Abstract

The first commercial post combustion CO₂ capture plant, based on regenerable amine technology, designed by Shell Cansolv was started successfully in Q3, 2013. Subsequently, the plant conceded 72 hrs warranty test run and since then, the CO₂ capture plant has been running smoothly. The plant performance met requirements for a successful warranty test run and in most cases results were considerably better than expected.

The CO₂ capture facility is designed to capture 170 tonnes of CO₂/day from a gas-fired boiler’s emissions, however, due to boiler limitations, the plant is running at a capacity of 120 tonnes of CO₂/day. The capture facility is equipped with a prescrubber followed by an absorber and water wash on the capture side. CO₂ was captured using counter current exchange with the Cansolv DC-103 solvent, which was regenerated in the stripper. At normal operation, the average CO₂ capture was maintained at around 90%, however, CO₂ capture as high as 98% is achieved. The average specific steam consumption over the Performance Test period was noticed as <1.05 kg of steam/per kg of CO₂ captured. The average CO₂ product purity was greater than 99.0%, more specifically as high as 99.8%.

The capture unit is equipped with a semi-batch thermal reclaimer (TR) unit to remove ionic and non-ionic degradation products from DC-103 solvent. The average amine recovery from thermal reclaimer unit was 99.75% with a maximum of 99.8%. The CO₂ capture performance, energy consumption, Amine recovery from Thermal Reclaimer, and operational philosophy exercised at the CO₂ capture plant will help Shell Cansolv to optimize the design of the CO₂ Capture unit further. Learning’s from first commercial CO₂ capture plant will help Shell Cansolv to successful start-up of upcoming commercial projects.

© 2014 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).

Keywords: DC-103; CO₂; Amine; Steam; Thermal Reclaimer; Purity;

* Corresponding author. Tel.: +1-514-382-4411 ext. 262; fax: +1-514-382-5363.
E-mail address: ajay.a.singh@shell.com
1. Introduction

The Shell Cansolv proprietary DC-103 solvent is a regenerable amine based solvent, developed to capture carbon di-oxide (CO₂) from any low pressure stationary source and produces a treated gas stream, lean in CO₂. Cansolv DC-103 is a binary mixture comprised of 50 wt% of amine and 50% of water.

One of the client’s chemical plant requires high concentrated CO₂ as a raw material and steam as a energy for their manufacturing process. However, a projected maintenance shutdown at the company’s carbon dioxide supplier meant that the plant might have to suspend operations, or at least reduce capacity significantly, until the supplier came back on stream, a consequence that would have a serious impact on its revenues. The chemical plant was also dependent on an industrial neighbour for steam supply but had suffered costly supply interruptions owing to unplanned boiler shutdowns. In order to avoid disruption to its plant operations, client developed a concept to become independent on steam and carbon dioxide supply to the chemical plant. It was proposed to build a natural gas fired boiler to generate 21 bar steam and capture CO₂ from resulting flue gas. The Shell Cansolv CO₂ capture technology was selected to capture CO₂ from the flue gas, due to its low energy demand, low emission, no restriction on use of technology and a proposal to form a long-term partnership for improving the technology. The client entered into a licensing agreement for the use of the technology and a material supply agreement for the supply of the Cansolv absorbent DC-103. This marked the first commercial license agreement in the chemical industry for the Cansolv CO₂ Capture System.

Shell Cansolv CO₂ capture technology helped client to become independent on CO₂ and enable client to “individually steer” its chemical production.

Cansolv DC-103 amine based CO₂ capture technology was deployed to the chemical plant to capture up to 170 tonnes of CO₂ per day, from a flue gas containing about 9-11% CO₂ on a wet basis, coming out from a natural gas-fired boiler. However, due to the limitation on boiler capacity, the plant runs at 120 tonnes of CO₂ capture per day.

The plant was started successfully in Q3, 2013 and since then, the Shell Cansolv CO₂ capture plant has been running smoothly. The plant has provided a unique opportunity for Shell Cansolv to monitor the plant performance over a period of time, validate the design envelop, capture learnings and & optimize the design envelop further. The present article covers the following sections.

Section 2 will discuss the process plant line-up, which includes pre-scrubber, absorber, water wash, regenerator lean flash, condensate flash and mechanical vapour compression (MVR). Section 3 will discuss the plant performance which includes CO₂ capture rate, steam consumption, amine emission, CO₂ purity, and performance of
the Thermal Reclaimer Unit. Section 4 will summarize the learnings attained from the capture plant. Section 5 will cover the conclusion.

