SOLVENT RECLAIMING AT A POST COMBUSTION CO$_2$ CAPTURE PLANT AT TWENCE (WTE FACILITY)

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Abstract

Solvent degradation in post combustion CO$_2$ capture (PCCC) impacts process economics and the environment. The degradation of solvents and the accumulation of degradation products leads to reduced cyclic capacity, change of solvent characteristics like viscosity and density, increased fouling and increased corrosivity [1]. This accumulation can be mitigated by solvent replacement, which is simple and effective, but affects process economics adversely, and leads to losses of non-degraded solvent. Thus, techniques like thermal reclaiming, which allow for recovering most of the non-degraded solvent while removing degradation products and impurities to a large extent, are seen as a preferred solvent management strategy.

Solvent thermal reclaiming was implemented at the PCCC pilot at Twence, a Waste-To-Energy plant in the east of The Netherlands. A standalone batch reclaiming unit was designed based on laboratory experiments and a ProTreat® model. From the laboratory experiments it was found that dilution of degraded MEA solvent (DMS) enhances MEA recovery, as expected and in line with previous literature [2]. This dilution, however, increases the energy demand of the reclaimer. Heat integration was carried out in ProTreat® to preheat the dilution water with the recovered MEA stream. The reclaimer commissioning campaign was carried out at Twence and it was found that the reclaimer was effective in removing impurities such as formate, acetate, oxalate, metals (Fe, Cr, Ni) and impurities (chloride, nitrate and nitrite) to below detection limit. The reclaimer was operated with different operating conditions: without dilution, with dilution and with neutralization with sodium hydroxide. As expected, addition of sodium hydroxide at the start of the reclaiming campaign led to enhanced MEA recovery (~20 wt% MEA in the distillate).

Keywords: CO$_2$ capture, aerosol-based emissions, solvent management, thermal reclaiming

1. Introduction

Post combustion CO$_2$ capture (PCCC) is critical for reduction of greenhouse gas emissions. Amine-based CO$_2$ capture has been implemented for capture of CO$_2$ from several types of flue gas sources. This method of CO$_2$ capture, using 30wt% monoethanolamine (MEA) is also being used at Twence, a Waste-To-Energy plant located in the east of The Netherlands. The PCCC pilot at Twence was commissioned in 2014. This pilot reduces the CO$_2$ footprint of the CHP (combined heat and power generation from waste incineration), thereby enabling renewable energy generation, circularity and production of biobased and CO$_2$ based products (Figure 1) [3].

The current CO$_2$ pilot installation at Twence captures up to 500 kg/h of CO$_2$ by treating 1.5 vol% of flue gas from a waste incinerator line. It is a multi-component hybrid system, which can produce liquid CO$_2$ and/or sodium bicarbonate. The liquefied CO$_2$ can be sold as a product to greenhouses and the sodium bicarbonate is used to remove acidic contaminants from the flue gas. The PCC pilot installation at Twence is shown in Figure 2.
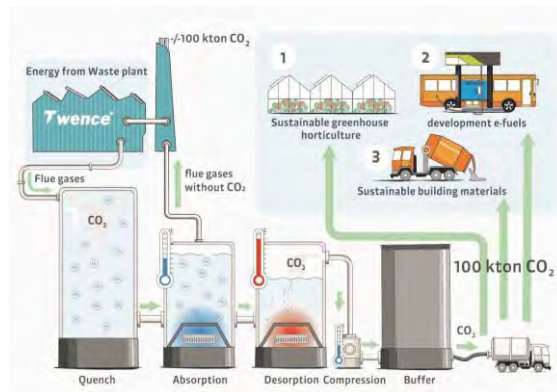

Figure 1 - CO$_2$ Utilization at Twence [4]

Solvent degradation affects the overall economic and environmental impact of PCCC. Amine based solvents degrade through three main mechanisms – thermal, oxidative and thermal degradation with CO$_2$ [5]. These mechanisms lead to the formation of degradation products that accumulate in the solvent over time, causing reduced solvent capacity [6], change of solvent properties like viscosity and density, increased fouling and corrosivity etc. The accumulation of the degradation products can also accelerate degradation due to increase

in corrosion [1]. This leads to additional costs due to solvent replacement and increased maintenance.
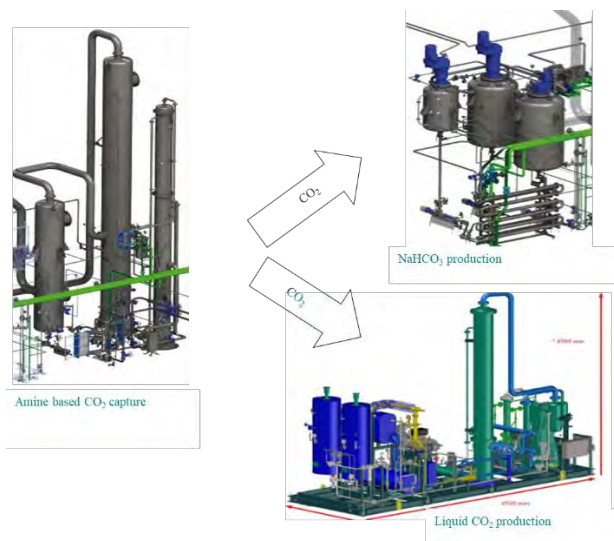

