SUBTASK 6.1 – STRATEGIC STUDIES

Final Report

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SUBTASK 6.1 – STRATEGIC STUDIES

ABSTRACT

The Energy & Environmental Research Center (EERC) has recently completed 7 years of research through the Cooperative Agreement with the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) focused on fossil energy technology development and demonstration. To support a significant number of the different activities being considered within all of our research contracts with NETL, a subtask (6.1 – Strategic Studies) was created to focus on small research efforts that came up throughout the year that would support an existing EERC–NETL project or would help to develop a new concept for inclusion in future efforts.

This subtask was funded through the EERC–DOE Joint Program on Research and Development for Fossil Energy-Related Resources Cooperative Agreement No. DE-FC26-08NT43291.

TABLE OF CONTENTS

Continued…

TABLE OF CONTENTS (continued)

SUBTASK 6.1 – STRATEGIC STUDIES

EXECUTIVE SUMMARY

The Energy & Environmental Research Center (EERC) has recently completed 7 years of research through the Cooperative Agreement with the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) focused on fossil energy technology development and demonstration. The goal of the Strategic Studies subtask (Subtask 6.1) was to provide support for small, focused efforts that address some of the most pressing needs faced by fossil energy. The wide range of topics addressed by Subtask 6.1 reflect of the dynamic nature of the fossil energy industry. Since the inception of Subtask 6.1, the energy picture in the United States has changed dramatically. Coal use for electrical generation has decreased from 48.3% in 2008 to 38.9% in 2014.[1] The bulk of this new demand has been offset by an increase in the use of natural gas for electrical generation which has increased from 21.5% to 27.5% in the same time period, with a peak in 2012 of 30.4%, while coal was 37.5%. Over the same time frame, domestic oil production has grown from approximately 5 MMbbl/day in 2008 to 9 MMbbl/day in 2014. The mounting environmental pressures that coal is facing, including significant pressure to address climate change concerns, combined with the technology-based increases in domestic oil and gas production are the primary drivers for these dramatic shifts in the energy picture in the United States and world. DOE has been a key partner in the development of the technologies that are changing the energy picture, and the EERC's strong partnership with DOE over three decades has been based on a firm foundation of practical applied research that enjoys the support and partnership of industry, resulting in rapid and efficient deployment of new technologies.

To support a significant number of the different activities being considered within all of our research contracts with NETL, a subtask (6.1 – Strategic Studies) was created to focus on small research efforts that came up throughout the year which would support an existing EERC–NETL project or would help to develop a new concept for potential inclusion in future efforts. The Strategic Studies topics that were investigated herein focused on the development of small amounts of key data and information that will attract the interest of the fossil energy research and industrial community.

This subtask conducted two activities, Activity 1 – Systems Engineering and Activity 2 – Ministudies:

- Activity 1 – Systems Engineering evaluated alternative processes and technologies to determine if research activities were worthy of additional investment. For technologies near commercialization, work involved the optimization of configurations or operating conditions, validation of laboratory and pilot plant data, and scale-up assistance to ensure that appropriate data were obtained and that the product cost and quality met the requirements of industry partners or other users.
- Activity 2 – Ministudies, included performing small paper studies on topics of interest to DOE, particularly emerging concepts and technologies that may affect domestic energy supplies.

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[1] U.S. Energy Information Administration. Short-Term Energy Outlook. www.eia.gov/forecasts/steo/pdf/steo_full.pdf (accessed May 2015).

Over the last 7 years, under Activity 2, 20 ministudies were conducted. These efforts ranged from quick experiments to gain fundamental knowledge to support a current effort, to literature reviews, to a few larger engineering efforts. In the last 4 years, the studies have focused exclusively on carbon capture and storage.

The range of ministudies projects conducted can be classified into three broad categories: Novel Carbon Capture Studies, Novel Carbon Storage Studies, and Preliminary Engineering Studies. The following is a list of the research projects conducted classified as described above:

