.4- 3489) MJ/ton $CO_2$ when tested on flue gases from coal as well as low degradation levels and consequently low amine emissions. Equipment sizes were also compared especially for the DCC, absorber, stripper and other units, where the trend is going towards smaller capture units that can be easily manufactured, transported and erected at the lowest time and cost possible such as the MTU designed by Aker Solutions. The Just-Catch modular unit by Aker solutions showed much better performance in terms of regeneration energy as well as the smaller size as seen in Figure 2.3.

This study also involved the different configurations and technologies which were tested by different pilots such as LVC, absorber inter-stage cooling, stripper inter-stage heating and energy integration. In addition, enhancement on the stripper side included increasing the stripper pressure, throttling the rich solvent at the stripper's entrance and adding a secondary stripper to further release the $CO_2$ within the lean solvent. Moreover, shifting the position of the flue gas blower from upstream the DCC to downstream the absorber had a great influence on decreasing the power consumption of the fan and reducing the corrosion. All these, showed the possibility of designing mobile pilot plants that are much smaller in size compared to non-modular ones which could reduce the time needed for studying the feasibility of implementing a full-scale capture unit as well as the cost of capturing i.e., the SRD and consequently, reduce the Levelized Cost of Electricity (LCOE).

With the increase of the share of renewables comes the necessity of the fossil-fired power plants to ramp up and down to compensate the supply-side peaks resulting from the prediction errors especially for solar and wind. Consequently, capture units should be also flexible with the change in $CO_2$ concentration and flue gas flowrates to guarantee the high carbon capture efficiency while reducing the energy penalties. Various start-up and shut down scenarios were discussed here in addition to various scenarios for regenerating the solvent at peak hours such as storing $CO_2$ in the solvent through adding lean solvent to the system to increase the L/G ratio or flue gas by pass.

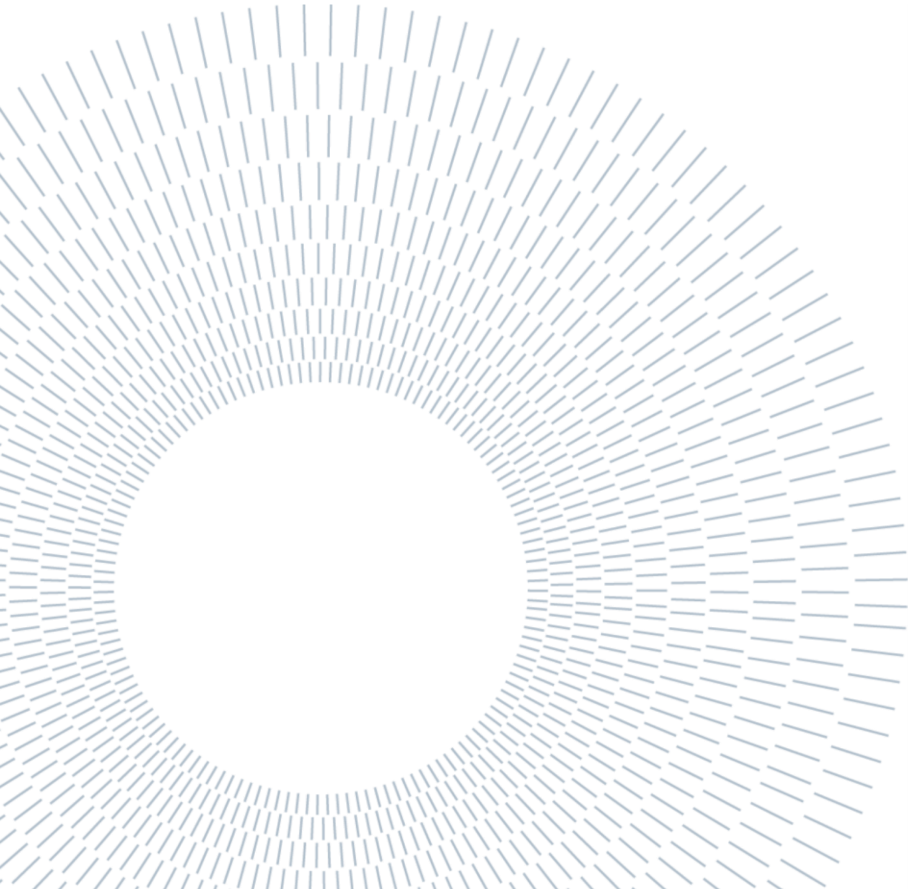
Amine emissions were discussed in this work where various technologies to reduce these emissions in all its forms such as liquid entrainment, vapor (volatile) emissions and aerosols emissions. A comparison between the different number of beds and height of the water and acid wash sections in each pilot was included as well as the new technologies dedicated to the elimination of aerosol emissions such as dry beds on the absorber side, Brownian diffusion filters upstream the capture unit as well as adjusting some operating parameters to reduce the formation of aerosols.

