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Bench Scale Development of a High-Performance Drop-in Solvent for Flue Gas CO_2 Capture

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Abstract

Susteon has developed a drop-in high performance, water-lean, mixed amine solvent (trademarked as Sustenol™) with fast absorption and desorption kinetics for significantly improved CO_2 capture efficiency for flue gas streams with a low CO_2 concentration (~4 vol%) such as flue gas from natural gas combined cycle (NGCC) power plants. Amine-based solvent absorption technology is the most mature and reliable technology for CO_2 capture at a large scale such as from a power plant flue gas; however, the amine absorption process requires large absorption columns which result in high capital costs and energy requirements (typically >3.0 GJ/tonne of CO_2). Using a design of experiments methodology, Sustenol™ solvent was optimized for a significantly lower energy for regeneration. Furthermore, the solvent exhibits significantly lower sensible heat in addition to having three times higher absorption kinetics compared to 30 wt% monoethanolamine (MEA) solvent. The optimized Sustenol™ also shows a higher dynamic CO_2 absorption capacity of ~0.5 mol_{CO2}/mol_{amine} compared to 0.25 mol_{CO2}/mol_{amine} for 30 wt% MEA. Additionally, the solvent exhibits high oxidative, thermal and hydrothermal stability leading to lower solvent loss and emissions compared to the current leading solvents. These advancements have resulted in a solvent regeneration energy of 2.16 GJ/tonne of CO_2 which is >30% lower than current state-of-the-art commercial and emerging solvents. A rate-based thermodynamic process model developed in Aspen Plus™ was experimentally validated with bench and pilot-scale testing results. This process model was used to develop a high-fidelity technoeconomic analysis (TEA) for post-combustion CO_2 capture from a 687 MW_e NGCC power plant. This TEA indicated the cost of CO_2 capture by Sustenol™ for 97% CO_2 removal at \$54/tonne and for 90% removal at \$49/tonne, with a pathway to achieve \$45/tonne of CO_2 with continued process and solvent advancements.

Keywords: water-lean solvent; NGCC flue gas; CO_2 capture; absorber efficiency; CO_2 desorption, specific regeneration duty, thermal and oxidative stability.

1. Introduction

Amine-based solvent CO_2 capture is one of the most practiced point source capture methods with its roots tracing back to the 1930s when monoethanolamine (MEA) was first used to treat acid gases from refineries [1]. Despite its maturity and ongoing governmental incentives for CO_2 capture and sequestration, such as the United States Section 45Q tax credit, widespread adoption remains limited due to overall high CO_2 capture costs for flue gas streams. These costs

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stem from high capital cost primarily due to large column diameter and height requirements dictated by lower CO_2 absorption rates and from high operating costs due to high energy requirements for solvent regeneration and significant solvent degradation resulting into high solvent make up rates [2,3].

Due to the technology maturity, the amine solvent-based CO_2 capture process has become well optimized through advancements such as intercooling the solvent in the absorption column to maintain high absorption rates and new stripping column designs to allow for integrated heat recovery from the exiting CO_2 stream to minimize the heat energy requirements of the system [2,4,5]. Furthermore, entirely new designs of the capture process have been proposed such as the use of a rotating packed bed reactor which employs centripetal acceleration of the solvent through a packed bed to minimize column height requirements resulting in significantly lower capital costs [6]. Despite these advancements, the high CO_2 capture costs persist, leading much of the current research to focus on further solvent development.

To address the cost issues in amine-based CO_2 capture, solvent development and optimization need to focus on several key properties: (1) CO_2 working capacity of the solvent, (2) rate of absorption of CO_2, (3) solvent degradation rate, and (4) enthalpy of CO_2 absorption [7]. The CO_2 absorption rate determines the height of packing required and size of the absorber columns. The oxidative, thermal, and hydrothermal degradation rates of the solvent directly determine solvent make up rate. For a conventional reboiler design, a lower enthalpy of CO_2 absorption is critical in reducing the amount of steam needed for solvent regeneration [5,8]. Furthermore, CO_2 working capacity of the solvent determines the circulation rate in the capture process. Key attributes of an optimal solvent include a lower water percent for increased CO_2 working capacity while maintaining low viscosity, avoiding precipitation, and low degradation rates.

Amine moieties are the most salient CO_2 capture agents in solvents due to the nitrogen group's high reactivity towards CO_2 while being regenerable at relatively low regeneration temperatures (<150°C) compared to other CO_2 capture agents such as metal hydroxide salts [9]. The chemical structure of amine moiety results in differing CO_2 capture properties among a wide variety of amines. Primary amines (such as MEA) capture CO_2 through carbamate formation leading to their characteristically high CO_2 absorption rates which makes them the most used CO_2 capture solvents [9]. However, they require high energy regeneration, have a lower working capacity, and generally exhibit high degradation and corrosion rates. Secondary amines also capture CO_2 through carbamate formation with a lower absorption rate and working capacity than primary amines but exhibit stronger stability compared to primary amines; however, they suffer from NOx-induced (present in most of the combustion flue gases) oxidative degradation and carcinogenic nitrosamine formation. Tertiary amines, such as methyl diethanolamine (MDEA) and triethanolamine (TEA), capture CO_2 through bicarbonate formation, offering high stability and high working capacity with low heat of absorption, but suffer from very slow CO_2 absorption rates [9].

