

Demonstrating STAR – 3rd generation CO₂ capture solvent

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Executive Summary

CO₂ capture from industrial flue gases using absorption solvents is already commercially deployed. Typical solvents used are amine based aqueous solutions being MEA the benchmark for this application. However, issues with solvent degradation and high regeneration energy pose a challenge on the faster implementation of the technology. The choice of absorption solvent and process configuration is decisive for CO₂ capture cost and implementation.

Ammonia-based solvents can be tailored to the flue gas and the size of WtE plants and are cost-effective. Aqueous ammonia is a very stable solvent not affected by thermal or oxidative degradation, unlike amine-based systems. High regeneration temperatures allow for the release of CO₂ at higher pressure (e.g., 150° and 20 bar), leading to a potential reduction in energy requirement and the capital costs of CO₂ compression and liquefaction, which is an important feature for the small to medium size plants typical of the WtE sector. The drawbacks include high volatility that can cause emissions, high energy for ammonia recovery, slower kinetics and crystal formation. Therefore, the main objective of this task is to demonstrate a strategy for solving the ammonia volatility issue as well as the slow kinetics reducing costs associated to this technology. A novel strategy to avoid ammonia losses due to volatility is to add components to the solvent that will lower the ammonia vapour pressure.

TNO developed a novel third generation solvent called STAR (Taurine-modified Ammonia System for Regular temperature operation) which is an ammonia-based CO₂ capture solvent, promoted by taurine. Taurine belongs to the family of amino acids and its addition is expected to reduce the amount of free ammonia in the solvent, thus reducing emissions, and to improve the CO₂ mass transfer, thus leading to smaller absorber columns. Emission reduction and absorber height reduction lead to both OPEX and CAPEX savings.

Lab scale tests (vapor-liquid equilibrium) have confirmed the benefits already reported in literature. The proposed STAR compositions can be used to desorb CO₂ at about 10 bar at 120°C. TNO has also operated a bench-scale CO₂ capture plant and demonstrated CO₂ desorption up to 5,8 bar – the operational limit of the system.

In NEWEST-CCUS, the so-called TNO's Miniplant was used for demonstration of STAR during continuous operation. Different solvent concentrations, flue gas composition and stripper pressures were used during the campaigns. This report presents the results of these campaigns at TNO using STAR as a solvent and concludes that the challenging nature of the solvent does not make it a good candidate for further research. CO₂ capture systems consisting of a volatile gas (co-solvent) for pressure elevation and blends with piperazine have been presented in the literature as options for high pressure. However, taking into account the added process complexity, operational costs and HSE aspects, render those systems less likely to be adapted than the benchmark MEA.

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1 Introduction

CO₂ capture from industrial flue gases using absorption solvents is already commercially deployed. Typical solvents used are amine based aqueous solutions being MEA the benchmark for this application. However, issues with solvent degradation and high regeneration energy pose a challenge on the faster implementation of the technology. The choice of absorption solvent and process configuration is decisive for CO₂ capture cost and implementation.

Ammonia-based solvents can be tailored to the flue gas and the size of WtE plants and are cost-effective. Aqueous ammonia is a very stable solvent thermally and chemically [1], unlike amine-based systems. High regeneration temperatures allow for the release of CO₂ at higher pressure (e.g., 150°C and 20 bar), leading to a potential reduction in energy requirement and the capital costs of CO₂ compression and liquefaction, which is an important feature for the small to medium size plants typical of the WtE sector. Downsides of the ammonia system are the high volatility of the solvent, which requires a chilling unit for ammonia recovery downstream the absorber, and the slow kinetics rate of the reaction between ammonia and CO₂, leading to high absorber columns [2]. Therefore, the main objective of this task is to demonstrate a strategy for solving the ammonia volatility issue as well as the slow kinetics reducing costs associated to this technology. A novel strategy to avoid ammonia losses due to volatility is to add components to the solvent that will lower the ammonia vapour pressure.

TNO developed a novel third generation solvent called STAR (Taurine-modified Ammonia System for Regular temperature operation) which is an ammonia-based CO₂ capture solvent, promoted by taurine. Taurine belongs to the family of amino acids and its addition is expected to reduce the amount of free ammonia in the solvent, thus reducing emissions, and to improve the CO₂ mass transfer, thus leading to smaller absorber columns. Emission reduction and absorber height reduction lead to both OPEX and CAPEX savings.

Lab scale tests (vapor-liquid equilibrium) have confirmed the benefits already reported in literature[3]. TNO has also previously operated a lab scale CO₂ capture facility with STAR, with CO₂ desorption at 5 bar – which was the current operational limit at the stripper side. Within NEWEST, TNO task was to perform vapor-liquid equilibrium and mass transfer rates lab experiments. This would help determine the optimum composition of the solvent in terms of suppression of ammonia vapor pressure over the solvent, as well as enhancement of CO₂ absorption kinetics. In order to demonstrate the solvent further, a STAR campaign of approximately 200 hours, in which an artificial flue gas mixture mimicking the composition of a typical WtE flue gas was realized.

2 STAR Campaigns at TNO

In this section, the experimental setup and conditions used in the work are presented, followed by the results and discussion. Challenges faced and troubleshooting are also discussed.

2.1 STAR VLE Experiments

Prior to the Miniplant tests, Vapor-Liquid equilibrium experiments were performed. The VLE set-up consists of an 1L vessel, Figure 1, made of stainless steel, with stirring in both gas and liquid phases. The set-up can be operated at temperatures from ambient to 150 °C and at pressures up to 6 bar. The solvent is inserted in the equipment and CO₂ is added in steps in a fully automated procedure. Both absorption and desorption conditions are tested at different temperatures. At the end of the experiments, the maximum loading, solvent cyclic capacity and total gas pressure are obtained.

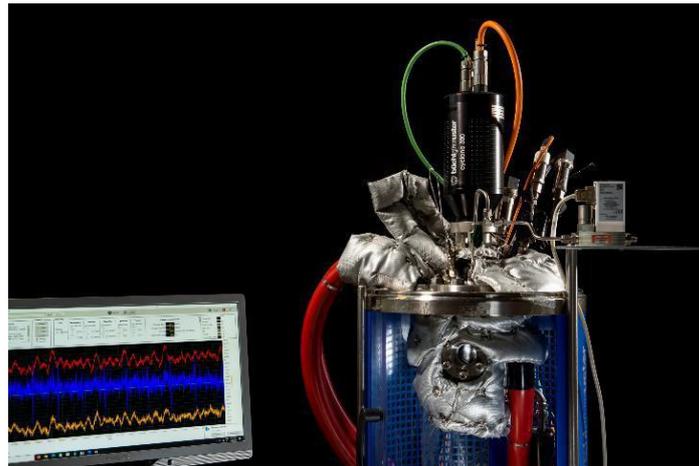


Figure 1 - VLE Setup

VLE experiments were done with both unloaded and CO₂-loaded STAR.

Figure 2 shows the vapor pressure of unloaded STAR. In this experiment, the concentration of STAR was 3M ammonia and 0.5M taurine. Since the VLE sensors have a maximum pressure limitation (6 bar), the experimental data is only available until 95°C.

