Skid-Scale Cryogenic Carbon Capture

Executive Summary

Wyoming Clean Coal Technologies
August 2014

UW Accounting ID: 1100-20352: SES
Project Sponsor: State of Wyoming
CFDA Number: Non-Federal
Project Title: Skid-Scale, Cryogenic Carbon Capture
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Abstract

The Cryogenic Carbon Capture™ (CCC) process is a retrofit, post-combustion technology that desublimates CO_2 in the flue gas, separates the resulting solid from the remaining light gases, pressurizes the solid CO_2, melts the CO_2 and warms the light gas, and completes the CO_2 pressurization with liquid CO_2. This skid-scale CCC system has demonstrated successful carbon capture of 90–99% from simulated (i.e., gas mixtures from gas cylinders), natural gas, coal, and coal/biomass flue gases where the CO_2 content varied from 5 to 18 vol%. The CCC system also obtained particulate and pollutant capture >95% for PM_4 and >98% for higher particulate sizes and SO_2. The CCC process has been successfully demonstrated at a skid-scale and is ready to be scaled up for pilot demonstration.

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Objectives & Methods

Task 1.1 Project Management

Manage the project and to establish and update the overall program status.

The deliverables from this task include progress reports (quarterly and annual), programmatic and technical conference calls and workshops, and to maintain the project scope and schedule.

Task 1.2 Contract

Finalize the details of the project contract.

Task 1.3.1 Heat Exchanger Design

Design and build the heat exchangers used in the process. This design will include trapping condensed moisture from the process and will incorporate the detailed designs for pollutants and solids, the design and construction of the latter two being the subject of other tasks.

The heat exchangers used in the process involve solids, liquids, and gases, and include internal phase changes, which lead to internal temperature profiles with significant curvature. Efficient design requires that temperature profiles through the heat exchangers remain as close to parallel as possible and nearly constant temperature differences, despite their significant curvature. This requires multi-phase systems on both sides of the heat exchanger and a refrigerant that involves blended components.

The deliverable from this task is a design for the multi-phase, multi-component heat exchangers used in this process.

Task 1.3.2 Pollutant Removal

Design and build the pollutant removal systems, which will be integral portions of the heat exchangers, but which must remove condensed-phase pollutants from the system.

Many of the pollutants condense at temperatures higher than those required to remove CO_2. Such condensation represents an advantage to the process in that it is a true multi-pollutant device. The design and operation much account for this behavior, both to remove the pollutants from the system in ways that minimize contamination of CO_2 and to maximize the potential salability or treatability for final disposal of the material.

The deliverables from this task includes detailed design and analysis of the pollutant removal characteristics of CCC.

Task 1.3.3 Refrigeration Cycle Design

Design a multi-component refrigeration cycle that provides efficient cooling capacity for the CCC process.

The phase changes involved in several stages of this process complicate the refrigeration cycle considerably. We are making good progress in developing a refrigeration cycle that deals with this problem. In particular, the use of a multi-component (mixed refrigerant) system allows heat transfer to occur with minimal entropy production and with reasonable effectiveness and small sizes. This task produces both theoretical and experimental development of this refrigeration cycle.

The deliverable from this task is a detailed refrigeration cycle design.

Task 1.3.4 Solids Handling

Design and build the solids handling (primarily dry ice handling) components of the system.

Most industrial gas handling systems avoid forming solids—a process that is integral to Cryogenic Carbon Capture™. Once formed and separated from the gas phase, the solids must be compressed and essentially extruded through heat exchanger tubes as it melts. Alternatively, we may be able to use a liquid that suppresses solid formation, greatly reducing the need for solid removal with a fluid bed, physical separation, or other scheme. This task will investigate these options.

The deliverable from this task is a detailed design for the solids handling and/or freezing point systems.

Task 1.3.5 Balance of Process Design

Design the balance of the process, most of which can be borrowed almost directly from current industrial practice.

Critical steps (e.g., drying residual moisture from the flue gas, piping and structural materials, insulation, particle–gas separation, diagnostics and controls, and similar items) do not differ greatly in this process from other installations in the gas processing industry. These processes will be designed and incorporated into our process under this task.

The deliverable from this task is the balance of process design details required to complete the integrated system.

Task 1.4 Energy Cost Estimates

Refine our process model for the CCC process using accurate and sophisticated algorithms for the transport, thermodynamics, and kinetics of all processes.

Even the most sophisticated commercial process modeling software lacks the tools necessary to model this process. Specifically, solids formation is not possible in many process simulators and is not well integrated into all process elements in those that include it at all. Aspen Plus is among the most capable of the simulators. Development of this technology used Aspen Plus, ProSim, ChemStations, and evaluation versions of several other simulators. None of these process simulation systems is capable of modeling the CCC process gracefully, largely because of the presence of solids. Aspen Plus can produce a reasonable approximation to the process. The results included here are a combination of such Aspen Plus simulations and custom calculations.