Novel Carbon Capture Studies

- Development of Novel Material Applications for Improving Performance of Distributed Liquid Production Process – Material Selection and Evaluation
- Synthesis of Hydrocarbon Fuel from Flue Gas CO_2 Using Renewable Energy Sources
- Economic Evaluation of CO_2 Capture Processes Using Aspen Icarus Process Evaluator
- Preliminary Evaluation of Using Supercritical Carbon Dioxide and Waste Organic Acids to Acidify Water for the Production of Simple Sugars from Switchgrass
- CO_2 Capture from Algae – Use as a Fish Food/Dietary Supplement
- Application and Use of Advances in Amines for Natural Gas Sweetening
- Investigation of Vapor-Phase Emissions from Amine-Based CO_2 Capture
- Optimization of Technology Development in the Context of Industrial CO_2 Sources
- Modification of Amine Solvent Stripping Process to Reduce Energy Input of CO_2 Capture
- CO_2 Capture Using Treated Activated Carbon and Electrically Driven Thermal Swing Adsorption (ETSA) Regeneration
- Review and Modeling of Precombustion Capture of CO_2 from Natural Gas-Fired Plants
- Assessment of the Operational Integration of CO_2 Capture at a Coal-Fired Utility

Novel Carbon Storage Studies

- Investigation of North Dakota Clays for Making Ceramic Proppants
- Evaluation of Clay-Based Cenospheres for Use in Hydraulic Fracturing
- Electrical Thermal Swing Adsorption (ETSA) Testing to Enhance CO_2 Flood Efficiency and Natural Gas Liquids (NGLs) Separation
- Measurement of CO_2 Adsorption Isotherms for Clays
- Development of an Analytical Approach to Differentiate Between Different Corrosion and Scale-Forming Mechanisms

Preliminary Engineering Studies

- Evaluation of Electric Vehicles and Other Fossil-Based Technologies as Near-Term Solutions to Reducing Foreign Oil Imports
- Zero-Energy Buildings
- Preliminary Evaluation of Non-Pt Alkaline Methanol Fuel

This subtask was funded through the EERC–DOE Joint Program on Research and Development for Fossil Energy-Related Resources Cooperative Agreement No. DE-FC26-08NT43291.

SUBTASK 6.1 – STRATEGIC STUDIES

INTRODUCTION AND BACKGROUND

The Energy & Environmental Research Center (EERC) has recently completed 7 years of research through the Cooperative Agreement with the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) focused on fossil energy technology development and demonstration. The goal of the Strategic Studies subtask (Subtask 6.1) was to provide support for small, focused efforts that address some of the most pressing needs faced by fossil energy. Summaries of the results of strategic studies activities are as follows:

SUMMARIES OF RESULTS

Activity 1 – Systems Engineering

Period of Performance: June 2008 – August 2010

The objective of this activity was to evaluated alternative processes and technologies to determine if research activities are worthy of additional investment. For technologies near commercialization, work involved the optimization of configurations or operating conditions, validation of laboratory and pilot plant data, and scale-up assistance to ensure that appropriate data were obtained and that the product cost and quality met the requirements of industry partners or other users.

A series of spreadsheet programs were previously developed at the EERC to recursively calculate energy, mass, and elemental balances for gasification and combustion systems. These programs operate on either Lotus or Excel, using an architecture that is adaptable to virtually any fuel or energy process. The user can define input and output streams and characterize their contents based on property correlations for 52 elements or compounds, along with fuels (coal, oil, or gas) and coal ash. Enthalpies are calculated for elements or compounds as a function of temperature based on regression equations derived from the JANAF tables. The correlation developed to calculate the enthalpy of a fuel on a moisture- and ash-free basis provides estimates of heating values that match experimental data better than the Dulong formula. Enthalpies for typical coal ash analyses for bituminous, subbituminous, and lignite coals are calculated based on enthalpies for the major constituents SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO. The relationships between inputs and outputs can be variously determined by fuel and product analyses, chemical equilibrium, or (less often) kinetics. The recursive calculations that are performed to balance elements, mass, and energy use either “Solver” in Excel or a Newton Raphson macro in Lotus. Elemental balances can be performed by changing the amount of any species in any stream containing that element. The energy balance can be performed by changing either amounts or temperatures. The design of a useful spreadsheet for a particular process application depends on making an appropriate choice of the species/streams or temperatures to be changed and the order in which they are changed—which is governed by knowledge and assumptions concerning how the process operates.

The program was used to predict mass and energy balances for oxygen-blown gasification of North Dakota lignite in the most suitable commercial gasifiers, including the dry-ash Lurgi gasifier, the slagging British Gas Lurgi gasifier, the KBR transport gasifier, and the Shell dry-feed entrained-flow gasifier. Calculations for the KBR gasifier included an intermediate-temperature oxygen-blown case, a high-temperature air-blown case, and a low-temperature air-blown case (for high-sodium lignite). In addition, calculations for the oxygen-blown KBR gasifier were performed to estimate the effects of coal moisture and ash on efficiency, gas composition, and oxygen demand.