CESAR-1 solvent developed by SINTEF in Norway is currently a leading amine-based CO_2 capture solvent formulated using a blend of 2-amino-2-methyl-1-propanol (AMP) and piperazine (PZ) in an aqueous solution. Initially designed to displace 30 wt% MEA-based CO_2 capture in pilot systems, it exhibits high working capacity and reaction kinetics; however, both AMP and PZ have been observed to precipitate out at high concentrations. The resulting solution is dilute and leads to less efficient CO_2 capture and requires higher regeneration energy (~3 GJ/tonne of CO_2) [10].

To address the costs associated with the current amine-based solvents for point source CO_2 capture, Susteon has been developing a novel solvent, Sustenol™ since 2021. This mixed amine solvent blend takes advantage of the high CO_2 capture rates of primary and secondary amines, while leveraging the higher working capacity, high oxidative and thermal stability, and lower regeneration energy requirement that tertiary amines bring.

2. Bench-Scale Experimental Testing

To develop and screen various solvent compositions, a 15 kg CO_2/day bench-scale absorber and stripping system was designed and built as shown in Figure 1.

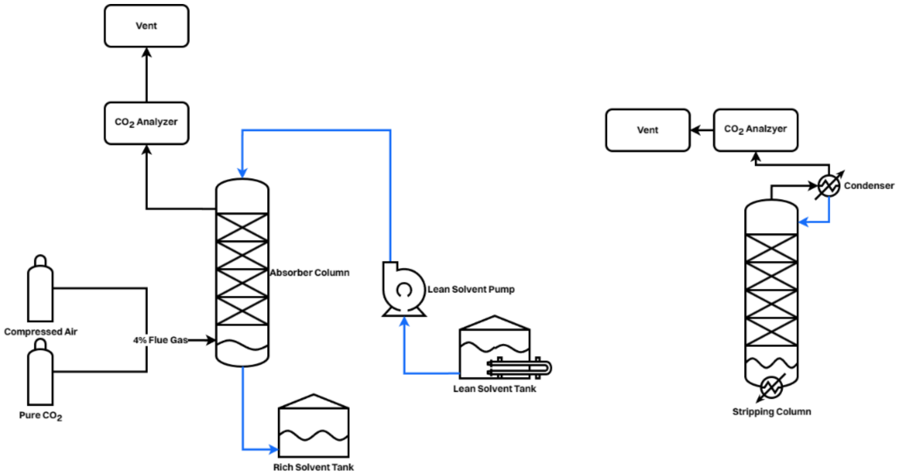


Fig. 1. Susteon Bench-Scale Solvent Test System. Left: Semi-batch Absorber Column. Right: Batch Stripping Column

A 5-foot tall, 1.5-inch inner diameter Schedule 80 PVC pipe was used as the absorber column with 4 feet of KUBER wire structured packing filling the column to increase the contact area between the solvent and the incoming flue gas. Mass flow controllers were used to mix compressed air and ultra-pure CO_2 to get the desired ~4.3% inlet CO_2 concentration and a total flowrate of 35-47 SLPM of the simulated flue gas was fed to the column for CO_2 capture testing. The lean solvent was heated to 40ºC to simulate a commercial amine plant. It was pumped into the column in a countercurrent fashion to the flue gas flow at varying flowrates to vary the mass of liquid / mass of flue gas (L/G) ratio. A Quantek NDIR CO_2 gas analyzer was used for absorber effluent gas to determine the CO_2 concentration to calculate percent CO_2 capture. To test thermal stability and the cyclic performance of the solvent, a stripping column was designed and constructed from a stainless-steel kettle with an 1800 W heater. The kettle was connected to an overhead condenser to maintain the water concentration of the solvent while releasing the CO_2 from the rich solvent.

Extensive physiochemical property measurements were conducted on the lean and rich solvents from the bench testing. In addition to viscosity and density measurements which were performed using a 10 mL pycnometer and NDJ-8S viscometer, respectively, a gas evolution titration system was used to determine CO_2 working capacity of the solvent. The heat of absorption of the solvent was measured using a THT µRC micro-reaction calorimeter with a gas injection port.

To perform vapor pressure and rate measurements, a stirred tank reactor was designed to allow the vessel to be closed and for pressure to be measured at elevated temperatures. Additionally, gas injection ports allowed CO_2 injection into the solvent tank, and the partial pressure of CO_2 was measured with respect to time and temperature to determine the rate of CO_2 absorption. The reactor was operated at a stirring speed of 1800 rpm and at temperatures up to 30ºC using tandem magnetic coupling stirring and modular electrical heating.