The deliverables from this task (and Stage Gate 1) are a refined energy analysis incorporating the advanced design of the skid-scale model.

Task 1.5 Stage Gate 1

Refine the energy analysis to incorporate the advanced design of the skid-scale model.

Task 1.6 Unit Construction and Manufacturing

Manage the construction of the skid-scale system.

The deliverables are completed unit operations devices prepared for integration into the process, as described in Task 1.3.

Task 1.7 Inspections and Testing

Integrate the unit operations constructed and to perform detailed functional testing.

The deliverable is an integrated series of unit operations with associated controls and diagnostics.

Task 1.8 Stage Gate 2

Documentation of a fully functional desublimating heat exchanger with 90% CO_2 capture.

Task 1.9 Validation and Verification of Unit Operations System and Model

Verify and validate both the mechanical system and the model. In this context, verification involves demonstrating that the physical components or model performs according to expectations or specifications. Validation involves demonstrating that the model or system as a whole accomplished the desired outcome.

These systems will first be validated using the combustion facilities locally available. The system will then be transported to Laramie, WY to validated in WRI's Combustion Test Facility under both coal-fired and coal/biomass co-fired conditions.

The deliverables from this task include detailed operational data that include at least the following: CO_2 and traditional capture efficiency as a function of temperature, operational results of each of the unit operations, materials and process information from operation at CCC conditions, and demonstrated performance including at least three types of coal and three operating conditions.

Results

Task 1.3.1 Heat Exchanger Design

SES has designed, developed, and patented several desublimating heat exchangers. The bubbling direct-contact heat exchanger is the most-developed design to date. CO_2 capture effectiveness above 99% has been shown in the bubbling desublimating heat exchanger built for this project (Figure 1). This heat exchanger works by bubbling pre-cooled flue gas through a colder cryogenic liquid. Cold liquid both cools the flue gas while also providing a mobile surface on which CO_2 can desublimate. Solid CO_2 is carried out of the heat exchanger by entrainment in the liquid.

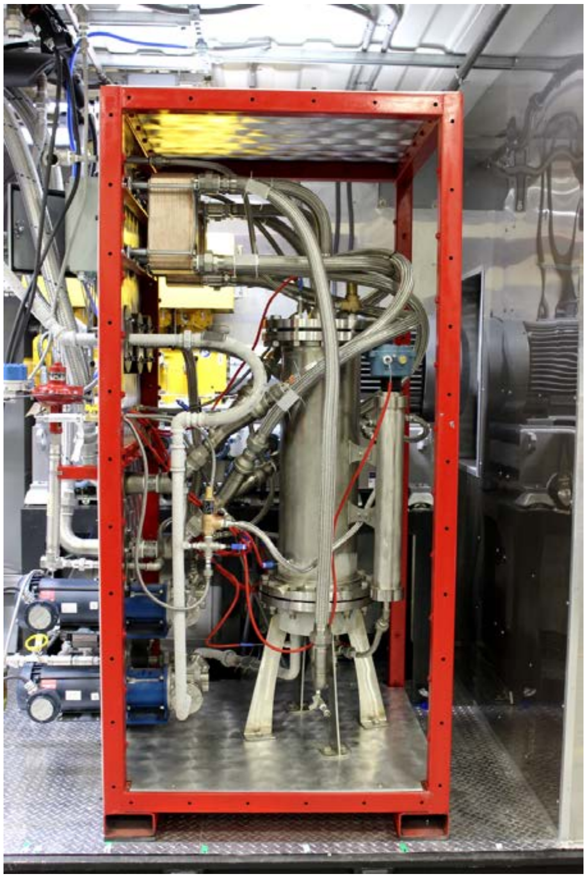

Figure 1. Completed single-stage desublimating heat exchanger inside the cold box frame. The loose-fill insulation and retaining walls were removed for this picture.

Task 1.3.2 Pollutant Removal

SES has further developed its in-house process model throughout this project. Detailed process models of CCC show that most major pollutants can be easily removed from flue gas streams. Throughout the process of cooling flue gas, every major pollutant—with the exception of CO and NO—condense out of the gas, making separation trivial. SO_2 capture tests (Figure 2) demonstrated that > 98% is captured using the CCC process.