Mass and energy balance closure for carbon capture units usually have ± 10% error due to the inaccuracy of some instrumentation and in particular gas and liquid analyzers. Thus, investing in highly accurate analyzers is crucial in reducing thus error to as low as possible. However, it is also governed by the budget available for instrumentation as some equipment can go up to $500,000 USD such as LC-MS and PTR-TOF-MS. In this study, a summary was made for the various types of instrumentation being used in flow, pressure, temperature and level measurements as well as liquid and gas analysis techniques and devices. Finally, an instrumentation proposal was made with 2 different scenarios where the first one assumes a limited budget of €250,000 while the other one assumed an unlimited budget which allowed for adopting very expensive technology.

A preliminary fitting on an absorber Aspen-plus model was done through plugging in results from TCM in which data was taken from Faramarzi et al. (2017) [35]. In this work, iterations were made by changing the global setup factors which are specific to the rate-based model such as the mass transfer condition factor ($\emptyset$) and the reaction condition factor (η). Moreover, iterations on the tuning factors were also done by changing the Interfacial area $a_j$, the heat transfer factor, the liquid mass transfer coefficient factor and the vapor mass transfer coefficient factor. By doing so, the temperature profile's average error was reduced from 10.61% to 4.36% while the error on the capture efficiency was slightly reduced by 0.5%. Similar results have been found by different combinations of the values of these factors than the ones reported in this study which means that even though this point is much better than the ones with the initial values set by default in the Aspen-plus model, yet it isn't the optimum point.

Finally, and as a suggestion for future work, this model should be tested with data from different tests done on different pilots such as Niederaussem, or the NCCC while taking into consideration the presence of interstage coolers on the absorber side. By doing so, a better fitting of the model can be achieved. Moreover, an optimization problem can be written where the objective function is to minimize each error at a time or the weighted average of the 4 errors.

Additional results found in the tables were taken from [37] [38] [39] [40][41] [42].



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# A. Appendix A

| | | number of absorbers | Absorber Interstage cooler | Absorber Diameter (m) | Absorber Height (m) | Type of packing in Absorber |
|---|---|---|---|---|---|---|
| **Next Generation Carbon Capture Technology (PDVU)** | | 2 + 3rd tower for water and Acid wash beds | yes | Not specified | Not specified | Not specified |
| **Niederaussem pilot plant** | | 1 | yes | Not specified | 40 | 4 beds |
| **WTE Fortum Oslo Varme (FOV's pilot)** | | 1 | yes | Not specified | 26 | Structured packing beds |
| **Technology Centre Mongstad (TCM)** | **Common Absorber for RFCC & CHP** | 1 | Not specified | 3.55 m × 2 m (Rectangular) | 62 (24m packing) | Flexipac 2X structured |
| | | 1 | - | 3.55 m × 2 m (Rectangular) | 62 (24m packing) | Flexipac 2X structured |
| | **Aker solution's MTU** | | Not specified | 0.4 | packing height Up to 18 | Not specified |

| | | number of absorbers | Absorber Interstage cooler | Absorber Diameter (m) | Absorber Height (m) | Type of packing in Absorber |
|---|---|---|---|---|---|---|
| **Aker Solutions' Mobile Test Unit (MTU) NORCEM** | | 1 | Not specified | 0.4 | 35 (18 "packing height") | Not specified |
| **Imperial College carbon capture pilot plant** | | 1 | Not specified | Not specified | Not specified | Not specified |
| **CASTOR- Esbjerg Pilot Plant** | | 1 | no | 1.1 | 34.5 | IMTP50 Random Packing |
| **CESAR- Esbjerg Pilot plant** | | 1 | yes | 1.1 | Not specified | Mellapak 2X Structured packing |
| **UK CCSRC PACT facility** | | 1 | no | Not specified | 6.5 "packing height" | 300mm diameter Sulzer Mellapak CC3 |
| **NCCC pilot plant** | Modular | 1 | yes (Gravity driven) | Not specified | Not specified | High-capacity structured packing (not specified) |
| | PSTU (non modular/mobile) | 1 | yes (2 stage cooling) | 0.641 | 3 beds (6.048 total packing height) | Mellapak 252.Y |
| **RECODEH2020** | | 1 | Not specified | Not specified | Not specified | Not specified |

| | | number of absorbers | Absorber Interstage cooler | Absorber Diameter (m) | Absorber Height (m) | Type of packing in Absorber |
|---|---|---|---|---|---|---|
| **LTD pilot plant University of Kaiserslautern pilot** | **Set I Gas-fired** | 1 | Not specified | 0.125 | 5 beds (4.25 m packing height) | structured packing BX 500 (Sulzer Chemtec) |
| | **Set II Coal-fired** | 1 | Not specified | 0.125 | 5 beds (4.25 m packing height) | structured packing BX 500 (Sulzer Chemtec) |
| **UK CAER, University of Kentucky** | | 1 | yes | 0.81 | 2 beds (12.19 m packing height) | Koch Glitsch structured packing |

Table A.1 Summary listing different absorber features of all the reviewed pilot plants.