In order to evaluate which pressure level could be reached at higher temperatures, the data points were fit into an Antoine equation (Equation 1). Both MEA and taurine thermally degrade faster above 120°C, therefore this temperature is considered as the maximum operational temperature.

$$P(\text{mbar}) = 10^{16.7037 - \frac{7964.16}{244.193 + T(K)}} \quad (1)$$

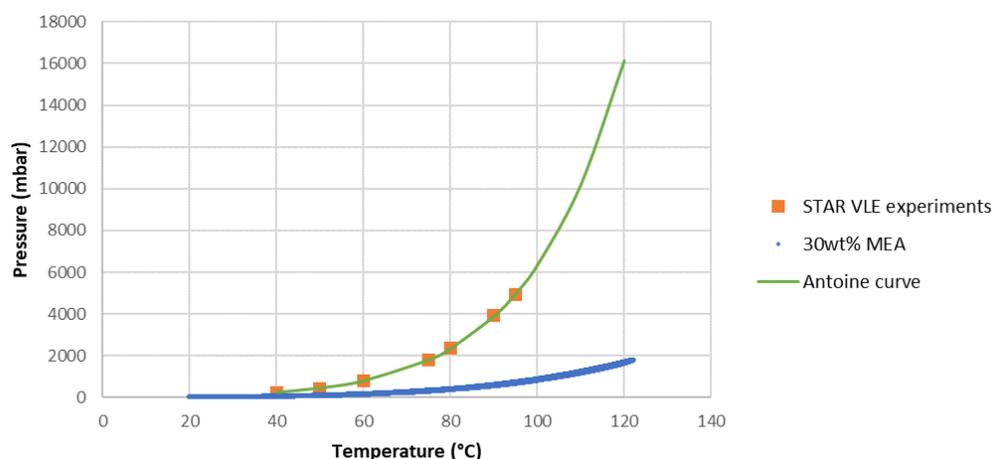


Figure 2 - Vapor curve of MEA and STAR

From Figure 2 it is possible to see that the vapor pressure of STAR is significantly higher than the one of MEA. This is expected, due to the presence of non-neutralized ammonia. This means that the design of a CO₂ capture technology based on STAR needs to pay particular attention to ammonia emissions.

Besides that, it is shown that the vapor pressure of the unloaded solvent is above the “target pressure” of 600kPa for desorption, from ca. 100°C onwards, and, for temperatures around 120°C, the values are expected to be ca. 1600kPa. However, to understand whether such pressures could be achieved in the desorber, the analysis of CO₂-loaded VLE data is needed.

Vapor-Liquid Equilibrium experiments with CO₂ loading done for ammonia (3M), MEA (30wt%) and STAR (3M ammonia + 0.5M taurine) at 40°C are presented in Figure 3 (total pressure) and Figure 4 (partial pressure of CO₂). Ammonia and MEA are shown for comparison.

Since the VLE is not equipped with a continuous gas sampling, it is not possible to measure the gas composition during the experiments. To calculate the CO₂ partial pressure (P_{CO_2}) on top of the solvent, it was assumed that the vapor pressure of the solvent remains constant, and that the CO₂ partial pressure is the difference between the total pressure (Figure 3) and the solvent’s pressure (measured at zero loading). This assumption brings uncertainties to the results, which are not very relevant for MEA, but become particularly important when considering the high volatility of ammonia and its reactivity towards CO₂.

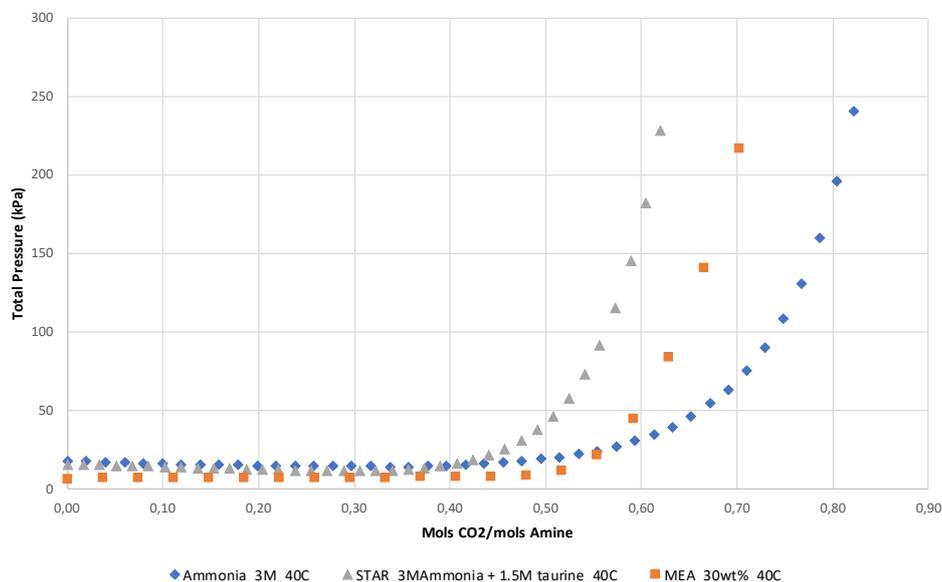


Figure 3 – Total pressure data for VLE experiments with ammonia, STAR (ammonia + taurine) and MEA at 40°C

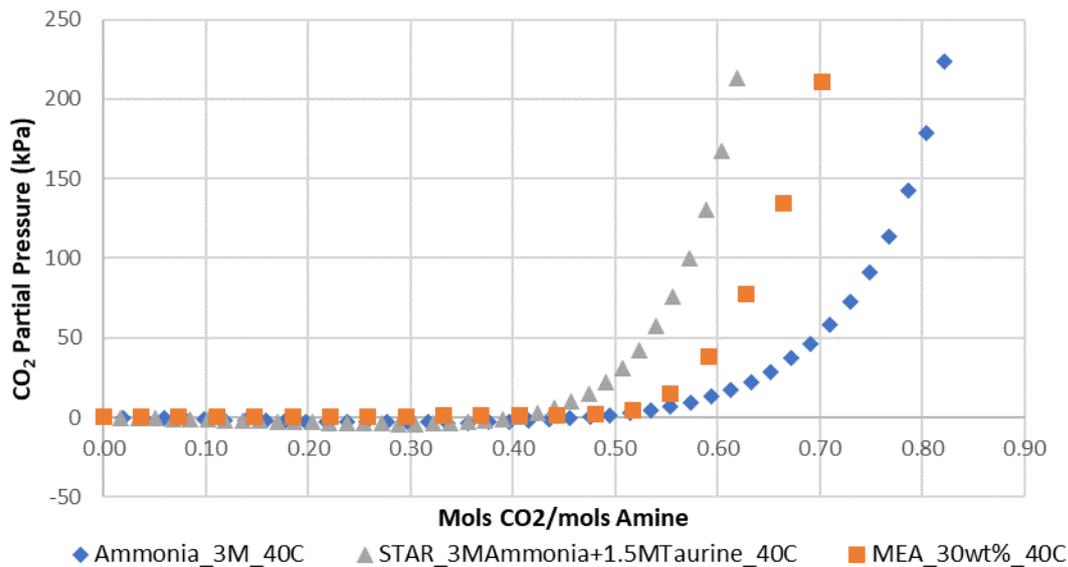


Figure 4 - CO₂ pressure data for VLE experiments with ammonia, STAR (ammonia + taurine) and MEA at 40°C

Comparing the three P_{CO_2} curves, it is observed that the STAR system has considerably lower loading as compared to both ammonia and MEA for a given pressure. Attempts to conduct VLE tests at 120°C, did not lead to any stable, useful data due to formation of ammonium carbonate crystals. As no data was obtained at high temperatures, the evaluation of the solvent cyclic performance was compromised, and therefore the optimization of the solvent concentration could not be done using this equipment. It was therefore decided to perform the solvent optimization tests in a parametric campaign using TNO's miniplant. Issues with ammonium carbonate crystals formation are well documented in literature, from lab scale tests to pilot campaigns operating with ammonia-based systems [4], [5]. The modifications performed at the miniplant in WP1, particularly the installation of a water wash downstream the stripper were believed to suffice for running with the STAR solvent in the miniplant. The miniplant campaign is described in item 2.2 of the present report.