A water-lean amine solvent for CO_2 capture was developed by using a blend of proprietary tertiary, primary, secondary, and hindered amines. Through iterative testing via a nested design of experiment matrix using the bench-scale absorber and stripping reactor, key properties such as CO_2 capture efficiency at various L/G ratios, solvent viscosity, heat of absorption, density, absorption rate, and regeneration energy were determined to optimize the concentration of each component in the solvent formulation. The facilities at the Pandit Deendayal Energy University (PDEU) in Gandhinagar, India were used to validate the bench-scale testing results in their one (1) tonne/day CO_2 pilot unit with a 40 kW reboiler capacity with simulated flue gas composition. Additional testing was conducted to measure CO_2 capture and regeneration energy requirements as well as performance stability over time.

3. Results

Figure 2 shows a comparison of the performance of Sustenol™ with the 30 wt% MEA solvent which was used a baseline. Higher CO_2 capture efficiencies were observed for Sustenol™ solvent at the same L/G ratio.

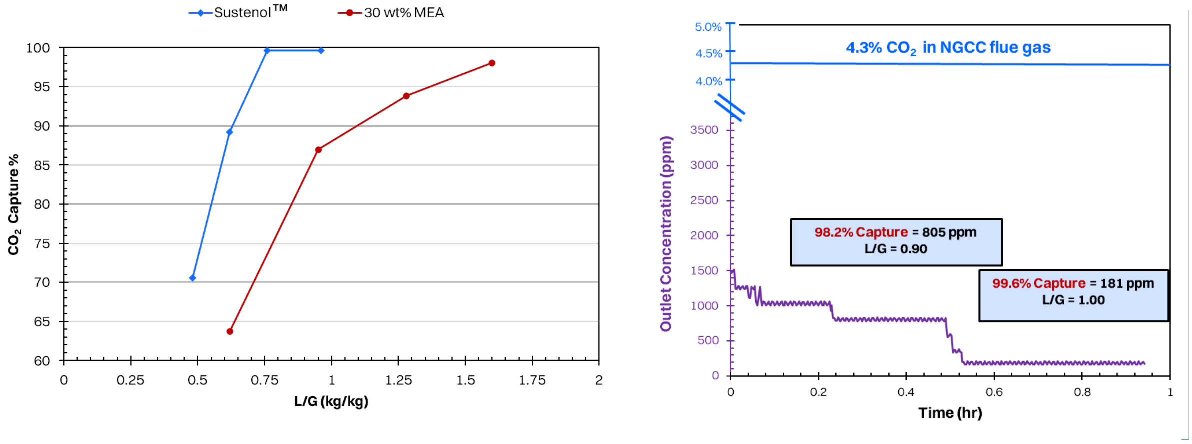


Fig. 2(a) CO_2 Capture Efficiency of 30 wt% MEA vs Sustenol^{TM} at various L/G Ratios
(b) PPM Level Capture of CO_2 using Sustenol™ from NGCC Flue Gas

From Figure 2(a), at the same solvent circulation rate at L/G of 0.6, Sustenol™ captures almost 90% of the CO_2 from a simulated NGCC flue gas (~4.3% CO_2) while 30 wt% MEA captures <65% CO_2. Furthermore, at an L/G ratio of 0.7, Sustenol™ captures ~97% CO_2 from this flue gas. As shown in Figure 2(b), Sustenol™ can capture 98.2% of CO_2 (with 805 ppmv CO_2 in the effluent) at an L/G ratio of 0.9 and 99.6% CO_2 capture at an L/G ratio of 1.0 producing an effluent with 181 ppmv of CO_2 which is lower than the CO_2 concentration in the ambient air (~420 ppmv). Therefore, it is possible to achieve net-zero or negative CO_2 emissions from NGCC plants with Sustenol™, clearly demonstrating its fast kinetics and high working capacity for CO_2 capture even with low (~4%) CO_2 concentration in the flue gas.

The significantly reduced regeneration energy of Sustenol^{TM} solvent was validated by lower heat capacity (kJ/kg/K) and heat of absorption (kJ/mol CO_2) that was observed during testing. Lower heat capacity in both the lean and rich conditions manifests into lower sensible heat which, in conjunction with the lower heat of absorption, resulted in a lower reboiler duty (GJ/tonne CO_2). These results are shown in Figure 3.