2. Plant description

The flue gas from a gas fired boiler, containing 9-11% CO₂ is routed to a booster fan to provide enough pressure to drive it through downstream equipment and out to the absorber stack. A prescrubber unit is installed downstream of booster fan to quench and sub cool the flue gas, prior to feed to the CO₂ absorber. This is to ensure proper CO₂ absorption and prevent excessive water evaporation from the amine solution in the CO₂ Absorber tower. The quenched and cooled gas is ducted to the CO₂ Absorber. CO₂ absorption from the flue gas occurs by counter-current contact with Cansolv DC-103 solvent in a vertical multi-level packed-bed column, where amine is fed on the top and flue gas enters at the bottom of the column. The absorber tower is equipped with 3 mass transfer beds, packed with Sulzer Mellapak M452Y packing. CO₂ is absorbed from the flue to amine and enriched CO₂ amine comes out from bottom of the absorber, whereas, lean in CO₂ flue gas comes out from the top of the absorber. CO₂ absorption is an exothermic reaction. To prevent heat accumulation in the tower, and to improve the amine absorption capacity, hot amine is collected on a chimney tray above the bottom packing section, pumped to the Intercooler, cooled by a water cooler and is returned back to the absorber to resume CO₂ absorption in the bottom packing section.

The treated flue gas leaving the top of the CO₂ absorption section passes through a water wash section, packed with Sulzer Mellapak M452Y packing. A water wash section, included at the top of the CO₂ Absorber is designed to capture any volatile and entrained amine mist from the flue gas. The treated flue gas leaving the Wash Water Section, flows upwards and is released to the atmosphere.

The CO₂ enriched amine from bottom of the absorber is heated in a lean-rich exchanger and sent to the CO₂ regenerator, where amine is regenerated by the heat provided by a reboiler and by a Mechanical Vapour Compressor (MVR). The regenerated (lean) amine from stripper bottom is send to a lean amine flash tank, where pressure is reduced and water vapour is generated. Water vapour released from the amine in the Lean Amine Flash Tank is compressed by the Mechanical Vapour Compressors (MVR). LP steam condensates from the Reboiler is collected in a Condensate Level Pot and routed through a pressure reducing valve to a Condensate Flash Pot, where it flashes to the same pressure as the Lean Amine Flash Tank. The flashed water vapour from Condensate Flash Pot is routed to the MVR, where it is compressed along with the lean amine flashed vapour coming from lean amine flash tank. The compressed vapour from MVR is introduced at the bottom of the CO₂ regenerator, to contribute to the stripping of the CO₂ and to minimize the steam requirement.

Overhead vapour from regenerator is cooled by an overhead condenser and the two-phase mixture is separated in an overhead reflux accumulator. The reflux is returned back to the regenerator whereas, vapour (CO₂ product) is sent to the CO₂ compression system.

Cansolv Absorbent DC-103 is subject to thermal degradation, oxidative degradation and degradation due to reaction with nitrite in solution. Amine degradation produces undesirable ionic and non-ionic degradation products over time that must be removed from the absorbent. Furthermore, other trace contaminants present in the gas, SO₂ for example, form ionic heat stable salts that must also be removed from solution. These ionic and non-ionic contaminants are removed by a vacuum distillation process, called Thermal Reclaimer Unit (TRU). The TRU boils off water and amine from DC-103 amine, to concentrate the degradation products into a mass that is then diluted in water for ease of disposal. The TRU is designed to operate in a semi-batch mode. The degraded amine product at the end of the TRU batch is collected at the bottom which consists of hot heavy liquid containing crystals of sodium salts. Dilution water is used to cool down the degraded product and to dissolve all salts and crystals before being disposed off.

A schematic of capture plant is shown in Figure 1.
Fig. 1. Shell Cansolv typical CO\textsubscript{2} capture process with lean flash and condensate flash lineup.

3. Plant performance

3.1. CO\textsubscript{2} capture

Figure 2 shows the plant performance in terms of % CO\textsubscript{2} captured during the warranty test run. The CO\textsubscript{2} capture plant was designed to capture 170 tonnes of CO\textsubscript{2} per day by removing 90% of the CO\textsubscript{2} from the flue gas generated by a natural gas fired boiler. However, due to boiler capacity limitations, the plant runs at a capacity close to 120 tons of CO\textsubscript{2} capture per day by removing 90% of the CO\textsubscript{2} from the flue gas generated by a natural gas fired boiler. The inlet and outlet CO\textsubscript{2} concentration (wet basis) in the flue gas to absorber is shown on the primary Y axes whereas, % CO\textsubscript{2} capture is shown on the secondary Y axes. The average concentration of CO\textsubscript{2} in the flue gas to the absorber was 9.1 vol% with a standard deviation of 0.26 vol%, whereas, average concentration of CO\textsubscript{2} in the flue gas in the absorber outlet was 0.85 vol% with a standard deviation of 0.22 vol%. The CO\textsubscript{2} capture was consistently maintained at around 90% (warranty figure), with an average removal of 91%.

3.2. Steam consumption

Figure 3 shows the plant performance in terms of steam requirement during the warranty test run. The steam flow was validated by a condensate level rise test, conducted at the end of the test run. The repeated condensate level rise test indicated that steam flow meter was under-predicting the steam flow by 13.4%. The steam flow and the stripping factor were therefore corrected by a factor of 13.4%. The corrected steam flow rate and stripping factor is shown in Figure 3.
Fig. 2. Inlet & Outlet CO₂ concentration and percent CO₂ capture in the absorber.