2.2 Miniplant Experiments

TNO's Miniplant is a CO₂ capture plant (up to 5 Nm³/h flue gas, 25 kg CO₂/day capture capacity) which allows for 24/7 continuous operation of the system. It enables tests of different solvents, multiple technologies for solvent management (oxygen removal, iron removal) and process quality control under realistic conditions at TRL5. However, the Miniplant was not fully prepared to be operated at higher pressures and with highly volatile solvents. Some of the equipment and instrumentation such as pumps, pressure sensors, heat exchangers, flow meters and valves were upgraded to allow for desorption at up to 10 bar. Wash columns were added on the outlet of both absorber and desorber columns. Typically, the washes are used as water washes aiming at reducing volatile emissions. In this work, the wash column on the outlet of the absorber was used as an acid wash (sulfuric acid) to ensure the low emission levels, while in the stripper the wash was operated as a water wash. Figure 5 illustrates the Miniplant after the necessary upgrade.



Figure 5 - TNO's Miniplant

2.2.1 Experimental conditions

The tests were realized with two different solvent concentrations for optimization: 3M ammonia + 1M taurine and 3M ammonia + 1.5M taurine. Table 1 shows the operational conditions during the campaigns. Synthetic flue gas was used with a total gas inlet of 2 Nm³/h, the CO₂ concentration was varied (12.5% in #1 and #2, 20% in #3 and 40% in #4) and the inlet flue gas temperature was kept at 20°C in all experiments. The liquid flow rate was also kept constant at 15 kg/h and the starting temperature in the reboiler was 120°C. The acid wash was operated with sulfuric acid at a concentration of 1M.

Table 1 - Experiment conditions during STAR campaigns at TNO

Experiment	Solvent concentration	Liquid lean (kg/h)	Air flow (NL/h)	CO ₂ flow (NL/h)
#1	3M ammonia + 1M taurine	15	1750	250
#2	3M ammonia + 1.5M taurine	15	1750	250
#3	3M ammonia + 1.5M taurine	15	1600	400

#4	3M ammonia + 1.5M taurine	15	1200	800
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2.3 Experimental results and discussion

The first set of experiments was done with 3M ammonia and 1M taurine and had a duration of 83 hours. Both liquid and gas flows were kept constant during the experiments. The CO₂ concentration in the gas was kept at 12.5%. The aim was to prove if higher pressures could be achieved with the solvent concentration proposed and also used the process conditions shown in Table 1. The pressure achieved in the stripper, reboiler temperature, lean and rich loadings, cyclic capacity and capture rate are reported in Table 2.

Table 2 - Experimental results from the Miniplant operation with 3M ammonia and 1M taurine

Parametric test	Date	Time	Desorber pressure (barg)	Desorber temperature (°C)	Lean Loading (mol/L)	Rich loading (mol/L)	Cyclic capacity (mol/L)	Capture rate (%)
a)	7-10-2020	12:55	8	122	0.99	1.23	0.24	~ 20
b)	22-10-2020	15:30	4.5	121	0.73	1.04	0.31	Up to 90
c)	28-11-2020	15:45	8	125	0.95	1.2	0.25	~ 20

The first test was done using 122°C in the stripper which gave a pressure of 8 barg. However, observing both lean and rich loadings, it is seen that the cyclic capacity of the solvent was not high enough (0.24 mol/L). Along with that, the CO₂ outlet from the stripper was not constant which could explain the high lean loadings, Figure 6. In order to check this hypothesis, the set pressure in the stripper was lowered to investigate if more CO₂ could be released. Although this approach increased the cyclic capacity, the value was still relatively low (0.31 mol/L). As a last attempt, the temperature was increased to impulse the desorption but once more, no significant change was observed and the cyclic capacity was the same as observed in test a). Typical rich loadings with MEA are XX mol/L, therefore the results of these tests indicate low CO₂ mass transfer in the system.

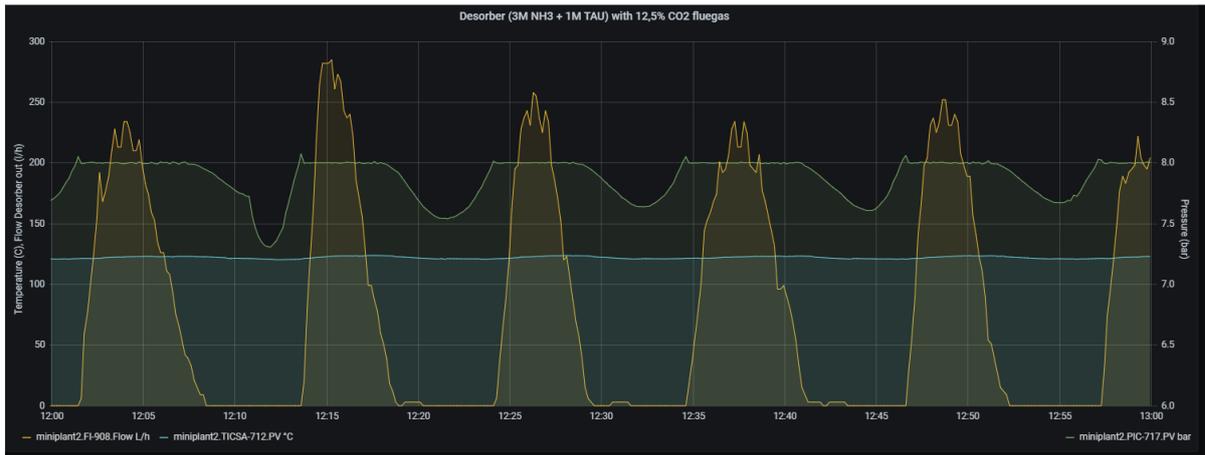


Figure 6 - Stripper temperature, pressure and outlet flow during the experiments with STAR (3M ammonia and 1M taurine)

For the operation at 8 barg, the capture rate is shown in Figure 7. A capture of 80% (red line) is the lower range accepted for the operation with TNO's Miniplant which is usually operating at values higher than 95% (orange line). The dotted lines show the actual capture rate during the experiments which fluctuates between 20 and 25% representing significantly low values for the process.



Figure 7 - Capture rate during STAR experiments (3M ammonia and 1M taurine) at 8 barg stripping pressure.

The next set of experiments was done using 3M ammonia and 1.5M taurine and the campaign lasted 45 hours. In this case, the stripper pressure was kept lower to enable stripping, however, the partial pressure of the CO₂ in the flue gas was increased from 12.5 vol% to 20 and 40vol%. This approach was followed as a measure to increase the loading of the solvent since the previous tests showed already a slow kinetics. The process conditions used are shown in Table 1. The pressure achieved in the stripper, reboiler temperature, lean and rich loadings, cyclic capacity and capture rate are reported in Table 3.

Table 3 - Experimental results from the Miniplant operation with 3M ammonia and 1.5M taurine

Experiment	Desorber pressure (bar)	Desorber temperature (°C)	Lean Loading (mol/L)	Rich loading (mol/L)	Cyclic capacity (mol/L)	Capture rate (%)
#2	4.5	120	0.79	1.18	0.39	~ 80
#3	4.5	120	0.77	1.2	0.43	~ 40
#4	4.5	120	0.76	1.23	0.47	~ 20

The results presented on Table 3 show that although the cyclic capacity was improved, the kinetics was still slow. In addition, the increase of the partial pressure of CO₂ in #3 and further in #4 did not lead to higher rich loadings. Since the amount of CO₂ introduced increased while the cyclic capacity remained the same, the capture rate was decreased. This can also be seen while comparing the plots on Figure 8.