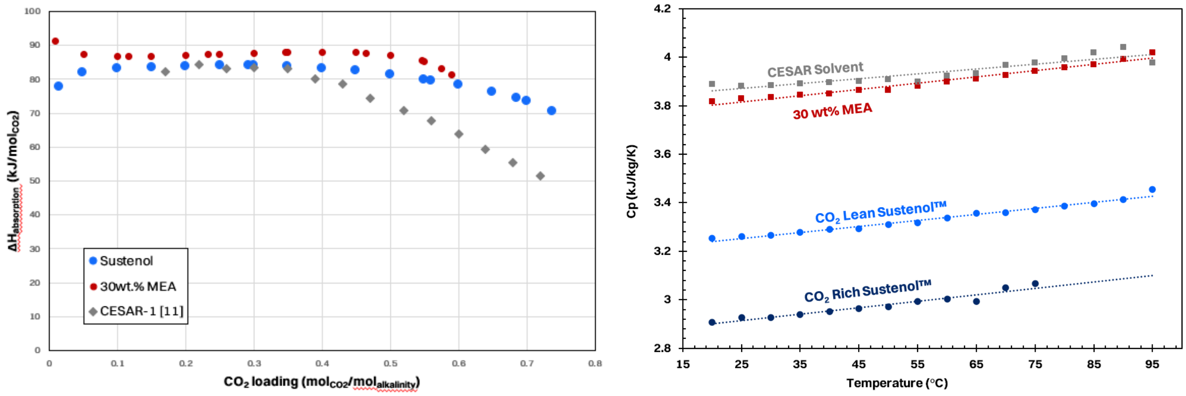


Fig. 3(a) Heat of Absorption of 30 wt% MEA and CESAR-1 vs Sustenol^{TM} at various CO_2 Loadings
(b) Heat Capacity of Sustenol^{TM} vs. 30 wt% MEA and CESAR-1 [11].

At 75ºC, Sustenol™ has lower heat of absorption across all tested CO_2 loadings compared to both CESAR-1 and 30 wt% MEA solvent formulations. Data from the micro-reaction calorimeter showed a 17% decrease in heat capacity for Sustenol™ over the temperature range from 15-95ºC. The heat of absorption and heat capacity results obtained were used to estimate the overall regeneration energy/reboiler duty from Equation 1 and plotted in Figure 4 [10].

$$Q_T = \underbrace{\frac{C_p\ \Delta T}{\Delta\alpha}\frac{M_{sol}}{M_{CO_2}}\frac{1}{x_{sol}}}_{\text{Sensible Heat}} + \underbrace{\Delta H_{vap,\,H2O}\frac{p_{H_2O}}{p_{CO_2}}\frac{1}{M_{CO_2}}}_{\text{Vaporization Heat}} + \underbrace{\frac{\Delta H_{abs,\,CO_2}}{M_{CO_2}}}_{\text{Absorption Heat}} \qquad (1)$$

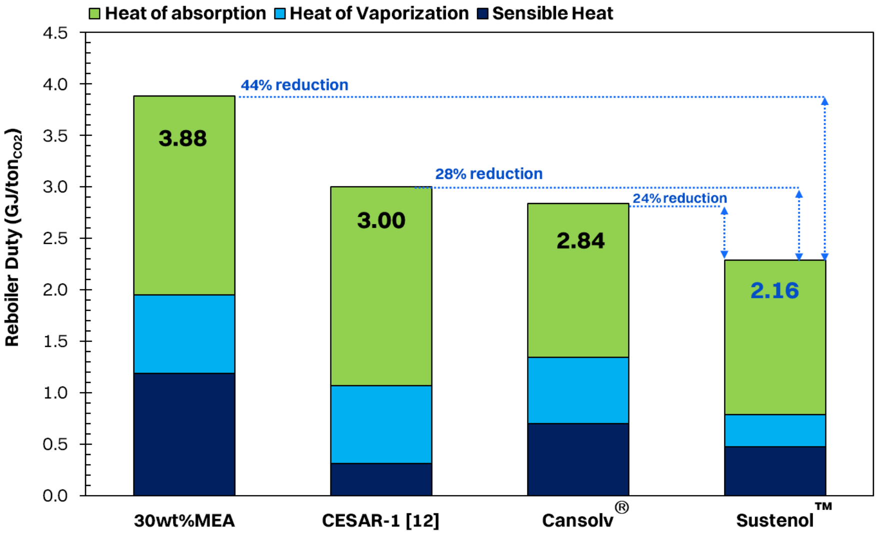


Fig. 4. Estimated Regeneration Energy for NGCC Flue Gas CO_2 Capture [12].

A comparison was made to current CO_2 capture solvents, including 30 wt% MEA, CESAR-1, and Cansolv® to estimate reduction in the regeneration energy with Sustenol™. The reboiler duty was reduced from 3.88 GJ/tonne CO_2 for the 30 wt% MEA to 2.16 GJ/tonne CO_2 with Sustenol™ indicating a 44% reduction. Similarly, as shown In Figure 4, the reboiler duty for Sustenol™ is >20% lower than the Cansolv® and CESAR-1 solvents.

In addition to high working capacity and lower heat of regeneration, second order absorption reaction kinetics were measured for the 30 wt% MEA, CESAR-1, and Sustenol™ solvents and are shown in Figure 5(b). Solvent kinetics were determined from the vapor-liquid equilibria (VLE) data and associated rate constants along the length of the absorber packing. From the VLE data, the estimated working capacity of Sustenol™ was 0.44 mol_{CO2}/mol_{amine} as shown in Figure 5 (a). From the results presented in Figure 5(b), Sustenol™ exhibits nearly triple the reaction kinetics that of 30 wt% MEA solvent at 25ºC. CESAR-1 appears to have a higher reaction rate than both 30 wt% MEA and Sustenol™ primarily due to its high piperazine content, but it suffers from high reboiler duty as shown in Figure 4.