# B. Appendix B

| | | number of strippers | Stripper Height (m) | Stripper Diameter (m) | stripper pressure (barg) | Type of packing in Stripper |
|---|---|---|---|---|---|---|
| **Next Generation Carbon Capture Technology (PDVU)** | | 1 | | 0.4 | 1-1.5 | |
| **Niederaussem pilot plant** | | 1 | Not specified | Not specified | MEA, GUSTAV,ludwig (1.5-2 bara)`<br>**CESAR1 (1.75)** | |
| **WTE Fortum Oslo Varme (FOV's pilot)** | | 1 | 17 | | 1 | |
| **Technology Centre Mongstad (TCM)** | **CHP configuration** | 1 | 30 (8m packing) | small stripper 1.3 | 1.9-2 Bara | Flexipac 2X structured |
| | **RFCC configuration** | 1 | 30 (8m packing) | large stripper 2.2 | **-** | Flexipac 2X structured |
| | **Aker solution's MTU** | 1 | 8 "packing height" | 0.32 | | |

| | | number of strippers | Stripper Height (m) | Stripper Diameter (m) | stripper pressure (barg) | Type of packing in Stripper |
|---|---|---|---|---|---|---|
| **Aker Solutions' Mobile Test Unit (MTU) NORCEM** | | 1 | 8 "packing height" | 0.32 | Not specified | |
| **Imperial College carbon capture pilot** | | 1 | | | | |
| **CASTOR- Esbjerg Pilot Plant** | | 1 | 2 X 5 m | 1.1 | 1.89 bar(a) | IMTP50 random packing |
| **CESAR- Esbjerg Pilot plant** | | 1 | | 1.1 | 1.9 bar | |
| **UK CCSRC PACT facility** | | 1 | 6 "packing height" | Not specified | 0.37–0.47 | 300mm diameter Intalox IMTP25 random packing |
| **NCCC pilot plant** | **Modular** | 1 | | | 3.4 bara | |
| | **PSTU (non modular/mobile)** | 1 | 0.641 | 0.591 | | 2 beds (6.048 total packing height) |
| **RECODEH2020** | | 1 | | | | |
| **LTD pilot plant University of Kaiserslautern pilot** | | 1 | 3 beds (2.55 m packing height) | 0.125 | | structured packing BX 500 (Sulzer Chemtec) |
| | | 1 | 3 beds (2.55 m packing height) | 0.125 | | |

| | number of strippers | Stripper Height (m) | Stripper Diameter (m) | stripper pressure (barg) | Type of packing in Stripper |
|---|---|---|---|---|---|
| **UK CAER, University of Kentucky** | 2 | Primary:- 2 beds (9.75m packing height) Secondary 2 beds (8.84 m packing height) | primary 0.66 m Secondary 0.71 m | MEA30%<br>[Primary: 2.1,2.5, 3.5]<br>MEA40%<br>[Primary: 1.5, 2.5]<br>H3-1<br>[Primary 1.5, 2.1, 2.5]<br>Primary :- (1.4 - 1.7 bara ) Max 2.1 bara, Secondary :- (~1bara) | Koch Glitsch structured packing (both primary & secondary) |

Table B.1 Summary listing different stripper features of all the reviewed pilot plants.

# C. Appendix C

| | Type of solvent used | Solvent provider | lean amine inlet Temperature ◦C | Solvent filter | Solvent flow rate | Solvent degradation rate | amine emissions | Reclaimer |
|---|---|---|---|---|---|---|---|---|
| **Next Generation** C.C **Technology (PDVU)** | MEA 35% | Shell Cansolv, MHI, Fluor, Aker | 40 | No | Not specified | | | Yes |
| **Niederaussem pilot plant** | MEA, Gustav 200, Ludwig 540, OASE® blue solvent, **CESAR-1** | BASF | 40 | Mechanical & carbon filters | CESAR-1 (2400-2600 kg/hr) | Not specified | Not specified | No |
| **WTE Fortum Oslo Varme (FOV's pilot)** | DC-103 | Shell CANSOLV | **-** | Carbon filters | | 10% (>5% WT) at the end of the campaign | < 0.4 ppmv | No |