Fig. 3. Steam flow (kg/hr) and specific steam consumption (kg of steam/kg of CO₂) during performance test run.
The average steam consumption for the proposed line-up in Figure 1 over the performance test run was 4,700 kg/hr with a standard deviation of 191 kg/hr. The average stripping factor was 1.05 kg of steam per kg of CO₂ delivered, with a standard deviation of 0.06 kg of steam per kg of CO₂ delivered. This corresponds to an average energy (steam) requirement of 2.33 GJ/ton of CO₂ capture.

3.3. Amine Emissions

Amine emission from absorber to stack was done iso-kinetically. The gas sampling set-up used was a hybrid of a modified EPA Method 5 sampling system on the front end, coupled with an ice bathed impingers set, followed by special sorbent tubes on the back end (shown in Figure 4 below). The modified Method 5 portion of the system collects droplets and any vapor that is condensable at ice-bath temperatures; while the sorbent-tube back end collects any remaining (non-condensable) vapour.

The average amine emission measured via stack was very low and it was in sub ppm level.

![Fig. 4. Hybrid Gas sampling set-up used for amine emission measurement.](image)

3.4. CO₂ Purity

The CO₂ product coming out of the stripper overhead reflux accumulator is routed to a compression train which compress the CO₂ product, before it is routed to the chemical unit. Samples of dried and compressed CO₂ were taken throughout the performance test period. The CO₂ purity results are shown in Figure 5. The average CO₂ purity measured was 99.8% with a standard deviation of 0.18%.
3.5. Thermal Reclaimer Unit

Thermal reclaimer is a vacuum distillation unit used to remove the ionic and non-ionic degradation products from amine. Non-ionic degradation products are build-up in amine due to thermal degradation, oxidative degradation and degradation due to reaction with nitrite in solution. Whereas, ionic degradation products like sulphate, nitrates are build-up due to the presence of trace components like SO$_2$ and NO$_2$ in the flue gas. These ionic and non-ionic contaminants are removed in a TRU, which boils off water and amine from DC-103 amine and recover it from top of the vacuum distillation column whereas degradation products are concentrated and recovered from the bottom.

During the vacuum distillation process, a portion of amine is not recovered and lost through the column bottom. The design and operating condition of vacuum distillation column is very important to maximize the amine recovery and to minimize the operational challenges e.g., fouling/plugging of column bottom.

Thermal reclaimer design deployed for this commercial unit is of a semi-batch type which operates for 15-20 days in series. At the end of the run, amine flow to TRU is stopped and unit operates in batch mode to boil off residual amine from TRU bottom. At this stage of operation, steam sparging at TRU bottom is used to maximize the amine recovery. Steam sparging also helps to promotes mixing and dissolution of the degraded products and crystals.

Wash water is injected to clean the TRU internals and the coils and to cool down the degradation products before it can be disposed off. The TRU is inspected to assess the level of fouling/plugging on the heating coils and column walls, before next batch commence.

An average amine recovery of 99.75%, with a maximum of 99.8% of amine recovery from TRU was achieved.
4. Learnings from the capture plant

The design and operational learnings gained from first commercial plant will help Shell Cansolv to further optimize the CO₂ capture process and will bring more value to customers. Some of the learning’s captured here are:

- % CO₂ capture was consistently maintained at 90% or higher, without over stripping of the amine in the regenerator.
- Lean flash MVR line-up for Cansolv DC-103 solvent can reduce the steam consumption by 33%.
- Lean Flash MVR plus condensate flash line up can reduce the steam consumption by 38%.
- Average steam consumption of 1.05 kg of steam/kg of CO₂ was recorded. Steam flow meter reading was corrected by condensate measurement from condensate level control measurement. The steam flow recorded at plant after correction was much lower than the warranty value.
- The thermal reclaimer unit was designed to recover 99.5% amine. The TRU performance was satisfactory with an average amine recovery of 99.75%. Appropriate design margin with TRU allows for a higher processing rate. Higher TRU processing rate allows to build-up higher concentration of degradation products in amine, providing operational flexibility to the plant in case TRU is out of operation for more number of days than expected. Higher processing rate also helps to reduce the number of TRU batches/year, and hence lower amine loss.
- The thermal reclaimer unit (TRU) should be operated close to 190-200 C bottom temperature to maximize the amine recovery.

5. Conclusion

Shell Cansolv CO₂ capture technology has a wide range of potential applications in refining, chemical and power sector, where it can help businesses to lower their carbon intensity and meet stringent greenhouse gas abatement regulations by removing CO₂ from their flue gas streams.

The performance tests were passed with very impressive results on capture rate, steam consumption and TRU recovery, all the performance criteria outperformed the guarantee. Furthermore, the purity of the final carbon dioxide product was greater than 99.75%, which was also above design expectations. More importantly, client is now independent of external CO₂ supplies and can individually steer its production of the chemical plant. The technological and engineering learning’s gathered from first commercial CO₂ capture plant, provide Cansolv with additional technological information and will help to deliver future projects with even better efficiency.

6. References