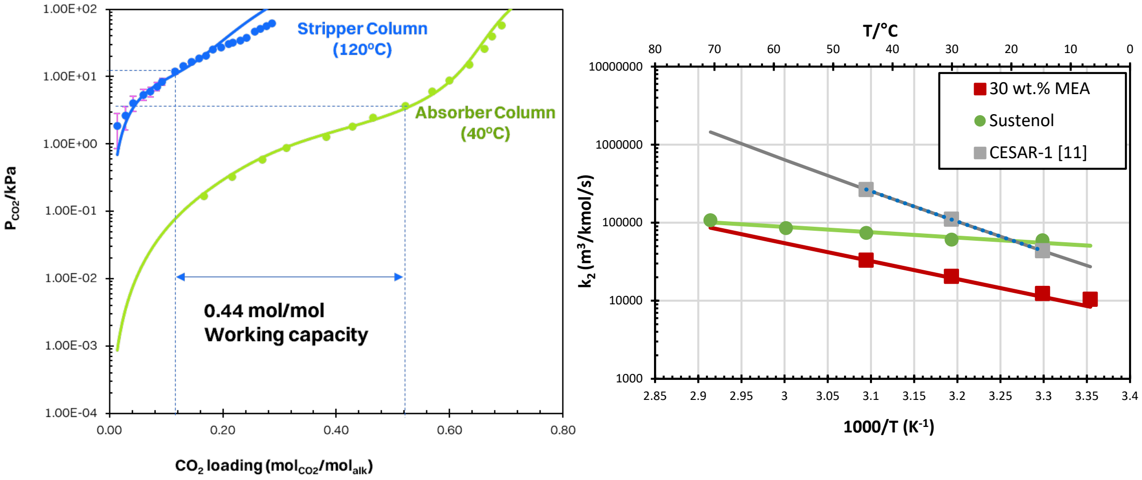


Fig. 5(a) Sustenol^{TM} VLE from Data taken from Absorber and Stripper Columns
(b) Sustenol^{TM} Reaction Kinetics vs 30 wt% MEA and CESAR-1 [13].

Following the in-house laboratory evaluation of Sustenol^{TM} at Susteon at 15 kg/day CO_2 at bench-scale, pilot-scale testing of 30 wt% MEA and Sustenol™ solvents was conducted at PDEU in their nominal 1 tonne/day CO_2 continuous pilot plant. This 1 tonne/day capacity pilot plant was designed for a 13% CO_2 concentration flue gas (coal combustion flue gas). This pilot unit has an absorber with 10-inch diameter and 13 feet height and a stripper with 10-inch diameter and 6 feet height. For a ~4% CO_2 containing flue gas, the capacity of this pilot plant was about 350 kg/day. Simulated NGCC flue gas conditions used in the pilot scale testing are given in Table 1. These pilot plant tests were aimed to compare Sustenol^{TM} solvent's CO_2 capture performance at various L/G ratios and regeneration heat duty with the bench-sale test results obtained in Susteon laboratory.

Table 1. Test conditions used in the pilot scale

Flue gas flow rate	1000-4000 slpm
Flue gas CO_2 conc.	4.0 vol%
Flue gas inlet T	35-40°C
Flue gas inlet P	1.0 psig
Solvent inlet T	40°C
Liquid flow rate	3-10 lpm
Flue gas H_2O conc.	5-7 vol%
Flue gas O_2 conc.	8-12 vol%
Flue gas N_2 conc.	70-80 vol%
L/G (kg/kg) range	0.7-4

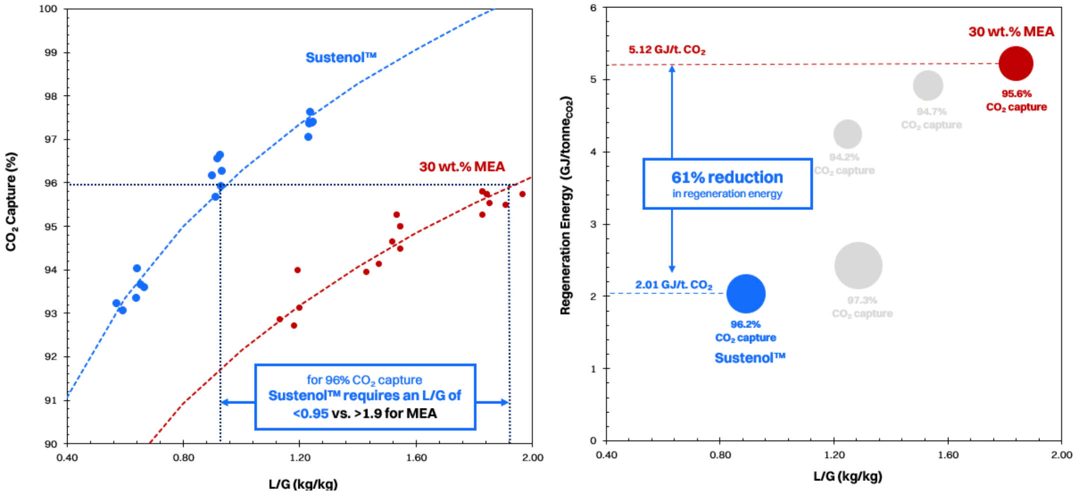


Fig. 6(a) CO_2 Capture Performance Comparison between 30 wt% MEA and Sustenol^{TM} at various L/G Ratios
(b) Regeneration Heat Duty for Sustenol vs 30 wt% MEA.