The program was further used to analyze run data for low-quality Bulgarian lignite (high ash, high moisture, and nonreactive) tested in oxygen-blown mode in the EERC's transport reactor development unit. The important findings of the balance calculations for Bulgarian lignite were that 1) carbon conversion based on gas production was much lower than that based on carbon in ash, indicating that carbon was building up in the reactor during the run period; 2) very low values of both gas heating value and cold-gas efficiency were related to low carbon conversion and heat loss in ash; and 3) the hydrogen content of the product gas was far below that predicted by the water–gas shift equilibrium, suggesting that the gasifier was having to be operated in a partial combustion mode to maintain the temperature of the gasifier. Removal of CO_2 from the product gas was calculated to provide a low yield of gas with an acceptable heating value. The recommendation given to the Bulgarian power industry was to use this low-quality fuel in a circulating fluidized-bed combustor (CFBC); follow-up tests were successfully run under a separate joint venture project in the 400-lb/hr CFBC at the EERC.

Activity 2 – Ministudies

This activity focused on performing small, intense studies on topics of interest to DOE utilizing EERC areas of expertise. These studies focused on technology areas that are not at a stage where they are likely to garner cash investment from commercial sources but do attract commercial interest and potential.

DOE NETL is funding research into next generation CO_2 enhanced oil recovery (EOR) technologies "that can increase recovery from existing CO_2 EOR projects and accelerate application of the process to other mature oil fields around the country. Ideally, these new projects will not only add to the nation's oil supply but also serve as storage locations for captured CO_2 from power plants and industrial processes, reducing CO_2 emissions" (U.S. Department of Energy National Energy Technology Laboratory, 2015).

While the recent (the last 4 years) ministudies dealt with some aspect of carbon capture and storage, earlier studies ranged more broadly and are reported in the "Preliminary Engineering Studies" category.

For each of the following activities, the period of performance and an identifier to the final report is listed in addition to a brief summary of the activities conducted. Depending upon the size and scope of the project, the final reports range from a short write-up within a quarterly report to a separate final report. Since these projects and reports occurred over a period of 7 years, it is noted that the assumptions and conclusions may be dated, and no effort was made to redo any past studies with the most recent information.

Novel Carbon Capture Studies

Activity 2.1 – Development of Novel Material Applications for Improving Performance of Distributed Liquid Production Process – Material Selection and Evaluation

Period of Performance: January–December 2009

Final Report: Appendix A of October–December 2009 Quarterly Report

Author: Nikhil Patel

Brief Summary: Certain natural and anthropogenic materials like activated carbon (AC) and zeolites are known for their unique mass and energy transport characteristics because of their intrinsic molecular structure and active surface areas. The unique properties of such materials can be utilized in developing innovative regenerative-type adsorption–desorption systems. As one of the major applications, this process is aimed at upgrading syngas by removing diluents and improving the H_2 concentration required for improving product yields for liquid fuels and chemicals synthesized based on the Fischer–Tropsch synthesis process. The development of cost-effective materials and processes is critical in establishing economically viable processes at the distributed scale.

The EERC has successfully developed and tested an advanced fixed-bed gasifier capable of utilizing a vast range of feedstocks, including high-moisture coal and biomass, for such applications. This gasifier is the enabling technology in the tightly integrated energy and indirect liquefaction processes. Utilizing a shift reactor to improve H_2 concentration is found to have insignificant impact on improving liquid yield unless the CO_2 produced as reaction by-products is removed, since it is a syngas diluent that also deteriorates synthesis catalyst performance. In order to make a distributed-scale liquid production process economically viable, the development of a low-cost CO_2 removal process becomes imperative. This project aimed at determining a low-cost material that can be used for distributed applications. One such material could be produced in the gasifier itself.

A comparative packed-bed study conducted to understand adsorption–desorption characteristics of new carbon material obtained as a by-product of turkey waste gasification proved the material capable of achieving comparable or better performance than commercial AC, indicating a possible role in the cyclic process. The removal of soluble inorganics improved performance of the turkey litter char. The two zeolites tested were found to have differences in achieving complete breakthrough; however, both materials showed comparatively longer CO_2 desorption time.