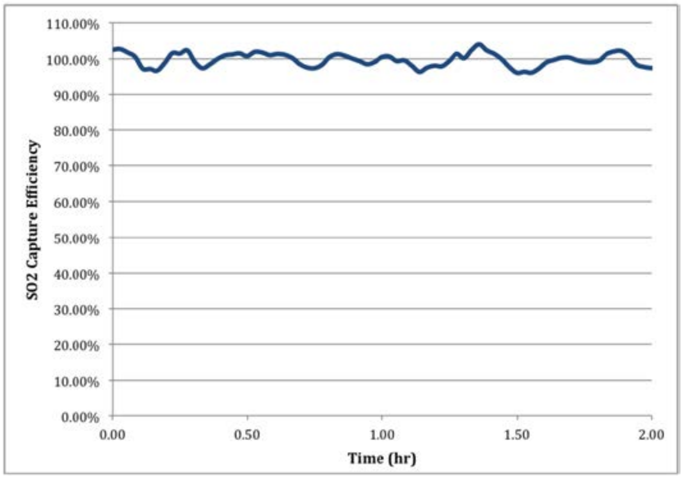

Figure 2. Experimental SO_2 capture results. The incoming gas stream had an SO_2 concentration of 450 ppm. After passing through the desublimating heat exchanger, the clean gas SO_2 concentration was too low to accurately measure, resulting in a perceived capture efficiency above 100% at times. The weighted average capture was 99.8%.

As part of the CCC process, flue gas is bubbled first through water and then through a cryogenic liquid. This contact between the gas and liquid streams captures particulates out of the gas stream. Figure 3 shows the capture of particulates, grouped into different particle sizes.

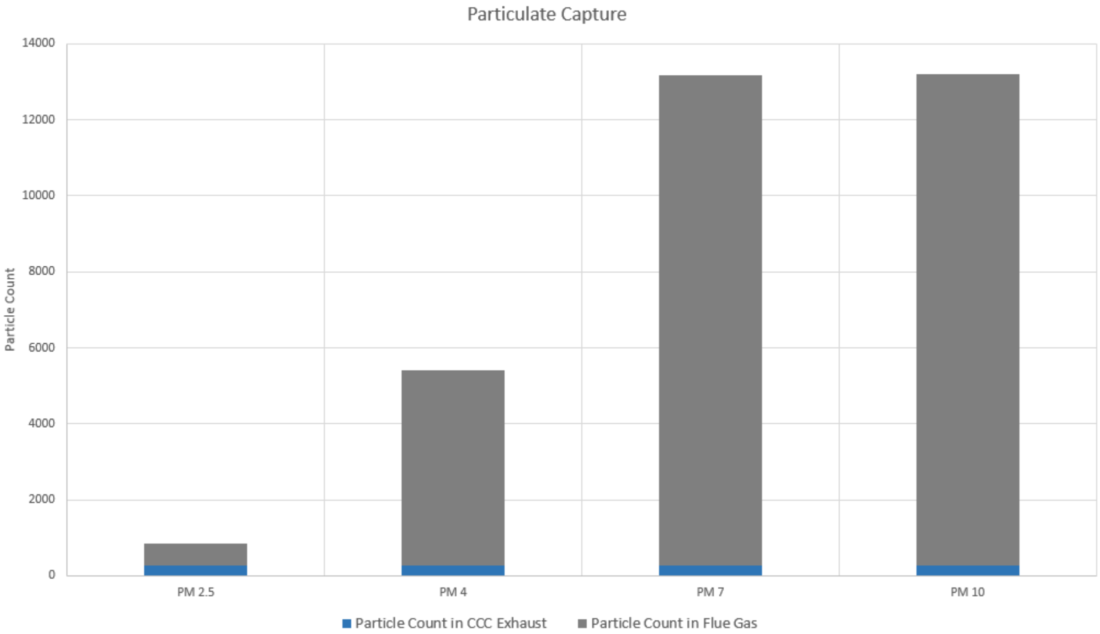

Figure 3. Experimental particulate capture results. Dramatic reductions in $PM_{2.5}$ through PM_{10} are achieved with CCC.

Task 1.3.3 Refrigeration Cycle Design

CCC requires refrigeration down to temperatures as low as –145 °C. Operating fluids for temperatures this low are very limited. Two commercially available Stirling Cryogenics SPC-4 cryogenerators (Figure 4) were selected to cool the contact liquid in the skid-scale system. This option is economical, robust, and easily integrated into the skid system and avoids the very high cost of designing and building a custom refrigeration cycle at this scale. However, these systems do not as effectively recover the cooling capacity of the returning stream and, therefore, they are not as efficient as a custom-built traditional system.

Figure 4. Stirling SPC-4 cryogenerator used to provide all lower-temperature cooling in the ECL skid.

SES and contractor L.A. Roser have designed a refrigeration cycle to leverage the latent heat of CO_2 melting to improve the CCC cycle efficiency. R-14 (carbon tetraflouride) is the working fluid, condensing at −50 °C against the melting CO_2, greatly reducing the required compressor pressure ratio compared with condensing at ambient temperatures. Detailed designs of a small-scale R-14 loop have been completed by refrigeration experts at L.A. Roser (funded under this project), and construction of the skid-mounted demonstration has begun (under ARPA-E funding). A successful demonstration of the R-14 refrigeration loop will dramatically improve the demonstrated efficiency of the CCC process.