As shown in Figure 6(a), Sustenol^{TM} required an L/G ratio of ~0.95 to achieve 96% CO_2 capture from a simulated flue gas containing 4.3% CO_2, compared to an L/G ratio of 1.9 for the 30 wt% MEA for the same 96% CO_2 capture. This finding validated the bench-scale test results, demonstrating that Sustenol^{TM} is a more efficient solvent for CO_2 capture. Furthermore, the heat duty required to regenerate Sustenol^{TM} was 2.01 GJ/tonne CO_2, compared to 5.12 GJ/tonne CO_2 for 30 wt% MEA. This observed 61% reduction in regeneration heat duty is consistent with the bench-scale test results. This pilot-scale testing confirmed lower regeneration heat duty and higher CO_2 capture efficiency of Sustenol^{TM}.

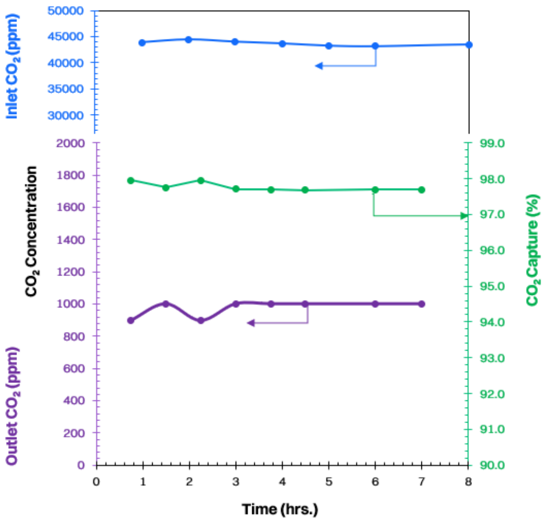


Fig. 7. CO_2 Capture Performance over 7 hrs. Continuous Operation at PDEU

Further testing was conducted at PDEU to evaluate solvent performance over a period of 7 hours continuous operation. Figure 7 shows the test results including inlet and outlet CO_2 concentrations as well as the percent CO_2 capture performance as a function of time. The inlet and outlet CO_2 concentrations and CO_2 capture efficiency remained relatively stable over the 7-hour period of continuous operation during the pilot testing. Notably, Sustenol^{TM} consistently captured >97% CO_2 from the simulated flue gas, validating the bench-scale test results. Preliminary testing for thermal and oxidative stability was also conducted which showed no significant degradation. However, this testing was for a short period of time and further degradation/stability testing is planned for early 2025. Total accumulated bench-scale testing of the Sustenol™ solvent was >300 hours with no signs of degradation.

4. Modeling and Technoeconomic Analysis

A rate-based thermodynamic process model was built in Aspen Plus^{TM} to estimate the CO_2 capture costs using Sustenol^{TM} as a drop-in solvent in existing amine-based CO_2 capture systems. This model was rigorously validated with the experimental results obtained in bench-scale and pilot-scale test units as discussed above. This evaluation culminated in a techno-economic analysis (TEA) of Sustenol^{TM} and its comparison with 30 wt% MEA and Cansolv® solvent systems. Basis of the TEA and CO_2 capture cost for various solvents were taken from the 2021 NETL report from the U.S. Department of Energy as well as studies published in the International Journal of Greenhouse Gas Control [14, 15, 16]. The overall costs of CO_2 capture using each solvent were calculated and are shown in Figure 8.

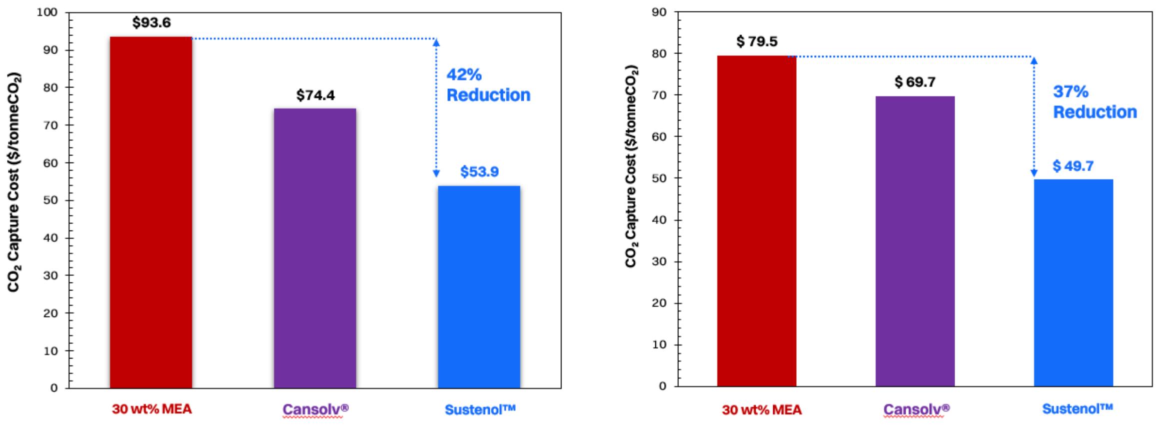


Fig. 8. (a) Capture costs for 97% CO_2 capture; (b) capture costs for 90% CO_2 capture [14,15,16].