| | | Type of solvent used | Solvent provider | lean amine inlet Temperature ◦C | Solvent filter | Solvent flow rate | Solvent degradation rate | amine emissions | Reclaimer |
|---|---|---|---|---|---|---|---|---|---|
| **Technology Centre Mongstad (TCM)** | **CHP** | **30% MEA,**<br>**S21,**<br>**S26** | SOLVit (S21&S26) | 37 | Carbon filters | 28,200–60,100 (Kg/hr) | **30% MEA** :- 2.6 kg amine/t CO2<br>**S21**:- 0.5-0.6 kg amine/ t CO2,<br>**S26** :- 0.2-0.3 kg amine/t CO2 | < 0.1 mg/Nm3 in total, nitrosamines and nitramines 0.1 µg/Nm3 | **Yes** (>80% HSS, impurities and degradation prducts Removed) |
| | **RFCC** | **-** | Not specified | **-** | Carbon filters | **-** | **-** | **-** | **-** |
| | **Aker solutions' MTU** | | | | | **3.6 (m3/h)** | | total amine emissions 1-4 ppm with anti-mist technology and > 200ppm without it | |
| **Aker Solutions' Mobile Test Unit (MTU) NORCEM** | | S26_1 | SINTEF Materials & Chemistry | 40 | Not specified | 3.6 (m3/h) | HSS< 0.01mol/kg ( amine consumption = 0.15-0.20 kg/ton CO2 captured) | (0.3-0.46 mg/Nm3) | Yes |

| | | Type of solvent used | Solvent provider | lean amine inlet Temperature ◦C | Solvent filter | Solvent flow rate | Solvent degradation rate | amine emissions | Reclaimer |
|---|---|---|---|---|---|---|---|---|---|
| **Imperial College carbon capture pilot plant** | | MEA | Not specified | | Yes but not specified | | | | Not specified |
| **CASTOR- Esbjerg Pilot Plant** | | MEA 30%<br>CASTOR-1<br>**CASTOR-2** | BASF | Not specified | 2 Mechanical filters + organic filter | Max :-40, optimized :- 15.5 (m3/h) | **MEA** :- 0.55-1.3 %w/w<br>**CASTOR-2 :-** 0.48-0.65 %w/w | NH3 (25 mg/Nm3) | Yes |
| **CESAR- Esbjerg Pilot plant** | | MEA 30%<br>CESAR-1<br>CESAR-2 | BASF | | 2 Mechanical filters | Max 26, optimized :- 12.5 m3/hr | | | |
| **UK CCSRC PACT facility** | | MEA 30% | Not specified | 40 | Carbon filters | 1000-1200 l/hr | | Not specified | No |
| **NCCC pilot plant** | Modular | OASE® blue solvent | BASF | 40-60 | Yes but not specified | | | 0.0116 (kg amine/MT CO2) | yes (but optional) |
| | PSTU (non modular/ mobile) | ION solvent | ION Engineering | | | | | | |
| **RECODEH2020** | | | io-li-tec | | | | | | |
| | | Type of solvent used | Solvent provider | lean amine inlet | Solvent filter | Solvent flow rate | Solvent degradation rate | amine emissions | Reclaimer |

| | | | | Temperature ◦C | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **LTD pilot plant University of Kaiserslautern pilot** | **Set I Gas-fired** | MEA 30%<br>CESAR-1<br>CESAR-2 | BASF | 40 | | 35-200 kg/hr | | | |
| | **Set II Coal-fired** | | | 40 | | 75-275 kg/hr | | | |
| **UK CAER, University of Kentucky** | | MEA 30%<br>MEA 40%<br>Hitachi H3-1<br>CAER<br>CDRmax | Mitsubishi Hitachi Power Systems | 20 - 36 (40 Max) | Carbon filters, Cartridge Filter | MEA 30% 13159 kg/hr H3-1 10701.5 kg/hr | H3-1 has 70% lower degradation rate than MEA | MEA--> Aerosols & no nitrosamines (below FTIR 1ppmv limit), NH3 (12.4 – 282 ppmV)<br>H3-1→ Nitrosamine | yes |