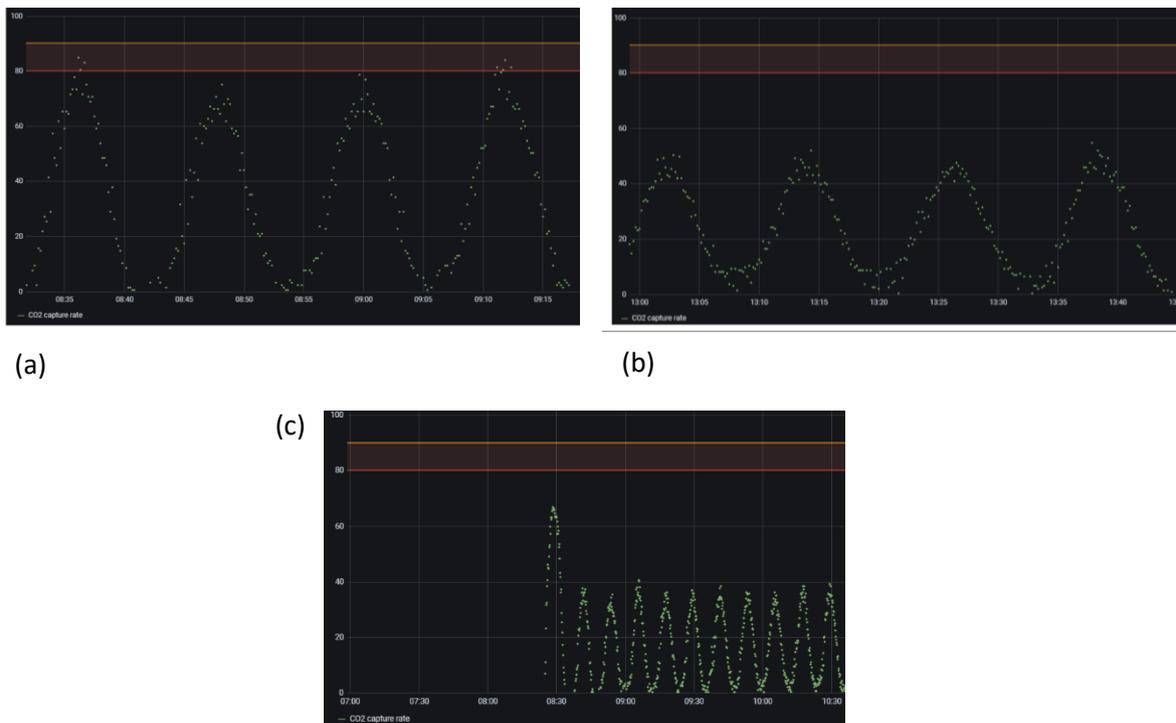


Figure 8 - Capture rate at (a) CO₂ 12,5%, (b) CO₂ 20% and (c) CO₂ at 40%

Since the increase in CO₂ partial pressure in the inlet did not show a significant improvement in the loadings, this leads to a conclusion that there is also a mass transfer limitation due to the height of the absorber column of the Miniplant. To overcome this problem, a higher column is needed.

2.4 Operational challenges and troubleshooting

Several issues were encountered during operation. The campaigns were not stable due to ammonia leakages and emissions. The solution in the acid wash was quickly neutralized by the large amount of ammonia escaping from the absorber and it was often replaced to avoid ammonia emissions to the

surroundings. Along with that, ammonium carbonate was formed which led to blockage of lines due to crystallization(Figure 9), provoking delays in the operation. Different strategies were used, such as the addition of heated lines around the valves, however, the formation of crystals could not be avoided.

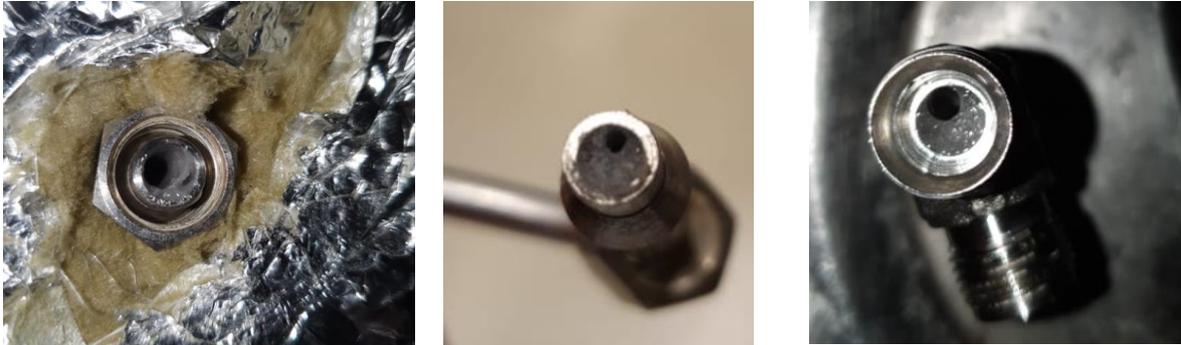


Figure 9 - Line blockage due to crystallization during operation

The operation of STAR showed to be complex even with the use of taurine. The emissions and formation of crystals could not be controlled, the kinetics did not show a significant improvement, mass transfer limitations did not allowed for demonstration of representative cyclic capacities and, at higher pressures, the CO₂ stripping was not continuous. Therefore, the campaigns with STAR were stopped and not run for 300 hours as proposed in order to screen different solvents that could be used as substitutes.

2.5 STAR way forward

Even though it was decided to terminate the development of STAR, high pressure stripping can create significant impact in the CO₂ capture costs. For this reason, a desk study was performed to search for new routes that could lead to this condition. One route was focused on the process (co-solvent stripping) and the other one focused on solvent formulation (use of piperazine).

2.5.1 Co-solvent Stripping

Co-solvent stripping describes a process which operates at high pressure and the pressure is delivered inside the stripper by an additional compound introduced in the system. This compound is (relatively) inert and volatile leading to higher stripping pressure without significantly affecting the chemical equilibrium between CO₂ and the amine. Such process was first mentioned in 2006 and recently resurfaced, both times from the CO₂ capture research group of NTNU (Tobiesen & Svendsen, 2006; Wanderley & Knuutila, 2021).

The methodology followed in this work is explained hereafter. First, the process modifications required in a traditional plant to accommodate the use of co-solvent were assessed and different scenarios were evaluated. Based on them and additional considerations related to HSE (Health, Safety and the Environment), the main criteria for co-solvent selection were decided. In the next step, using the Aspen Databank, a plethora of candidate co-solvents was generated and screened against the criteria previously formulated. Four different process concepts were considered, while five components were identified as potential co-solvents and used for each one of the process concepts investigation. The analysis was performed using an MEA system at its conventional operational conditions.

Conventional process modifications and co-solvent selection criteria

The introduction of an additional component in the CO₂ capture process implies several process modifications. The modifications identified concern the desorption part of the process, since it is required that the co-solvent remains in the stripper side so as not to affect the absorber operations and flue gas purification taking place in the absorber, and very importantly, to avoid emissions of the co-solvent to the atmosphere. The reboiler, stripping column and a condenser on the top of the stripper are considered as the main parts of the conventional process. Reboiler temperature is 120°C and condenser temperature is 40°C.

One additional required equipment is a flash tank for the lean solvent to ensure that no co-solvent ends up in the absorber side. For the possibilities around the condenser, there are three options depending on the state of the solvent:

I. the co-solvent is in gaseous phase at condenser conditions and it must be separated from CO₂ by either an adsorption step or cryogenics. Such separation significantly increases the complexity of the process, while an additional compressor is required to send the separated co-solvent back to the stripper. Thus, one criterion for the co-solvent selection is to be liquid at condenser conditions.