Figure 2 - PCCC pilot installation at Twence

Additionally, the solvent replacement leads to large volumes of waste that adversely impacts overall process economics. Thermal reclaiming of amine based solvents is an effective counter measure that can recover up to 90% of amines from the degraded solvent [1], [7], [8]. Thermal reclaiming has been demonstrated for different solvents, and is considered a mature and effective method for reclaiming MEA [2]. This reduces the costs associated with solvent replacement and also the environmental impact due to reduction of waste streams. A stand-alone batch thermal reclaiming unit was designed to reclaim degraded solvent from the Twence PCCC pilot installation. This unit was commissioned at Twence in April 2021 and results of the experimental campaign are discussed in this work.

2. Solvent Management

2.1 Laboratory experiments

Laboratory experiments were carried out at TNO to determine the optimum operating conditions to reclaim degraded solvent, obtained from the Twence pilot PCCC plant. Experiments were carried in a batch wise evaporator operated at atmospheric pressure. The operating temperature was maintained at 130°C. This was done to limit the thermal degradation which occurs at higher temperatures [9]. The aim of the experiments was to recover at least 90% MEA. Initial experiments indicated that dilution of degraded MEA with water assists the thermal reclaiming process. Thus, a series of experiments with different dilution factors were carried out for a fixed batch time. As shown in Figure 3, dilution factors above 5 lead to MEA recovery greater than 90%.
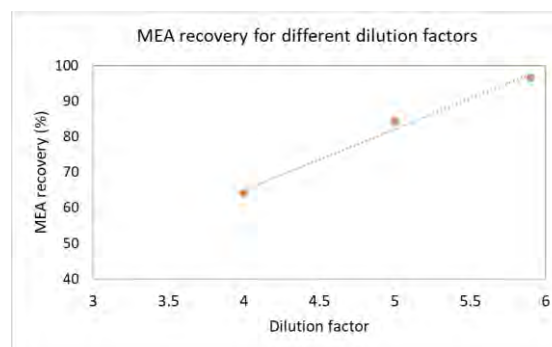

Figure 3 - MEA recovery for different dilution factors

However, this dilution greatly increases the energy consumption and, thus, a standalone thermal reclaiming system is expected to have a high energy demand and associated operational costs. To minimize these costs heat integration with the stripper of the capture plant is recommended [10]. It should be noticed, however, that for the current work heat integration with the PCCC plant was not performed.

3.2 Reclaimer Modelling

In order to reduce the cost of thermal reclaiming, it was decided to pre-heat the dilution water with the hot reclaimer MEA stream. A model was created in ProTreat® to determine the size of the equipment (heat exchanger, reclaimer vessel) required for this integration and achieving 90% MEA recovery. Figure 4 shows this model where a stream of lean degraded MEA is mixed with preheated dilution water is sent to a reclaiming vessel.
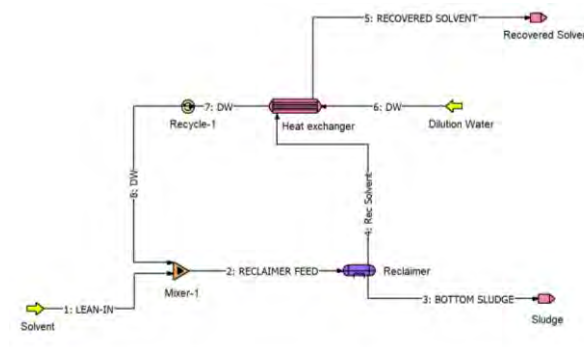

Figure 4 - ProTreat® model for MEA recovery

The dilution water is preheated to 110°C with the top stream of the reclaimer.