Table C.1 Summary of Solvent parameters and comparison points

# D. Appendix.D

| Real TCM Data | |
|---|---|
| **Height(m)** | T (°C) |
| **24** | 39.7 |
| **23.5** | 47.4 |
| **22.5** | 51.7 |
| **21.5** | 51.6 |
| **20.5** | 50.5 |
| **19.5** | 49.9 |
| **18.5** | 48.9 |
| **17.5** | 47.2 |
| **16.5** | 46 |
| **15.5** | 44.4 |
| **14.5** | 43.1 |
| **13.5** | 42.2 |
| **12.5** | 40.9 |
| **11.5** | 40.6 |
| **10.5** | 41.6 |
| **9.5** | 37.4 |
| **8.5** | 37.1 |
| **7.5** | 35.9 |
| **6.5** | 34.3 |
| **5.5** | 34.1 |
| **4.5** | 33.8 |
| **3.5** | 32.9 |
| **2.5** | 33.2 |
| **1.5** | 32.5 |
| **0.5** | 32.4 |

Table D.2 Temperature profile along the absorber's packing height in TCM

| Solvent | Total solvent loss (kg amine/ton CO2) | Operating hours before reclaiming |
|---|---|---|
| **MEA** | 2.6 | < 1000 |
| **S21** | 0.6 | 3600 |
| **S26** | 0.3 | 3300 |

Table D.1 Results from Aker Solutions campaigns for MEA, S21 and S26 solvents.

# E. Appendix.E

| Next Generation C.C Technology (PDVU) | Niederaussem pilot plant | WTE Fortum Oslo Varme (FOV's pilot) | Technology Centre Mongstad (TCM) | Aker Solutions' Mobile Test Unit (MTU) NORCEM | CASTOR-Esbjerg Pilot Plant | CESAR-Esbjerg Pilot plant | UK CAER, University of Kentucky | NCCC Pilot plant |
|---|---|---|---|---|---|---|---|---|
| **10,000** | 10000 (40,000 hrs with OASE@ blue) | 5,100 | 10,000 | 4320 | 4000 | 6000 | (+ 2000 hrs ) | Modular :- 6764<br>-PSTU >1000 |

Table E.1 UK CAER University of Kentucky pilot's test campaigns

| | Testing hours | Absorber L/G (kg/kg) | Primary Stripper Pressure (psia) | Inlet CO2 Concentration (vol%) |
|---|---|---|---|---|
| **MEA30%** | 1217 | 3.5,4 and 5 | 30,36 and 51 | 12, 14 and 16 |
| **MEA40%** | - | 3.2,3.5 and 4 | 22 and 36 | 14 |
| **H3-1** | 1493 | 3.1,3.7 and 4 | 22,30 and 36 | 12, 14 and 16 |
| **CAER SOLVENT** | - | 3.5-5 | 30 and 36 | 14 and 16 |

Table E.2 Test duration of pilot plants

# F. Appendix F

| | Steam consumption (MJ/ton CO2 captured) | Steam supply | L.P steam temp ◦C | L.P steam Pressure (barg) | Reboiler Type | Reboiler Temperature ◦C | Max reboiler steam flow |
|---|---|---|---|---|---|---|---|
| **Next Generation Carbon Capture Technology (PDVU)** | - | on-site packaged boiler plant | 140-150 | 3.5 | | | |
| **Niederaussem pilot plant** | (3500-3800) MEA,<br>(2800 - 3700) Gustav 200,<br>(2700- 3000) Ludwig 540,<br>(3000-3300) CESAR1,<br>(2500) OASE blue | Separate steam generator | not applied | not applied | Electrically powered reboiler | | |
| **WTE Fortum Oslo Varme (FOV's pilot)** | - | Separate steam generator | - | - | Not specified | 122 | |

| | | Steam consumption (MJ/ton CO2 captured) | Steam supply | L.P steam temp ◦C | L.P steam Pressure (barg) | Reboiler Type | Reboiler Temperature ◦C | Max reboiler steam flow |
|---|---|---|---|---|---|---|---|---|
| **Technology Centre Mongstad (TCM)** | **CHP** | MEA :- (3740 -4490) = 2260-11,890 MJ/h,<br>S21&S26 :- 3400 | Extracted from steam turbine | 140-160 | - | Welded plate thermosiphon HX | 110-125 | 1000–5000 kg/hr |
| | **RFCC** | - | Extracted from steam turbine | - | - | Welded plate thermosiphon HX | - | - |
| | **Aker's MTU** | | | | | | | |
| **Aker Solutions' Mobile Test Unit (MTU) NORCEM** | | 2700- 2800 MJ/ t CO2 (energy required by electric reboiler) | not applied | not applied | not applied | Electrically powered reboiler | | not applied |
| **CASTOR- Esbjerg Pilot Plant** | | (3650-3900) MJ/ ton CO2 | Not specified | 127.43 | 2.5 | thermosyphon reboiler | 120 | 2500 kg/h @2.5 bar |
| **CESAR- Esbjerg Pilot plant** | | 2900MJ/ ton CO2 | | 143.63 | 4 bara | | | |
| **UK CCSRC PACT facility** | | 6200–6800 MJ/tCO2 | Extracted from LP steam turbine | 124 (pressurized water) | Not specified | Shell & tube (not specified) | approximately 120 | 10 m3/hr |