II. the co-solvent is at liquid phase at condenser conditions and all condensate is pumped back to the top of the stripper for the rectification section of the column. Here, no additional equipment is required.

III. the co-solvent is at liquid phase at condenser conditions and it is then separated from the rest of the condensate (mainly water and low amine amounts) to be introduced to the reboiler. For this scenario, a simple gravity separator could be used if the co-solvent is immiscible with water/amine.

For II. and III., possible co-solvent entrainment in the CO₂ stream after the condenser has not been studied. Besides additional process equipment, larger size of the conventional equipment would be required to accommodate the higher flowrates due to the co-solvent.

HSE-related criteria were also set. The solvent should be easy and safe to handle, non-toxic to humans and aquatic life, non-carcinogenic, non-causing genetic anomalies or organ failures and non-explosive. Moreover, obvious but worth-mentioning criterion is the co-solvent's non-reactivity towards CO₂. Ideally, the co-solvent should be also non-flammable and immiscible with water for easy separation for condensate but also for eliminating entrainment to the absorber side.

Taking into account the first criterion of a liquid co-solvent at condenser conditions, and using the Aspen databases, four groups of components were assessed based on their boiling point (B.P.), as shown below. Next to each group, the component which was selected for further analysis, based on the rest of the criteria, is shown. For the calculations, the vapor pressure of the compound and its heat of vaporization is needed, therefore their availability also played its role on the component selection.

- a) B.P. from 40 to 50°C: 3-methoxy-1-propene (B.P.: 46°C, CAS #: 627-40-7)
- b) B.P. from 50 to 60°C: 4-methyl-1-pentene (B.P.: 54°C, CAS #: 691-37-2)
- c) B.P. from 60 to 70°C: 1,4-hexadiene (B.P.: 66°C, CAS #: 592-45-0)
- d) B.P. from 70 to 80°C: cyclohexane* (B.P.: 81°C, CAS #: 110-82-7)

*cyclohexane was selected due to its known immiscibility with water, although it is toxic to aquatic life.

Overall, finding a component for each temperature group fulfilling all criteria is a challenging exercise, while all candidate co-solvents are flammable.

Process concepts and results

The evaluated process schemes are illustrated in Figure 10 to Figure 12. They describe the four process concepts evaluated in this study for each one the candidate co-solvents selected:

1. The co-solvent is vaporized in the reboiler (120°C) and it does not condense in the stripping column. The temperature in the top of the stripper is 100°C, which is typical in MEA operation. (see Figure 10)
2. The co-solvent is vaporized in the reboiler (120°C) and it partially condenses in the stripping column. The temperature in the top of the stripper is 100°C, which is typical in MEA operation. (see Figure 11)
3. The co-solvent is vaporized in the reboiler (120°C) and it partially condenses in the stripping column, while the split rich configuration is used, leading to lower temperature (80°C) in the top of the stripper than the conventional (100°C).
4. The co-solvent is vaporized in the reboiler (120°C), it partially condenses in the stripping column, then being directed to a compressor (heat pump) where the pressure is tripled and the temperature is increased to 140°C. The stream partially condenses and the condensation heat is exploited through a heat exchanger to heat up the lean amine (and thus reduce the energy demand in the reboiler). (see Figure 12)

Since the simulation sheets would have to be validated with experimental data for the studied system, and no experimental data are available for such a co-solvent system, the evaluation was performed by calculating mass and energy flows from fundamental properties using Excel. Figure 10 to Figure 12 illustrate the process schemes, but no simulations have been performed. Further, as explained in the previous section, an alternative process scheme does not include a condensate separation unit but rather it is as a whole injected back to the top of the stripper.

For the analysis, the calculation basis assumes that the partial pressure of water and carbon dioxide are similar to the case without co-solvent ($P_{H_2O}+P_{CO_2}=1.9$ bar). The total pressure achieved in the desorber is 10 bar, therefore the co-solvent contributes with 8.1 bar in the system. Moreover, the reboiler operates at 120°C and the condenser at 40°C. The acceptance criteria is that the energy required to add in the process to vaporize the co-solvent is no higher than the energy demands required in a compressor after the desorber to pressurize the gas from 2 bar to 10 bar, i.e. <0.4 MJ_{th}/kgCO₂ (electrical energy demand in the compressors is 0.13 MJ_{el}/kg, which using the Carnot efficiency of 0.31, corresponds to the equivalent thermal energy of 0.4 MJ_{th}/kg) . The heat of vaporization for each candidate co-solvent was calculated by ΔH_{vap} equations from nist.gov, except for component a) and b) where the value at STP and 47°C, respectively, were used.

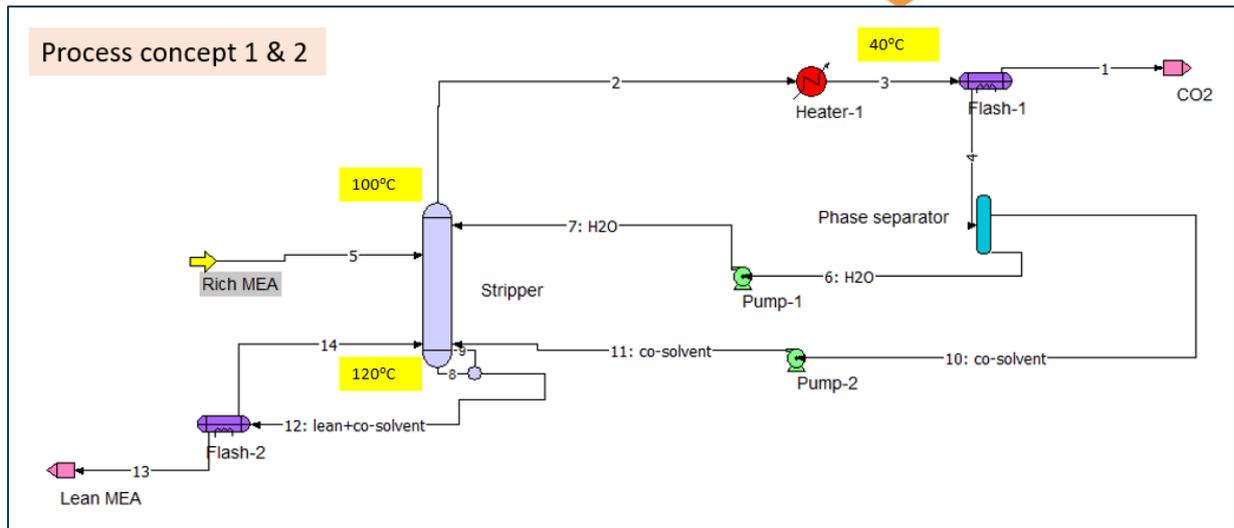


Figure 10 - Process scheme and assumed temperatures for Process Concept 1 and Process Concept 2. It is noted that no simulations have been performed due to lack of experimental data for model validation.