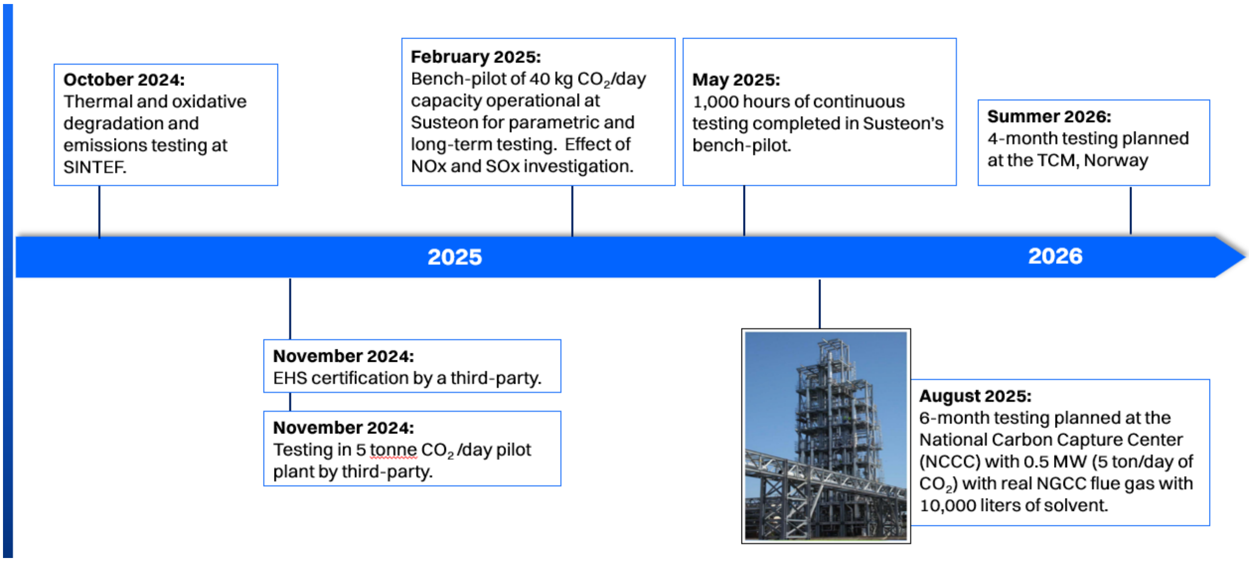
Previous TEAs reported for 30 wt% MEA and Cansolv® showed that the costs for 97% CO_2 capture were \$93.00 and \$74.40 per tonne of CO_2, respectively. For 90% capture, the costs decreased to \$79.50/tonne CO_2 for 30 wt% MEA and \$69.70 per tonne of CO_2 for Cansolv® [14, 15, 16]. The TEA conducted in this study using the experimentally validated process model showed lower CO_2 capture costs for both 90% and 97% capture using Sustenol™ compared to 30 wt% MEA and Cansolv® as shown in Figure 8. Specifically, the cost for 97% CO_2 capture estimated at \$53.90 per tonne of CO_2 is 42% lower than 30 wt% MEA. These TEA findings built upon the previous studies on commercial CO_2 capture solvents [14, 15, 16] demonstrate that Sustenol™ solvent's unique attributes can significantly reduce the cost of CO_2 capture from NGCC flue gas (~4% CO_2). Additional TEA work done by Susteon for other higher CO_2 concentration flue gases (cement plants, coal combustion, recovery boiler in paper and pulp industry, etc.) indicates further reduction in the CO_2 capture cost below \$40 per tonne and in some cases as low as \$35 per tonne.

5. Technology Roadmap

As reported here, Sustenol™ solvent has been developed from the Technology Readiness Level (TRL) of 2 to current TRL 5 since 2021. Initial bench-scale and pilot-scale testing has demonstrated its superior properties and performance for CO_2 capture from a simulated NGCC flue gas. The development work is continuing to further de-risk this technology. A technology roadmap is shown in Figure 9. Susteon has signed a solvent manufacturing agreement with a major contract manufacturer who has successfully produced 5,000 liters of Sustenol™ solvent and is currently producing 10,000 liters for the testing at NCCC. Furthermore, Susteon has obtained a comprehensive U.S. patent on the composition of the Sustenol™ solvent with associated international filings.