| | | **Steam consumption (MJ/ton CO2 captured)** | **Steam supply** | **L.P steam temp ◦C** | **L.P steam Pressure (barg)** | **Reboiler Type** | **Reboiler Temperature ◦C** | **Max reboiler steam flow** |
|---|---|---|---|---|---|---|---|---|
| **NCCC pilot plant** | **Modular** | OASE® blue solvent 2700 MJ/ton CO2 | Extracted from LP steam turbine | 130-175 | | 2 phase flow Plate and shell HEX with variable heat transfer area | | 1134 kg/hr |
| | **PSTU (non modular/mobile)** | ION solvent 2500 MJ/ t CO2 (design case) - 3600 MJ/ t CO2 (operating case) | Extracted from LP steam turbine | | | thermosyphon reboiler | | |
| **LTD pilot plant University of Kaiserslautern pilot** | **Gas fired (Set I)** | | | | | electrical heating elements for partial evaporation of the solvent | | |
| | **Coal fired (Set II)** | | | | | | | |
| **UK CAER, University of Kentucky** | | MEA 30% (2326 - 3721.6) MJ/ton CO2 , H3-1 (2093.4- 3489) **MJ/ton CO2** CDRmax (2900-3300)MJ/ton CO2 | Extracted from LP steam turbine | 121 | 25 psig | kettle type reboiler. | | [MEA 973 kg/hr] [H3-1 610 kg/hr] |

Table F.1 Reboiler and steam parameters.

# G. Appendix G

| | Flue gas Source (fuel used) | Flue Gas Capacity | Flue gas Temp at absorber inlet ◦C | $O_2$ content in Flue gas | $CO_2$ concentration in F.G | Flue gas Pre-treatment Wash | Flue gas Post-treatment Washing stages | Flue gas blower position |
|---|---|---|---|---|---|---|---|---|
| **Next Generation Carbon Capture Technology (PDVU)** | Waste, CCGT | Not specified | 40-45 | typical EFW & CCGT flue gas | typical EFW & CCGT flue gas | DCC with water | 1 water wash & 1 Sulfuric acid wash | Upstream the DCC |
| **Niederaussem pilot plant** | Lignite | 1552 Nm3/hr | 40 | 5 vol% dry | 12.5-14.2 | DCC Pre-scrubber (with NaOH) | 1 water wash | Upstream the absorber |
| **WTE Fortum Oslo Varme (FOV's pilot)** | Waste | 736 Nm3/hr | 40 | | | Pre-scrubber no caustic DCC | 1 water wash | Upstream the DCC |

| | Flue gas Source (fuel used) | Flue Gas Capacity | Flue gas Temp at absorber inlet ◦C | $O_2$ content in Flue gas | $CO_2$ concentration in F.G | Flue gas Pre-treatment Wash | Flue gas Post-treatment Washing stages | Flue gas blower position |
|---|---|---|---|---|---|---|---|---|
| **(TCM)<br>CHP configuration** | natural gas | 60000 Sm3/hr | 30 (optimum 25) | 14.4 mol% | 3.6-4.1 vol% | DCC with water (smaller) | **2** water wash **in absorber** (6m Flexipac 2Y HC structured packing) **1 in stripper** (1.6 m Flexipac 2Y HC structured packing) | Upstream the DCC |
| **(TCM)<br>RFCC configuration** | refinery RFCC | **-** | **-** | **-** | **13-14.5 % mol** | DCC with water (larger) | | |
| **TCM<br>Aker solution's MTU** | refinery RFCC | **Max 1000 Nm3/h** | **25** | | **14% CO2** | | 2 water wash + 1 Acid wash | |
| **Aker Solutions' Mobile Test Unit (MTU) NORCEM** | flue gas from the cement kiln | 427 up to 948 Nm3/hr | **-** | 7.5 Vol.-%, actual | 17.80% | yes | 2 water wash + 1 Acid wash | |