A sensitivity analysis was also carried out to determine the optimum operating pressure of the reclaiming vessel. According to Figure 5, it was observed that reclaiming efficiency increases at lower pressures. However, in the interest of costs, it was decided to operate the reclaimer at atmospheric conditions.
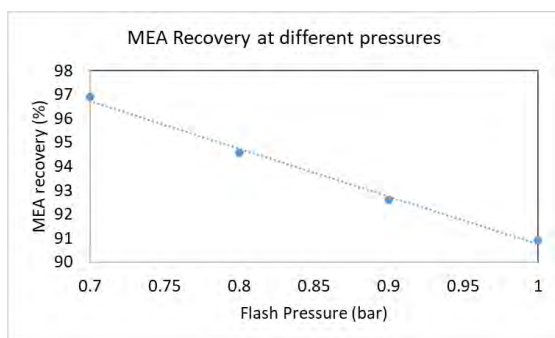
Figure 5 - MEA recovery at different reclaimer pressures

The model was also used to carry out a sensitivity study for dilution factor and was compared to the experimental results. Figure 6 illustrates that the model prediction follows the same trend as the experiments with better recoveries in the experiments. This may be attributed to the model not having an accurate representation of the degraded solvent (ProTreat® allows for including some heat stable salts to the simulations, but thermal degradation products are not present).
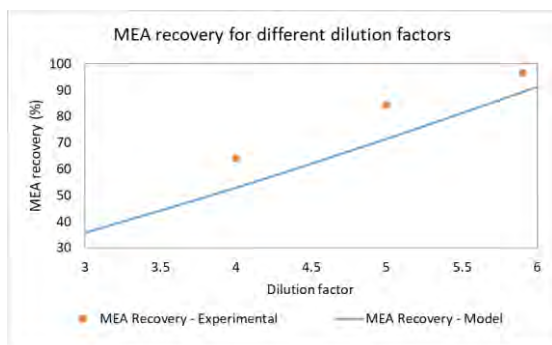

Figure 6 - Effect of dilution factor on reclaiming efficiency

3.3 Reclaiming campaign at Twence

A standalone batch reclaimer was designed and constructed based on prior laboratory experiments and the ProTreat® model results (Figure 7). The reclaimer has the capacity to process 0.5 m³ of degraded solvent per batch. Degraded MEA solvent from the Twence plant was treated in the batch reclaimer and the distillate was collected and analyzed. The reclaimer was heated using three electrical heating elements installed in the reclaimer sump. Different operational settings were investigated during the commissioning tests held over three days in March and April 2021.

Figure 7 - Batch reclaiming unit

At the start of the tests, degraded MEA was added to the reclaimer. The degraded MEA solvent was heated and it was observed that the reclaimer distillate comprised mostly of water and the amount of reclaimed MEA in the distillate marginally increased at higher temperatures.
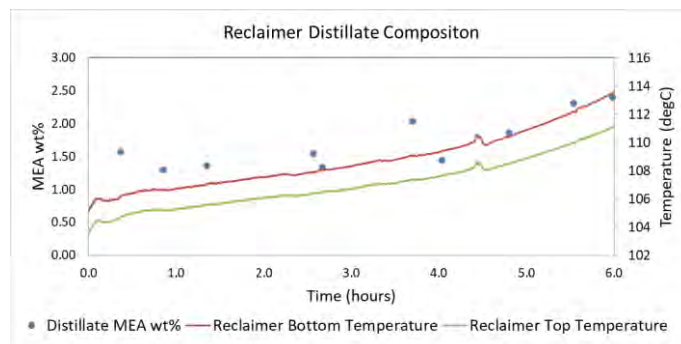

Figure 8- Reclaimer distillate composition with degraded MEA

Then, sodium hydroxide was added to the degraded MEA solvent to neutralize the solvent. Upon neutralization, the MEA recovery in the distillate increased considerably and the composition reached between 10wt% and 29wt% MEA. During this campaign the operating temperature of the reclaimer also increased. To maintain the temperature below 130°C, demi water was added to the reclaimer twice. The MEA recovery decreased immediately after the addition of water and then increased as shown in Figure 9.
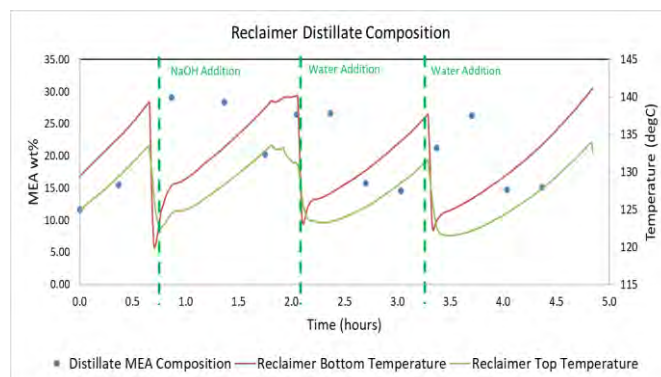

Figure 9 - Reclaimer distillate composition with neutralized MEA

Several samples were taken during the commissioning campaign and were analyzed for some degradation products, impurities and metals. The sludge at the bottom of the reclaimer was also analyzed. These results have been summarized in Table 1.