Task 1.3.4 Solids Handling

The bubbling desublimating heat exchanger generates a slurry of solid CO_2 and contact liquid. This slurry is easily pumped and pressurized much like a pure liquid. The skid-scale system boosts the slurry pressure to 10 bar in preparation for melting.

CO_2 must be separated from the contacting liquid before it is exhausted from the CCC process. To accomplish this on the skid-scale system, a custom auger filter was designed and fabricated (Figure 5). At the end of the auger screw, a slug of dense CO_2 solid is extruded into a melting chamber attached directly to the end of the auger body. Warm liquid CO_2 is sprayed into the chamber to melt the incoming solid CO_2, thus completing solids handling.

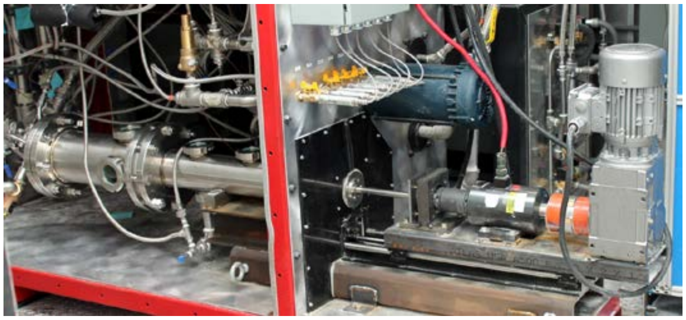

Figure 5. Completed auger filter assembly in the skid-scale system.

Figure 6. CO_2 *solid is extruded from the auger filter during testing.*

Figure 7. Solid CO_2 *captured and separated during testing of the skid-scale system.*

Task 1.3.5 Balance of Process Design

SES used industry best practices and high quality off-the-shelf components where possible to complete the balance of the process design. Safety always takes top priority at SES. This project required transporting the ECL skid to various flue gas sources. To simplify transportation, the system was designed to fit inside 3 half-sized high cube shipping containers. Two of the containers hold all the CCC process equipment. The other container holds a water chiller and air compressor, used for running the ECL skid in the SES lab or in the case that a host site does not have a cooling water and compressed air supply.

Figure 8. The coldbox container holds all 3 coldboxes and the cryogenerators. Hoses and cables connect the two containers.

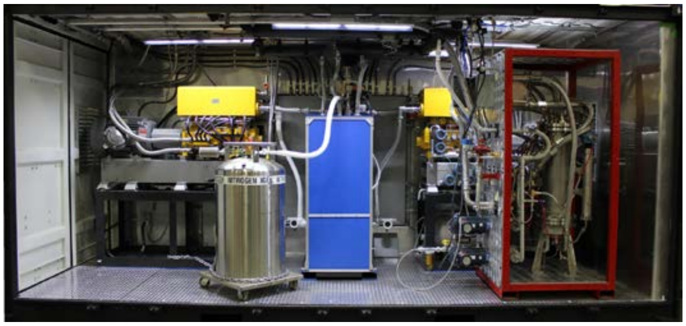

Figure 9. Inside the coldbox container during testing. The two cryogenerators can be seen in the back (yellow) with the nitrogen liquefaction coldbox (blue) between them. The desublimating heat exchanger and flue gas recuperators are in the coldbox on the right.

Figure 10. The pre-treatment container holds the flue gas pre-cooler, blower, and drier in the left half. The right half is dedicated to electrical control cabinets. Two large variable frequency drives can be seen on the right which drive the 60 horsepower cryogenerators.

Task 1.4 Energy Cost Estimates (Stage Gate 1)

The in-house model developed for the CCC process overcomes shortcomings in commercial simulators, of which the most significant is the lack of support for solids formation and destruction in heat exchangers and other process equipment other than reactors. This updated process software provides detailed analysis and design bases for the ECL process. All assumptions for the CCC simulations match NETL reports [1,2] as closely as possible to provide a one-to-one comparison between CCC and current state-of-the-art technologies reported by NETL. Based on these numbers, the energy penalty for amine capture and oxyfuel combustion are 1.407 GJ/tonne and 1.153 GJ/tonne, respectively, an increase of 77% and 45% over the non-integrated CCC ECL simulation.

Task 1.6 Unit Construction and Manufacturing

Most of the skid-scale equipment was either designed and fabricated, or purchased and customized in-house. The machine shop at SES was capable of manufacturing the majority of the custom parts, with some metal fabrication and labor-intensive precision machining contracted out to local shops. High-voltage electrical work was installed by professional electricians.