The combination of AC and zeolite-packed beds showed the highest peak H_2 concentration and improved CO_2 adsorption in contrast to individual material tests, thus establishing the possibility of combining the materials for improving the performance of the packed bed for biomass-to-liquid/coal-to-liquid applications.

Activity 2.2 – Synthesis of Hydrocarbon Fuel from Flue Gas CO_2 Using Renewable Energy Sources

Period of Performance: January–September 2009

Final Report: Appendix A of the July–September 2009 Quarterly Report

Authors: Ye Zhuang and Denny Laudal

Brief Summary: Increasing energy demand for hydrocarbon fuels is expected to continue because of their importance in the transportation and industrial sector. At the same time, environmental concerns over rising CO_2 concentrations in the atmosphere are driving efforts to reduce anthropogenic emissions of CO_2. The competing requirements of reducing CO_2 emission levels and increasing energy supply will require innovative technical and operational solutions.

In a sustainable carbon economy, energy from renewable energy sources such as wind and solar would be used to synthesize fuel from captured CO_2. When the fuel is consumed, CO_2 is released into the atmosphere. Thus a carbon-neutral cycle is completed. The CO_2-to-fuel reforming represents the storage of these energy sources as chemical energy. These carbon-neutral hydrocarbon fuels can be widely used within existing infrastructures without additional intense capital investment on infrastructure. Other advantages over battery technology or hydrogen include higher-energy density.

The capital investment for a methanol plant using CO_2 and H_2 is estimated to be the same as that of a conventional syngas-based plant, while the key factors are the availability of CO_2 and H_2. Capture and concentrated CO_2 with minimum energy input is a prerequisite for a CO_2-to-fuel process. The current amine process is energy-intensive, causes corrosion, and degrades over time. Development of a more efficient renewable CO_2 sorbent is needed. For example, polyethylenimine supported on nanostructure silica and other metal-organic frameworks have been found to have high CO_2 capacity; however, further improvements are necessary to reduce the cost for further scale-up.

Hydrogen production is another key component in chemical recycling of CO_2. Electrolysis is also energy-intensive. So far the best energy efficiency for hydrogen production using electrolysis is around 73%, and additional research and development efforts are needed to improve net efficiency. The cost of electricity would dictate the overall economics and will be the major driving factor for producing hydrogen.

Current studies have focused on reforming atmospheric CO_2 directly or concentrating atmospheric CO_2 and then reforming. Either case will suffer a low yield or additional energy penalty, respectively. Weimer et al. (1996) estimated that a total of 430 kJ is needed to produce 1 mole of methanol from atmospheric CO_2, resulting in an overall 44% system efficiency using the lower heating value. Meanwhile, not many studies have been done to see if it is feasible to use coal flue gas or biogas directly without additional concentration.

Activity 2.3 – Economic Evaluation of CO_2 Capture Processes Using Aspen Icarus Process Evaluator®

Period of Performance: April–September 2009

Final Report: Appendix B of the July–September 2009 Quarterly Report

Author: Greg Dvorak

Brief Summary: Development of economically feasible carbon capture technologies presents one of the biggest challenges to the fossil energy industry in the 21st century. Many existing technologies are capable of capturing carbon from coal-fired power plants, but most come at a high cost and high-energy penalty. Development and evaluation of new technologies is a critical step toward economical carbon capture. Software models developed by AspenTech are excellent tools for evaluating technologies from a technical and economic perspective. Aspen Plus® is used to develop carbon capture process flow models, including detailed mass and energy balances around the entire power generation system. The information developed is then exported to an Aspen Process Economic Analyzer (APEA) to size the equipment and determine the cost to run and build the system. The APEA software allows modelers to quickly generate equipment sizes and designs and calculate estimated capital and operating costs and allows for rapid evaluation of process alternatives to compare profitability.

As part of this subtask, APEA software was acquired from AspenTech. The final report details the results of two modeling runs generated with APEA. The first run evaluates the cost of specific equipment pieces for an oxygen-fired retrofit to a 500-MW coal-fired power plant. The second run evaluates the cost of a pilot-scale amine-based CO_2 capture system and compares the cost to actual expenses incurred during the construction of the system.

APEA is a good tool for sizing and evaluating the cost of CO_2 capture systems. The tool is more suited to developing cost comparisons as opposed to absolute cost estimates. AspenTech provides additional tools at additional cost, such as the Aspen Capital Cost Estimator, for determining detailed construction costs. Built-in tools allow the system to easily model compressors and calculate capital and operating costs. Absorber–stripper models that are developed in Aspen Plus are very easy to export to APEA for estimating capital costs, operating costs, utility consumption, raw material costs, and product costs.