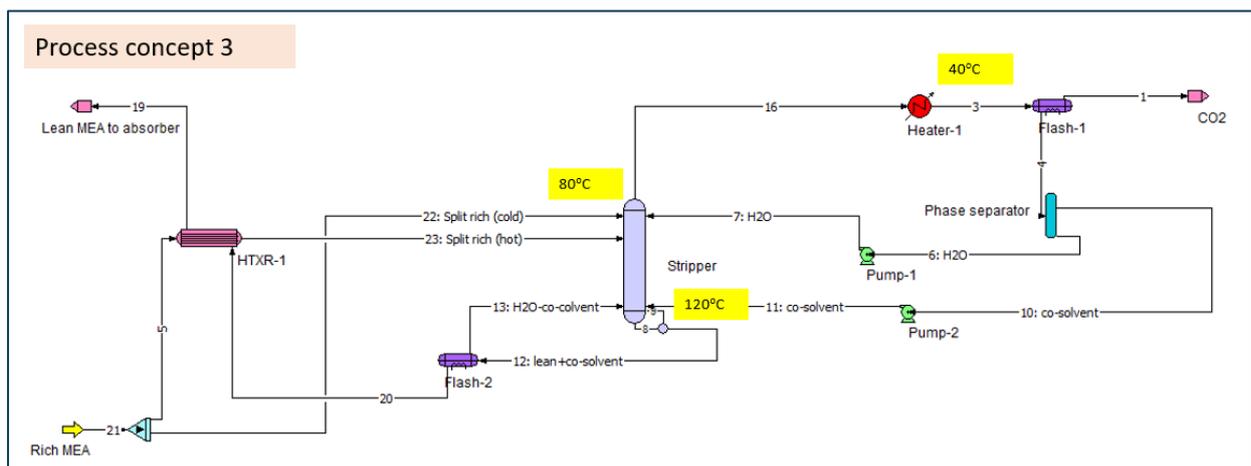


Figure 11 - Process scheme and assumed temperatures for Process Concept 3, using the rich split configuration. It is noted that no simulations have been performed due to lack of experimental data for model validation.

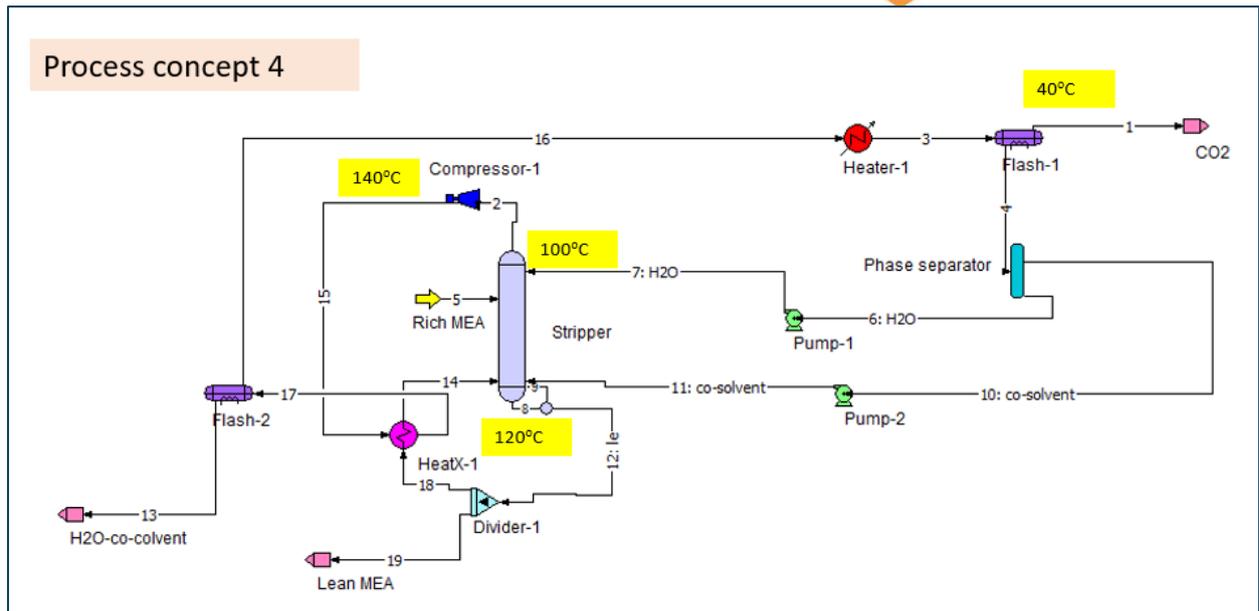


Figure 12 - Process scheme and assumed temperatures for Process Concept 4, using a heat pump configuration. It is noted that no simulations have been performed due to lack of experimental data for model validation.

Process Concept 1 is not feasible, since the energy demand (co-solvent vaporization energy) for the four cases (four candidate co-solvents) is calculated to be 5.5, 5.8, 6.4 and 6.8 MJ/kgCO₂. This is higher than the acceptance criterion and represents the worst-case scenario, where the energy demand is 3 times higher than the one in a conventional plant. In this concept, all the energy provided in the reboiler to vaporize the co-solvent is being lost in the condenser. Therefore, Process Concepts 2, 3 and 4 assume partial condensation of the co-solvent in the stripper so as the condensation heat is used within the stripper to heat up the solvent.

In Process Concepts 2, 3 and 4, we aim in maximizing the amount of co-solvent that condenses along the column. The amount which condenses is calculated based on the co-solvent fraction in the vapor phase at 120°C (reboiler) and 100°C (top of the stripper), and it is limited by the temperature difference, ΔT , in the column (20°C). This is evaluated in Process Concept 2, where, for all four solvents, 31-38% of the co-solvent condenses, leading to additional required heat which is still above the acceptance criterion. A split rich stream configuration, where one part of the rich solvent is introduced to the stripper via the cross heat exchanger (hot rich), and the other part is introduced directly to the stripper (cold rich), can assist in overcoming the ΔT limitation. According to available simulations for an 200 kton/year industrial plant, such configuration would lead to a temperature of 80°C in the top of the stripper (Process Concept 3). Here, the amount of condensing co-solvent is increased to 62-64%. This corresponds to additional energy requirements for a), b), c) and d) of 2.2, 2.3, 2.5 and 2.7 MJ/kgCO₂. These values are significantly lower than in Process concept 2, but still higher than the acceptance criteria of 0.4 MJ/kgCO₂ additional heat.

Lastly, Process Concept 4, aims on using the latent heat of the co-solvent to increase/maintain the temperature of the lean solvent, by using a compressor to increase the solvent's temperature and then a cross heat exchanger coupled to a lean solvent loop. In this loop the lean solvent is partly heated up, thus aiming to decrease the reboiler requirements. This is a heat pump configuration, and it can be integrated with the CO₂ compression process, where the first compressor is the one being shown in Figure 12. In this concept, the amount which condenses is calculated based on the co-solvent

fraction in the vapor phase at 140°C (after the compressor) and 120°C (reboiler temperature), which is again limited to a $\Delta T=20^\circ\text{C}$. In this process concept, 48-50% of the co-solvent condenses, which is lower than the one for Process Concept 3, therefore the energy demand is again well above the acceptance criteria.

Based on the findings of this technical assessment, it was deemed unnecessary to continue with a more elaborative economic assessment.

2.5.2 Piperazine for high pressure stripping

This case study focused on investigation of conventional high pressure stripping i.e. use of solvents that allow for CO₂ stripping at higher pressures. The investigation included the study of a high-pressure system using aqueous piperazine (PZ) as a solvent to get an understanding of the plant size and associated costs. Piperazine was chosen since it is one of the few single solvent systems used for high pressure stripping at larger scales. These costs were compared with a case using MEA as a solvent at the same scale. Simulations were carried out in ProTreat® to model and optimize the case for capturing 200 kt per annum of CO₂ using 5m PZ. The sizing and costing of major equipment for this case were done using ASPEN Capital Cost Estimator. OPEX calculations were based on work done in previous projects like ALIGN CCUS.

A process model with 5m PZ was based on a FEED study presented by the group of Prof. Gary Rochelle in the University of Austin, Texas (Closmann et al., 2021). Figure 13 shows the flowsheet for this process. Flue gas with flow rate 2.05 kt/h at 110°C is fed to an absorber column. The flue gas composition has been given in Table 4.