Task 1.7 Inspections and Testing

Testing of the skid-scale system at the SES shop was conducted by recirculating a simulated flue gas. The desublimating heat exchanger captures CO_2 and delivers a nitrogen stream with a low CO_2 concentration. Before re-entering the front of the process, CO_2 is injected at any desired concentration. This setup allowed for continuous testing in the lab at minimal cost.

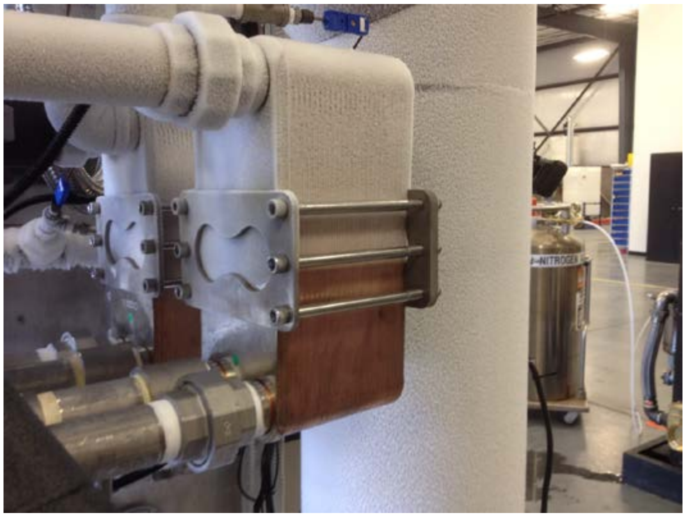

Figure 11. Gas recuperating heat exchangers being tested without insulation. The frost pattern on the exterior clearly shows the temperature gradient from warm (bottom) to cold (top).

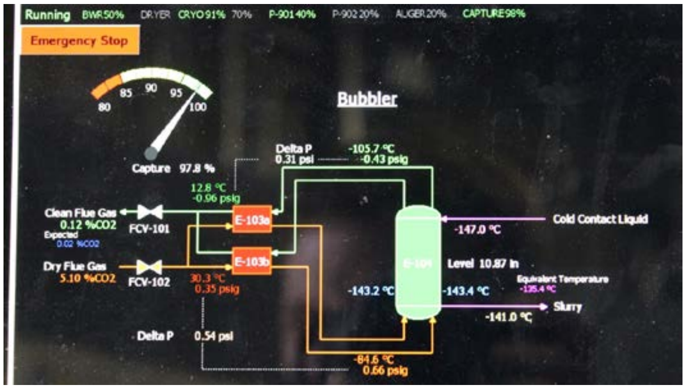

Figure 12. Touch-screen user interface showing real-time CO_2 capture rate and various process parameters.

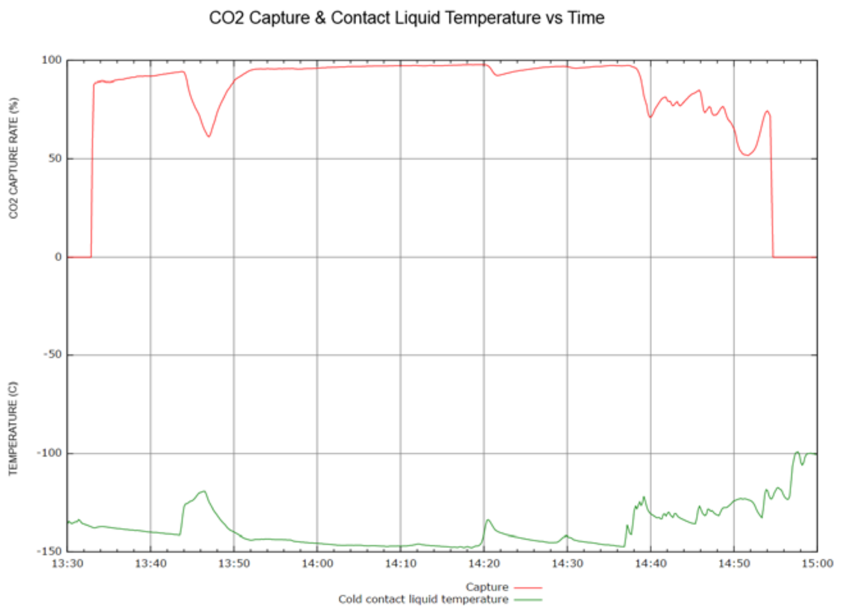

Figure 13. Plot of experimental data showing the correlation between contact liquid temperature entering the bubbler and CO_2 *capture rate. Rises in contact liquid temperature correspond to drops in capture efficiency.*

The energy storage capabilities of CCC depend in part on it transient behavior. The transient behavior of the skid during shakedown provides valuable information on the heat exchanger response times and other dynamic aspects of the system. These dynamics appear in Figure 14. This figure illustrates capture efficiency (left ordinate) and inlet flue gas CO_2 composition (right ordinate) as a function of time (abscissa). As indicated, the system responds to varying amounts of inlet CO_2 from near zero to nearly 18% within about 2 minutes, sometimes less. The capture system is also demonstrably robust to widely and rapidly varying inlet flue gas conditions. The full energy storage operation depends also on the transient response of the refrigeration system. This cannot be demonstrated until natural-gas-based refrigeration system is installed, which is not part of this project. Nevertheless, these data suggest that the system response time will be very rapid and that the system is robust to the inevitable process variations in commercial power generation systems.