The most important risk mitigation activities planned, include obtaining solvent testing data with actual flue gas for 1000s of hours of testing at large pilot and/or demonstration scale to: (1) demonstrate stable CO_2 capture performance at low L/G ratios, (2) validate regeneration heat duty (~2.2 GJ/tonne), (3) measure solvent emissions and any degradation products including formation of heat-stable salts, (4) determine its ecotoxicity and (5) determine corrosion with carbon and stainless steel and compatibility with the materials of construction. With these goals, Susteon has contracted with SINTEF (a Norwegian research institute which developed industry standard benchmarks for solvent degradation testing) to perform a comprehensive thermal and oxidative degradation testing of Sustenol™. In parallel, Susteon has contracted with an independent third-party to perform an environmental health and safety (EHS) certification using their standard protocols which were used for competing CO_2 capture solvents.

Additionally, Susteon is currently building a continuous 40 kg CO_2/day solvent capture unit which should be operational in February 2025 and will use this unit to perform 1,000 hours of continuous testing with the Sustenol™ solvent with a simulated NGCC flue gas. During this testing, in addition to measuring CO_2 capture performance and regeneration heat duty, Susteon will also measure solvent emissions as well as effect of trace contaminants in the flue gas. Following this testing, the Sustenol™ solvent will be tested at the National Carbon Capture Center (NCCC) using their Pilot Solvent Test Unit (PSTU), which captures 5 tonnes of CO_2/day from a slipstream (at 0.5 MWe) from the exhaust of the NGCC power plant for 6 months. This testing will be done to confirm the capture performance of Sustenol™ in real flue gas conditions and observe the emissions and solvent stability profile to de-risk the technology with an actual flue gas at 5 tonne/day scale. Following testing at NCCC, demonstration-scale testing is planned for 4 months at the Technology Centre Mongstad (TCM). This facility is a 100 tonne CO_2/day capture plant with a 10 MW reboiler that will further validate the solvent performance and its stability at scale for commercial deployment.



October 2024: Thermal and oxidative degradation and emissions testing at SINTEF.

November 2024: EHS certification by a third-party.

November 2024: Testing in 5 tonne CO_2 /day pilot plant by third-party.

February 2025: Bench-pilot of 40 kg CO_2/day capacity operational at Susteon for parametric and long-term testing. Effect of NOx and SOx investigation.

May 2025: 1,000 hours of continuous testing completed in Susteon's bench-pilot.

August 2025: 6-month testing planned at the National Carbon Capture Center (NCCC) with 0.5 MW (5 ton/day of CO_2) with real NGCC flue gas with 10,000 liters of solvent.

Summer 2026: 4-month testing planned at the TCM, Norway

Fig. 9. Technology Advancement Plans for Sustenol™

6. Conclusions

Susteon has developed Sustenol™, a drop-in high performance, water-lean, mixed amine solvent with fast absorption and desorption kinetics for >95% CO_2 capture efficiency for an NGCC flue gas (4% CO_2). The composition of the Sustenol™ solvent is optimized to reduce regeneration energy duty, to increase absorption reaction kinetics, enhance CO_2 absorption capacity and reduce thermal and oxidative degradation through a comprehensive design of experiment testing methodology. This optimization was achieved by conducting extensive testing in a bench-scale absorber column and characterization of physicochemical properties for both rich and lean solvent samples. Results obtained from the 15 kg/day CO_2 bench-scale column were then validated in a 1 tonne/day pilot plant at PDEU. At a low L/G ratio of 0.7, Sustenol™ exhibited >90% CO_2 removal from a simulated NGCC flue gas containing ~4% CO_2. The regeneration heat duty for Sustenol™ in bench-scale tests was ~2.16 GJ/tonne of CO_2, which was 44% lower than 30 wt% MEA. Pilot-scale testing at PDEU validated bench-scale testing results and demonstrated that Sustenol™ can achieve 96% CO_2 capture efficiency at half the L/G ratio than 30 wt% MEA. This PDEU testing also demonstrated a 61% reduction in regeneration energy using Sustenol™ compared to 30 wt% MEA in over 7 hours of continuous testing at >96% CO_2 capture from a simulated NGCC flue gas.

All results obtained from testing at bench and pilot scale were used to develop a comprehensive TEA for Sustenol™. This TEA showed an estimated 42% reduction in capture cost for 97% CO_2 removal from an NGCC flue gas and 37% reduction for 90% removal compared to the cost of capture using 30 wt% MEA. The TEA results demonstrated that CO_2 capture cost can be reduced to below $50/tonne using Sustenol™. Susteon has developed a technology roadmap to bring the cost of CO_2 capture to <$45/tonne for the NGCC flue gas with further advancements in the technology.

Susteon has developed a detailed technology roadmap to de-risk this technology for commercial deployment. These derisking activities include: comprehensive solvent degradation testing, long-term testing in pilot (5 tonne/day) and demonstration scale units (100 tonne/day) with actual NGCC flue gas and engineering design studies to qualify the Sustenol™ solvent as a drop-in solvent.

Acknowledgements

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