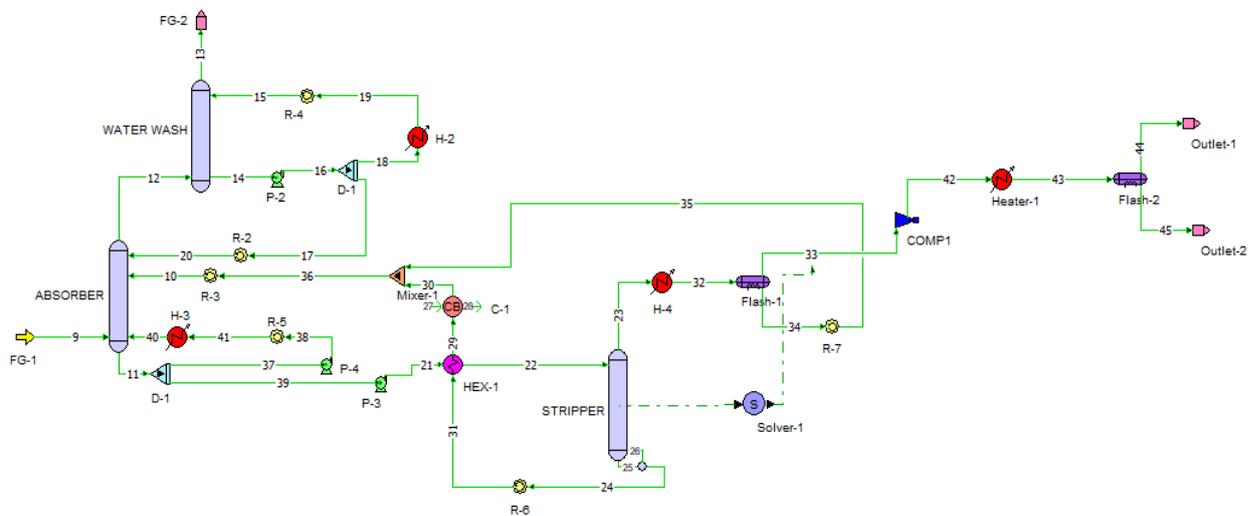


Figure 13: Flowsheet for CO₂ capture using 5m PZ

Table 4: Flue gas composition for PZ case study

Component	Mole Fraction
N ₂	0.7
CO ₂	0.1
O ₂	0.1
H ₂ O	0.1

The flue gas is cooled in the packed absorber column using pump around intercooling at the bottom of the column. In comparison a quench column is typically used for cases where MEA is used as a solvent. The absorber column has a packed height of 7.6 m and diameter of 6.4 m. A water wash with packing height of 3m and diameter of 0.5 m is used to recover any PZ from the off gases. As PZ is a hazardous substance it is key to prevent emissions from the capture plant.

The rich solvent from the bottom of the absorber column is spilt into two streams. 25% of this stream is cooled and fed back to the absorber column for intercooling. This pump-around contributes to the larger absorber diameter. The remainder of the rich solvent is pumped to the desorber column through a cross heat exchanger. In this heat exchanger, the rich stream is heated to 134.4°C. The rich solvent enters the stripper column at 7.5 bar. The stripper column has a packed height of 3m and diameter of 2.1m. The reboiler at the bottom of the stripper is operated at 148.5°C and 6 bar. This results in CO₂ being stripped at a higher pressure than the MEA case. The CO₂ product at the top of the stripper is at a pressure of 5.97 bar as opposed to 1.8 bar for MEA. The CO₂ product is then condensed and compressed to 20 bar using a single compressor. For the case of MEA, two compressors are needed.

The model described above was optimized to minimize the specific reboiler duty (SRD). An optimum SRD of 2.63 GJ/ton CO₂ captured was achieved at L/G ratio of 2.48. The rich loading achieved in this case was 0.78 molCO₂/molPZ with a corresponding lean loading of 0.44 molCO₂/molPZ. The optimization study has been presented in Figure 14.

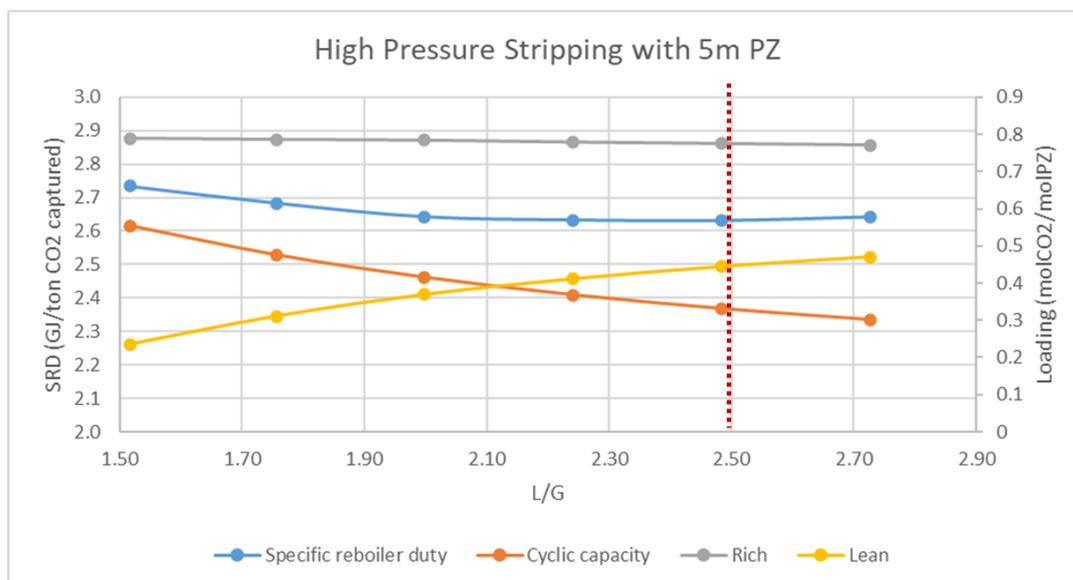


Figure 14 - Specific reboiler duties, loadings and cyclic capacity for 5m PZ

A techno-economic evaluation was carried out for this optimized case. Sizing and costing for main equipment like absorber, desorber, compressor and cross heat exchanger were done. Fixed factors established in ALIGN CCUS (Garcia et al, 2020) were used to include other auxiliary equipment. Based on this, a specific CAPEX of €6.8/tonCO₂ captured. The main contributor to the CAPEX is the absorber with water wash followed by the compressor, cross heat exchanger and desorber. This has been illustrated in Figure 15. For MEA with stripping at 2 bar, the specific CAPEX is €7.9/tonCO₂ captured.

The reduced costs for PZ are associated with fewer compressors, a smaller desorber column and no quench column for cooling the flue gas.