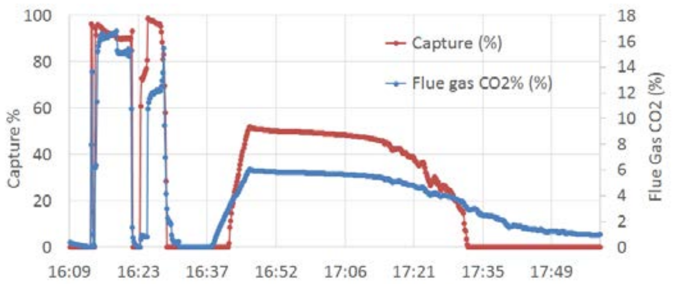

Figure 14. Capture efficiency (left ordinate) and inlet flue gas CO_2 composition (right ordinate) as a function of time (abscissa).

Task 1.8 Stage Gate 2

A heat exchanger demonstrating CO_2 capture above 90% was completed early in the project and improved upon throughout the remainder. CO_2 capture above 99% was demonstrated using flue gas from coal combustion. Figure 15 shows capture data above 90% from a fuel mixture of biomass and coal.

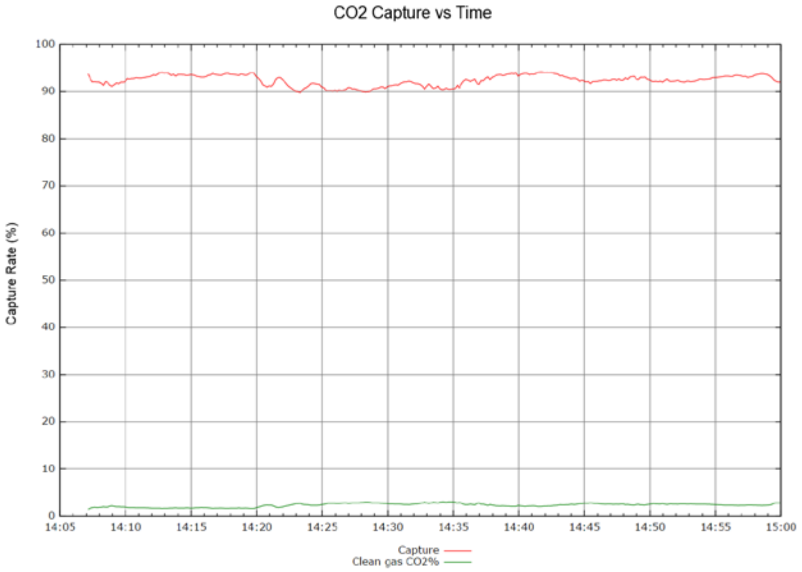

Figure 15. CO_2 capture rate versus time. Flue gas was from a 90% coal, 10% biomass fuel mixture.

Task 1.9 Validation and Verification of Unit Operations System and Model

Testing of the CCC system included both simulated and combustion flue gases. For the entire range of flue gas compositions, the CCC system successfully captured CO_2 at 90–99% and at outlet CO_2 concentrations less than 3 vol%, and many runs less than 1 vol% (Figure 16–Figure 18). The capture from the CCC process closely follows the predicted trends (Figure 19). The experimental capture is slightly lower than theory predicts due to expected, small, normal process inefficiencies.