Table 1 - Laboratory analysis for degraded MEA, distillate sample and sludge sample

Component (mg/kg)	Start sample	Distillate sample	Bottom Sludge Sample
Acetic Acid	641.5	< 10	1826.1
Formic acid	1454.4	< 10	5028.0
Oxalic acid	627.2	< 10	10436.8

Chloride	103.0	< 10	587.7
Nitrate	1116.9	< 10	5252.5
Nitrite	29.4	< 10	26.5
Chromium	0.78	< 0.02	27.70
Iron	3.67	< 0.09	140.68
Nickel	0.43	< 0.02	15.38

From the laboratory analysis it can be clearly seen that the reclaiming operation was successful in removal of degradation products and impurities listed above. The bottom sludge was observed to be more viscous than the start sample and as the analysis shows contains the degradation products and impurities accumulated in the bottom sludge (Table 1).

4. Conclusions

Amine loss due to solvent degradation has significant economic and environmental impacts. For large scale implementation of PCCC, it is important to reduce the impact of these issues.

Laboratory experiments were carried out to determine the optimum operating conditions. It was found that a dilution factor of 6 and operating temperature of 130°C at atmospheric pressure lead to MEA recovery greater than 90%. A model was developed in ProTreat® to optimize the design of the thermal reclaimer, including a heat integration strategy. This reduces the energy demand of the reclaiming unit. Based on the experiments and model results, a standalone thermal reclaimer was designed and operated at Twence. The overall energy demand can be further reduced by integrating the reclaimer with the stripper of the capture plant in industrial scale installations.

The reclaimer was successfully commissioned and the MEA recovery was enhanced after neutralization with sodium hydroxide. The amount of sodium hydroxide to be added for neutralization needs to be better estimated to improve the overall solvent recovery and enhance the reclaiming efficiency. The use of reclaiming allows for reduction of waste volumes thereby reducing the overall waste handling costs. Additionally, the reuse of reclaimed MEA also improves process economics.

The commissioning campaign at Twence provided a first insight into the operation of thermal reclaimers. The operational parameters for maximal solvent recovery, and the design of a process control philosophy will be investigated next. The possibility of using the reclaimer for continuous operation and for blends will be investigated in the future. This mobile batch reclaimer unit can be a valid instrument in evaluating reclaimability of different solvents, and TNO is evaluating the use of it in different research projects. The results of the commissioning campaign of the reclaimer at Twence contributes to the understanding of use of thermal reclaiming as a solvent management strategy for amine based post combustion CO_2 capture in the Waste-to-Energy sector.

References

[1] O. Gorset and V. Andersson, "Amine thermal reclamation; Technology development from lab to large-scale pilot testing," *Energy Procedia*, vol. 37, pp. 6357–6364, 2013, doi: 10.1016/j.egypro.2013.06.565.

[2] N. E. Flø *et al.*, "Results from MEA Degradation and Reclaiming Processes at the CO2 Technology Centre Mongstad," *Energy Procedia*, vol. 114, no. November 2016, pp. 1307–1324, 2017, doi: 10.1016/j.egypro.2017.03.1899.

[3] R. de Vries, A. Roeloffzen, and C. Offereins, "Carbon Capture and Usage (CCU) at Twence," in *ISWA World Congress Bilbao*, 2019.

[4] R. de Vries and W. de Jong, "CCU at Twence Status from Pilot to Demonstration," in *Workshop on EU funding opportunities for CCU projects*, 2019.

[5] S. A. Bedell, "Amine autoxidation in flue gas CO2 capture-Mechanistic lessons learned from other gas treating processes," *Int. J. Greenh. Gas Control*, vol. 5, no. 1, pp. 1–6, 2011, doi: 10.1016/j.ijggc.2010.01.007.

[6] A. L. Cummings and S. M. Mecum, "Increasing Profitablility and Improving Environmental Performance by Maintaining Amine Solvent Purity," in *Proceedings of the Laurance Reid Gas Conditioning Conference*, 2000, pp. 9–20.

[7] T. Wang, J. Hovland, and K. J. Jens, "Amine reclaiming technologies in post-combustion carbon dioxide capture," *J. Environ. Sci.*, vol. 27, pp. 276–289, 2015, doi: https://doi.org/10.1016/j.jes.2014.06.037.

[8] N. E. Flø *et al.*, "Results from MEA Degradation and Reclaiming Processes at the CO2Technology Centre Mongstad," *Energy Procedia*, vol. 114, no. November 2016, pp. 1307–1324, 2017, doi: 10.1016/j.egypro.2017.03.1899.

[9] G. Léonard, D. Toye, and G. Heyen, "Experimental study and kinetic model of monoethanolamine oxidative and thermal degradation for post-combustion CO2 capture," *Int. J. Greenh. Gas Control*, vol. 30, pp. 171–178, 2014, doi: 10.1016/j.ijggc.2014.09.014.

[10] CO2CRC Limted, "Retrofitting an Australian brown coal power station with post-combustion capture," 2018.