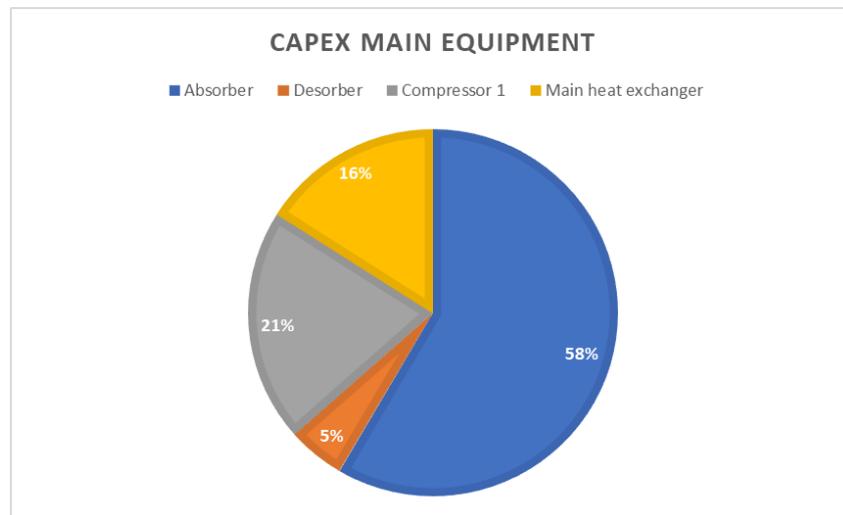


Figure 15 - Breakdown of CAPEX for main equipment for 5m PZ

Specific OPEX that includes labour costs, maintenance, insurance etc. was determined to be €2.7/tonCO₂. For MEA this cost was estimated to be €3.1/tonCO₂. The use of PZ also leads to a lower SRD of 2.63 GJ/ton CO₂ captured compared to 3.2 GJ/ton CO₂ captured for MEA. This leads to reduction in heat costs as well. Variable OPEX was calculated at heat prices of €4/GJ, €6/GJ and €8/GJ. Based on this, the variable OPEX is calculated to be €13/ton CO₂ captured, €18.3/ton CO₂ captured and €23.6/ton CO₂ captured, respectively. For MEA, if heat is available at €4/GJ, the variable OPEX is €18.3/ton CO₂ captured. Therefore, at the same energy cost of €4/GJ variable OPEX for PZ (€13/ton CO₂ captured) is less than that for MEA (€18.3/ton CO₂ captured). This results in a total cost of capture for PZ between €22.5/tonCO₂ captured and €33/tonCO₂ captured. Figure 16 shows the total cost of CO₂ capture for the various PZ cases and compares it with the MEA case with heat price of €4/GJ.

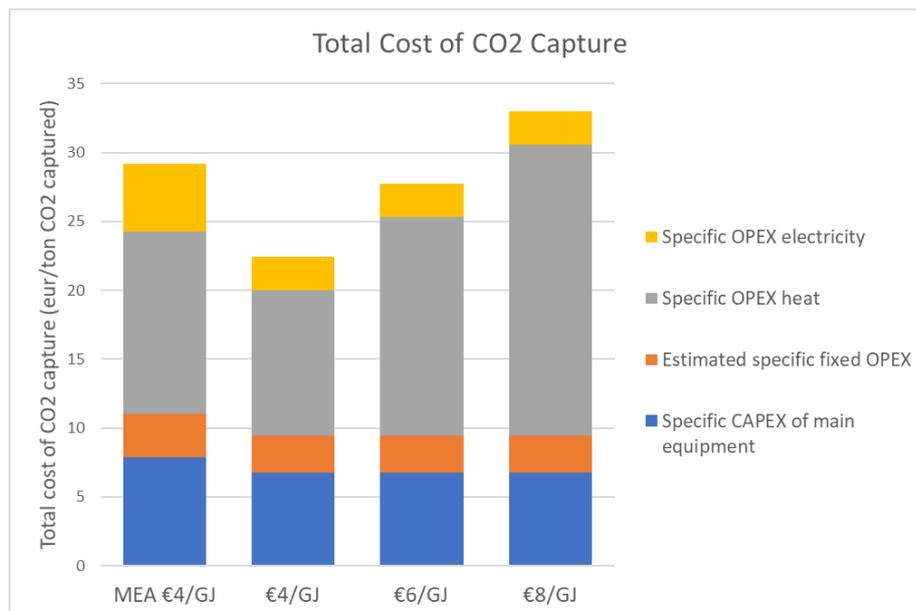


Figure 16 - Total cost of CO₂ capture for PZ and MEA

This case study shows that high pressure stripping with PZ leads to lower costs of CO₂ capture compared to MEA. However, experience suggests that use of PZ can lead to operational and environmental issues associated with crystallization of PZ and its hazardous nature. Being a secondary amine solvent, PZ leads to the formation of nitrosamines which accumulate in the solvent. Measures to control nitrosamine concentration include periodically increasing the reboiler temperature to destroy such compounds. Relatively more complexity in solvent handling is involved. The reduction in costs should be analysed with these aspects in mind as well. Investigation on conventional high pressure stripping shows that there are benefits associated with stripping CO₂ at pressures higher than 5 bar. However, a literature review shows that besides PZ, no promising single-phase systems have been identified that can deliver such performance at a large scale. However, solvents that exhibit two liquid phases have shown promising results. IFPEN's DMX[®] system is claimed to be able to strip CO₂ at up to 5 bar (Raynal et al, 2014), and the DEEA/MAPA system investigated by NTNU can strip CO₂ at least 4 bar (Liebenthal et al, 2012). The DMX system is currently being demonstrated in the 3D project (Home - 3D (3d-ccus.com)), whereas research on the DEEA/MAPA system has been discontinued by NTNU due to toxicity of MAPA. Research in finding a substitute for MAPA did not lead to promising results (personal communications with Prof. Hanna Knuutila).

3 Conclusions

The innovative solvent STAR proposed by TNO to enable stripping at higher pressures and lower compression costs was tested at TNO's Miniplant. Although pressures higher than 6 barg were achieved, stripping was not constant nor stable. Along with that, the addition of taurine did not prove to be sufficient to enhance solvent kinetics and cyclic capacity which lead to significant low loadings and capture rate. Challenges such as ammonia losses and formation of crystals increase the operation complexity and continuity. Therefore, it was decided not to go forward with STAR and to investigate different routes for operation at high pressures. Two different routes were studied: one focused on the process using co-solvent stripping and the other on the solvent formulation using of piperazine.

Adding a co-solvent into the amine capture systems shows no energy (economic) gains, while at the same time the complexity of the process would increase dramatically upon the introduction of an additional component. The study of the conventional high pressure stripping with aqueous piperazine shows that lower costs of CO₂ capture compared to MEA can be achieved, however, the use of piperazine is associated with health, safety and environmental concerns in addition to increased operational difficulty as opposed to MEA. However, no other suitable alternatives have been found in the literature.

Bibliography

[1] O. Augustsson *et al.*, "Chilled Ammonia Process Scale-up and Lessons Learned," *Energy Procedia*, vol. 114, pp. 5593–5615, 2017, doi: <https://doi.org/10.1016/j.egypro.2017.03.1699>.

[2] J.-F. Pérez-Calvo, D. Sutter, M. Gazzani, and M. Mazzotti, "Application of a Chilled Ammonia-based Process for CO₂ Capture to Cement Plants," *Energy Procedia*, vol. 114, pp. 6197–6205, 2017, doi: <https://doi.org/10.1016/j.egypro.2017.03.1757>.

[3] N. Yang, H. Yu, D. Xu, W. Conway, M. Maeder, and P. Feron, "Amino acids/NH₃ Mixtures for CO₂ Capture: Effect of Neutralization Methods on CO₂ Mass Transfer and NH₃ Vapour Loss," *Energy Procedia*, vol. 63, pp. 773–780, 2014, doi: <https://doi.org/10.1016/j.egypro.2014.11.086>.

[4] H. Yu and P. H. M. Feron, "12 - Aqueous ammonia-based post-combustion CO₂ capture," P. H. M. B. T.-A.-B. P. C. of C. D. Feron, Ed. Woodhead Publishing, 2016, pp. 283–301.

[5] H. Yu *et al.*, "Results from trialling aqueous NH₃ based post-combustion capture in a pilot plant at Munmorah power station: Absorption," *Chem. Eng. Res. Des.*, vol. 89, no. 8, pp. 1204–1215, 2011, doi: <https://doi.org/10.1016/j.cherd.2011.02.036>.