| | Flue gas Source (fuel used) | Flue Gas Capacity | Flue gas Temp at absorber inlet ◦C | $O_2$ content in Flue gas | $CO_2$ concentration in F.G | Flue gas Pre-treatment Wash | Flue gas Post-treatment Washing stages | Flue gas blower position |
|---|---|---|---|---|---|---|---|---|
| **CASTOR- Esbjerg Pilot Plant** | Pulverized Bituminous Coal | 5000 Nm3/hr | 47 | | 12% vol. (dry) | No DCC | 1 water wash in absorber (3 m) Mellapack 250Y structured packing.<br>1 in stripper (3 m) IMTP50 Random packing (diameter 0.8m "reduced" "not 1.1" | Downstream the absorber |
| **CESAR- Esbjerg Pilot plant** | Pulverized Bituminous Coal | 5000 Nm3/hr | | | 12% vol. (dry) | No DCC | 1 water wash in absorber Bubble cap trays & 1 in stripper | Downstream the absorber |
| **UK CCSRC PACT facility** | Coal | 200 Nm3/h | 42 | | 12% vol | No | No water wash after absorption or stripping | Upstream the absorber |

| | **Flue gas Source (fuel used)** | **Flue Gas Capacity** | **Flue gas Temp at absorber inlet ◦C** | **$O_2$ content in Flue gas** | **$CO_2$ concentration in F.G** | **Flue gas Pre-treatment Wash** | **Flue gas Post-treatment Washing stages** | **Flue gas blower position** |
|---|---|---|---|---|---|---|---|---|
| **NCCC pilot plant Modular** | Illinois No. 6 bituminous coal | 2673-5614 Nm3/hr | 30-40 | 6-8 mol% (dry) | (11-13) **mol% CO2 (dry)** | (DCC) with NaOH [**integrated in the absorber**] | 1 water wash in absorber, 1 water wash in stripper | Downstream the absorber |
| **NCCC PSTU (non modular/mobile)** | | | 68 | 4.5 mol% dry | 14 **mol% CO2 (dry)** | | 1 water wash after absorber | Upstream the DCC |
| **RECODEH2020** | flue gas from the cement kiln | 50Nm3/h | | | | | | |

| | Flue gas Source (fuel used) | Flue Gas Capacity | Flue gas Temp at absorber inlet ◦C | $O_2$ content in Flue gas | $CO_2$ concentration in F.G | Flue gas Pre-treatment Wash | Flue gas Post-treatment Washing stages | Flue gas blower position |
|---|---|---|---|---|---|---|---|---|
| **LTD pilot plant University of Kaiserslautern pilot** | gas fired (Set I) | 63.12 Nm3/h | 47 | | partial pressure 54 mbar | DCC with water | 1 water wash after absorber & 1 water wash in the stripper {0.42 m structured packing Mellapak 250.Y} | |
| | Coal fired (Set II) | 66.44 Nm3/h | 47 | | partial pressure 102 mbar | DCC with water | 1 water wash after absorber & 1 water wash in the stripper {0.42 m structured packing Mellapak 250.Y} | |
| **UK CAER, University of Kentucky** | Pulverized coal | 2230 Nm3/h | 30–35 °C avg [MEA30% 27.3] | 6 – 12 vol% dry | 14 dry vol%) | DCC with water & soda-ash solution | 1 water wash after absorber "external" i.e not integrated in the absorber | Upstream the DCC |

Table G.1 Flue gas characteristics for different pilot plants.