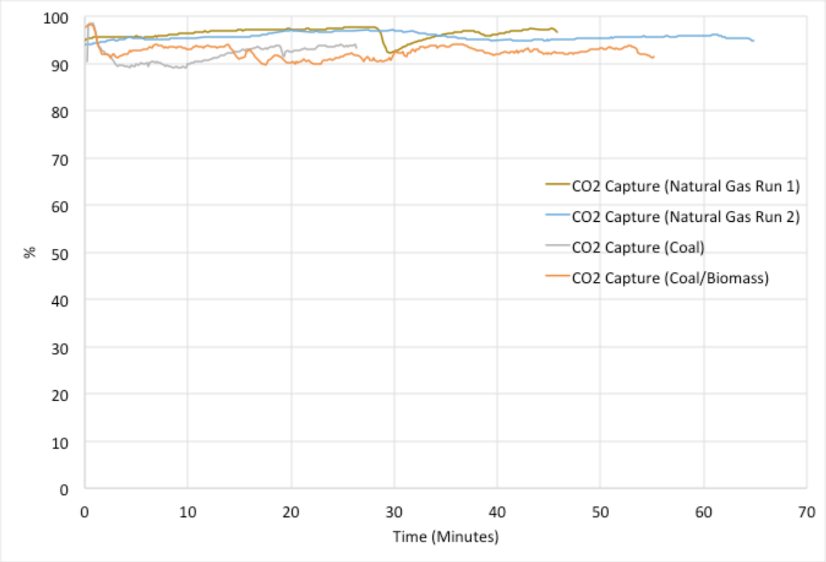

Figure 16. CO_2 capture from tests using natural gas, coal, or coal/biomass mixture.

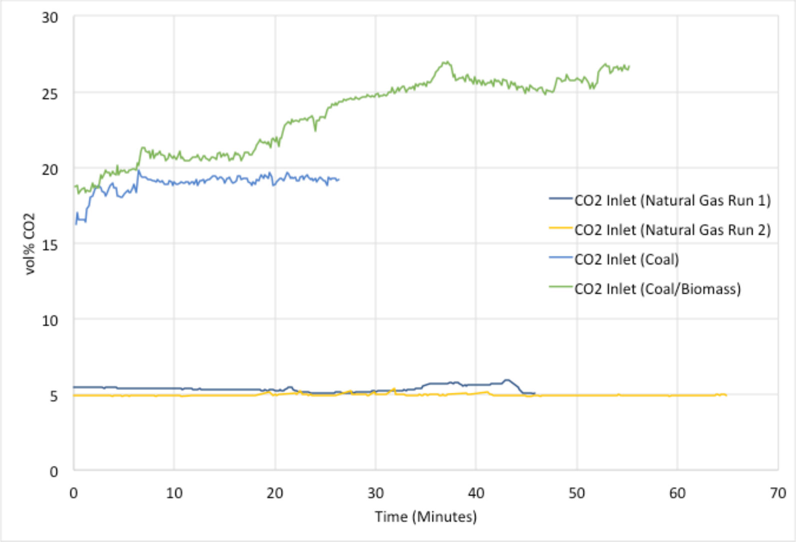

Figure 17. CO_2 concentration in the flue gas entering the CCC process from tests using natural gas, coal, or coal/biomass mixture.

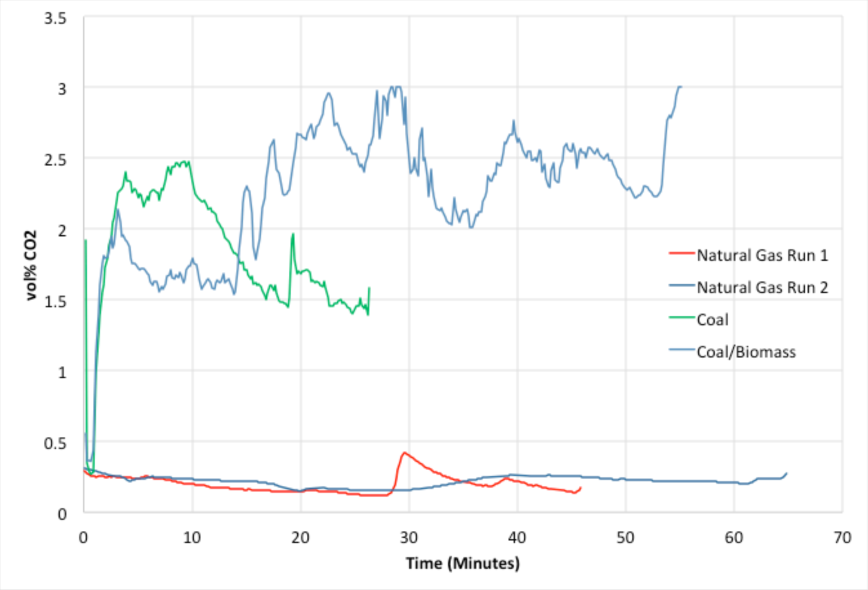

Figure 18. CO_2 outlet concentration exiting the CCC process from tests using natural gas, coal, or coal/biomass mixture.