# H. Appendix H

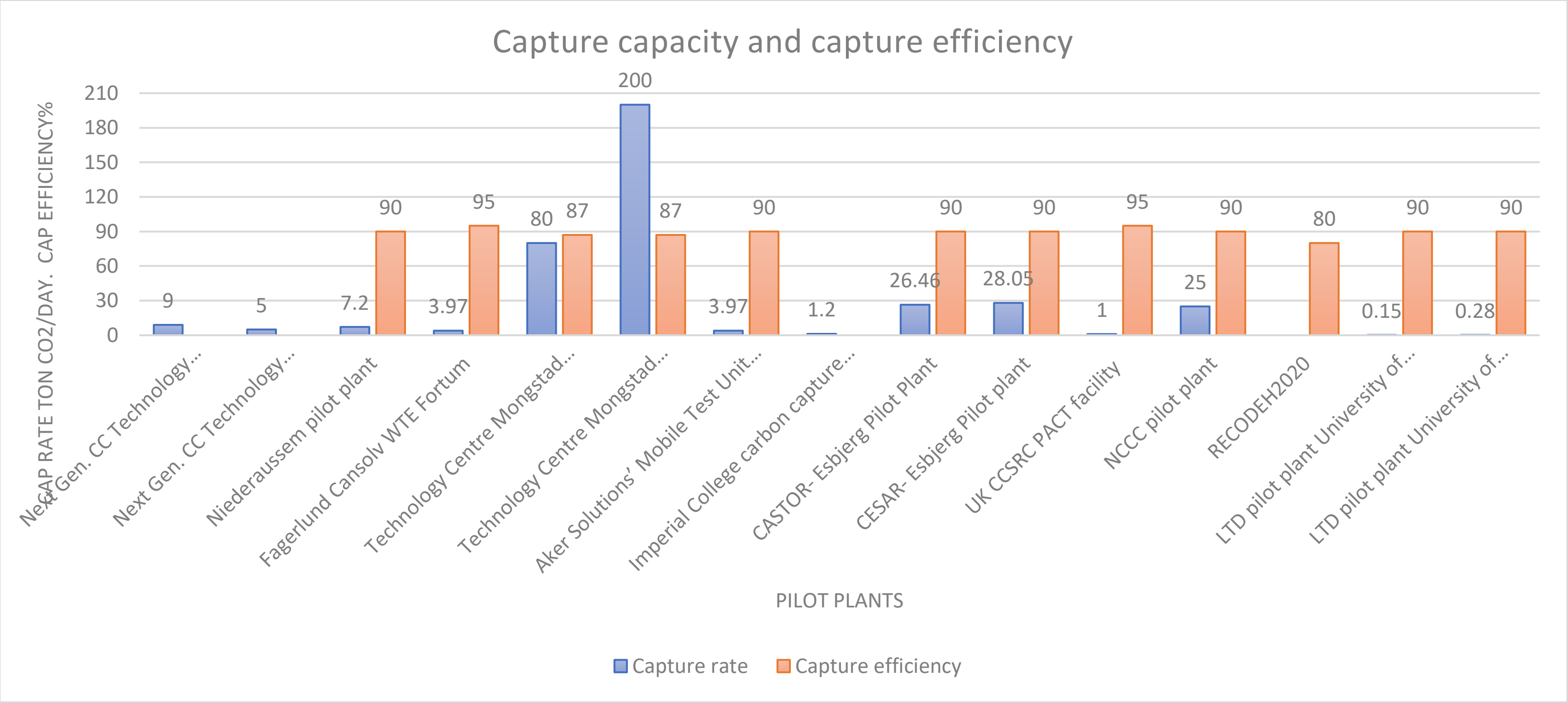

Figure H.1 Capture Capacity and efficiency for the studied pilots.

# List of Figures

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# 2. List of Symbols

| | |
|---|---|
| amino-methylated polyvinylamine (AMP) | 48 |
| Carbon Capture utilization and storage (CCUS) | 2 |
| Catalytic Cracker (RCC) | 16 |
| combined cycle gas turbine (CCGT) | 6 |
| combined heat and power (CHP) | 6 |
| Direct air capture (DAC) | 4 |
| direct contact coolers (DCC) | 6 |
| Enhanced oil recovery (EOR) | 5 |
| heat stable salts (HHS) | 10 |
| lean vapor compression (LVC) | 9 |
| Levelized Cost of Electricity (LCOE) | 108 |
| Levelized Cost Of Electricity (LCOE) | 15 |
| Mobile Test Units | |

(MTU) ........ 13
Monoethanolamine
(MEA) ........ 7
Net Zero Emissions
(NZE) ........ 1
Pre Deployment Verification Unit
**(PDVU)** ........ 17
Residual Fluid Catalytic Cracker
(RFCC) ........ 6
Solid Recovered Fuel
(SRF) ........ 2
specific reboiler duty
(SRD) ........ 51
Stripper Inter-stage Heating
(SIH) ........ 67
Technology Readiness Level
(TRL) ........ 12
The pilot solvent test unit
(PSTU) ........ 18
volatile organic compounds
(VOC) ........ 7
waste to energy
(WTE) ........ 2
Waste to Energy
(WTE) ........ 14

# 3. Acknowledgements

It has been a long journey since I started this master program in 2019 where I was full of doubts regarding my decision to take this energy path and moving out to a new country with all the challenges it brings. Moreover, the unexpected pandemic has further increased the difficulty of studying abroad with the lack of interaction with people and especially my classmates and professors. But despite all the obstacles that were brought by the COVID-19, yet there were always those people who never stopped believing in me even when I failed to believe in myself sometimes. This experience has taught me that one cannot walk through this life alone and that surrounding yourself with successful people who radiate positive energy and optimism is a must if you want to succeed as well. Above all these people, I would like to thank my mum, my dad and my two brothers who supported my trip financially and emotionally and never got tired of hearing my repeated complaints. To my family, I owe you my life and I wish to live for more moments in which I can make you happy.

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Now that I made it to the finish line, I would like to express my gratitude for Politecnico di Milano for giving me such an opportunity as well as the Italian government for granting me a scholarship without which I would have never made it.

I am so excited for the future and if I have learned anything from this experience, it would be that self-doubting is one’s worst enemy and that stress would never take one anywhere good. It’s good to work hard but it’s also important to rest and take it easy on yourself and believe that good things happen to those who dream big and work hard for it.

Mina