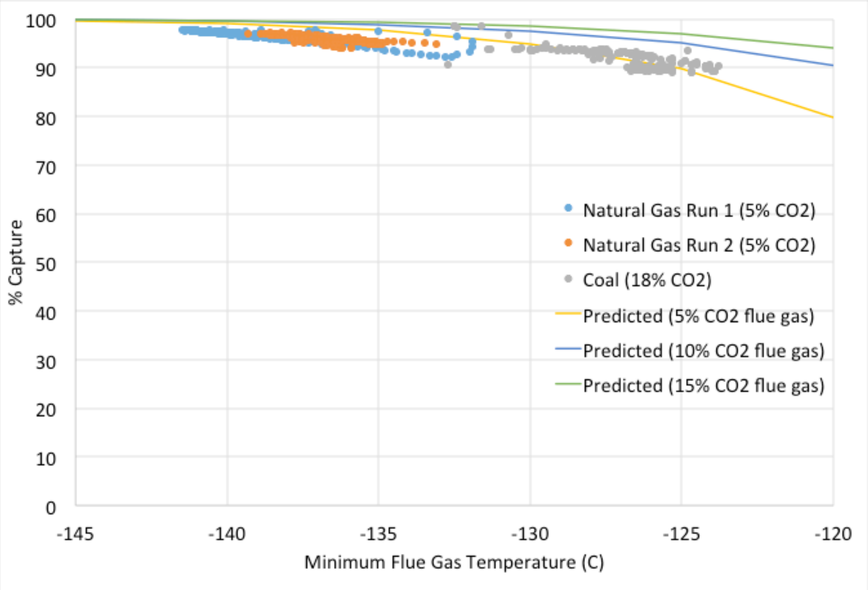

Figure 19. Theoretical predictions and experimental data showing CO_2 capture as a function of temperature.

The overall performance of the skid-scale CCC system clearly demonstrates that it is a robust process that can successfully capture CO_2 from a variety of flue gas compositions. Testing performed at the burner flow reactor (BFR) at BYU included processing flue gas from natural gas, Black Thunder coal, and a 90/10 wt% mixture of Black Thunder coal and fine hardwood sawdust. Unit operations and full-system testing, described in their respective sections, have provided fundamental insight into how the individual unit operations interact in the full system, which we will integrate as we scale up to a pilot demonstration.

Conclusions and Recommendations

The skid-scale ECL version of CCC process design, construction, and operation operated successfully on natural gas, coal, and biomass and blends of these fuels over a broad range of CO_2 contents (4–18%). The design involved three half-length (20 foot) high-cube containers, one housing the utilities, a second housing the gas conditioning and many of the controls, and the final housing the cold boxes and most of the CCC process proper. The construction included modular subsystems that can be mounted inside the three containers. Brigham Young University hosted the demonstration at their burner flow reactor facility during which natural gas, coal, and biomass provided flue gas. The vitiated flow included the pollutants and particulate typical of commercial power systems.

Most of the skid system design operates robustly, including the coolers, traditional heat exchangers, desublimating heat exchangers, controls and data acquisition, blower, dryer, and gas conditioning. The solids–liquids separation subsystem proved more difficult, which may be primarily because of our lack of experience operating it at this scale. We anticipate further refining this system during development of the energy storage subsystem and the larger scale versions of the process.

The computer models of the capture system provided accurate but slightly optimistic estimates of the capture efficiencies. The measured capture efficiencies generally were well above 90% during steady operation, but they were typically 1–2% less than the model predictions. The models assume equilibrium stage behavior in the heat exchangers, and we attribute the difference to the heat exchangers not quite reaching equilibrium.

Pollutant capture during operation included SO_x and particulate matter. Gaseous pollutant capture has been measured at all previous stages, and the skid operation proved similar to the early experience, which is that SO_x capture generally greatly exceeds CO_2 capture. The skid runs provided our first measured particulate capture results, which include over 98% capture of all particulates down to $PM_{2.5}$. Fume particles, particles less than 1 micron, were not as effectively captured, though the data suggest these measurements may be suspect.

On balance, the skid demonstrated both effective CO_2 capture and the ability to analyze the system accurately based on the in-house computer simulations. The latter will provide important scaling tools for larger-scale versions of the process.

We will resolve some residual issues with the skid operation in the earliest portion of the energy storage demonstrations. These include more robust demonstration of the transient behavior of the system, demonstration of the natural-gas-based coolant loop, improved solid–liquid separation robustness, improved particulate removal characterization, and increased operational experience and knowledge. Most of these are outside the scope of this project but in the scope of the eventual commercialization of this process.

The primary recommendation is that the CCC process commercialization continue to pilot and eventual commercial scale. The ECL version of the CCC process has overwhelming advantages compared to other processes in the areas of energy efficiency, economics, energy storage, additional pollutant capture, water conservation, and compatibility with the equipment and workforces at existing plants. More specific recommendation are to continue to optimize the solids–liquids separation process, improve the contacting efficiencies of the desublimating heat exchangers, and decrease the overall flue gas pressure drop in the process.

References

[1] US Department of Energy, N.E.T.L., Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity. Revision 2, November 2010.

[2] US Department of Energy, N.E.T.L., Pulverized Coal Oxycombustion Power Plants Volume 1: Bituminous Coal to Electricity Final Report. Revision 2, August 2008.