Activity 2.6 – Preliminary Evaluation of Using Supercritical Carbon Dioxide and Waste Organic Acids to Acidify Water for the Production of Simple Sugars from Switchgrass

Period of Performance: October 2009 – September 2010

Final Report: Appendix A of July–September 2010 Quarterly Report

Author: Steve Hawthorne

Brief Summary: The purpose of the project was to evaluate the potential for using hot water that has been acidified by pressurization with supercritical carbon dioxide as a replacement for added sulfuric acid to aid in the processing of cellulose sources to produce valuable products such as simple sugars. A range of reaction temperatures with water acidified with carbon dioxide at 4000 psi was investigated using a specially constructed laboratory reactor system for exposing samples. This system was designed to allow periodic collection of water extracts so that the effect of sequential changes in temperature (or pressure) can be determined with a single cell loading. Discussions were held to identify suitable substrates for initial testing, and it was determined that a cellulosic feedstock produced from municipal solid waste by Tempico, Inc., would be a better model sample for the initial tests rather than switchgrass. This product consists of very small, dry, compacted fibers from Tempico's process conducted with steam in a rotary pressure cooker. The material has low crystallinity and is the same as that used in recent tests by Gennencor that demonstrated high conversion to glucose in a fungal enzyme process. Use of this material thus enables a direct comparison of process efficiencies for a particular cellulosic waste by-product.

Acidification of hot water at 250°C by pressurizing with carbon dioxide at 4000 psi did not significantly affect the production of glucose and related products from pure cellulose, municipal waste-derived cellulose, and previously untreated hardwood shavings, but the same conditions show promise to replace sulfuric acid pretreatment of cellulosic (e.g., wood) lignin. However, further studies on enzyme hydrolysis of the residual cellulose would be needed to evaluate this approach.

Activity 2.8 – CO_2 Capture from Algae – Use as a Fish Food/Dietary Supplement

Period of Performance: July–September 2010

Final Report: Appendix B of July–September 2010 Quarterly Report

Author: Nicholas Ralston

Brief Summary: Power plants and certain CO_2-producing industries may soon be forced to reduce their emissions. One option being explored is algae-based carbon capture technology. In addition to carbon capture, two benefits of this technology are that the oil produced in algae can be processed into a renewable fuel and the remaining components of the algae can be used to make other products. While oil production from algae has not proven to be cost-efficient, culturing high-value algae products would offset the capital and operating costs of the process and could provide a positive cash flow to early adopters of CO_2-to-algae technologies.

The use of CO_2 to support growth of algae that produce omega-3 fatty acids appears to be an attractive alternative for a number of reasons. Considering the need for novel CO_2 capture technologies and that certain strains of algae are known to produce high-value forms of omega-3 fatty acids, we expect that economically important fish meal supplements could be produced from algae, thereby offering industries that utilize algae for CO_2 capture the opportunity to develop a potentially profitable product for their efforts. The economic value of these health-promoting fatty acids may provide a better product than algae utilized for biofuels. The possibility of using algae to produce omega-3 fatty acids for fish meal could also expand to other animal feedstocks as well as human supplements (algae use for production of omega-3 supplements already exists to some extent). We also expect that the algae biomass may be manipulated and utilized for its nutritive value.

Activity 2.9 – Application and Use of Advances in Amines for Natural Gas Sweetening

Period of Performance: January–March 2011

Final Report: Appendix A of the January–March 2011 Quarterly Report

Author: Denny Laudal

Brief Summary: Costs required to remove CO_2 from fossil-fueled power plants vary widely, but controlling CO_2 will be expensive. Research at the EERC is focused on reducing the costs/ton for CO_2 control. A commonly used CO_2 separation process involves amine absorption. In brief, flue gas streams and natural gas streams are contacted with an amine solution, and the CO_2 in these streams becomes bound to the amine groups in the solution. Consequently, the CO_2 content in the resulting gas stream is significantly reduced. Amine absorption is an effective technique to remove CO_2; however, this technique has notable flaws and inefficiencies. First, once the amine solution is saturated, the process to reactivate the solution (i.e., remove the bound CO_2 from the amine groups in the solution) for reuse requires a high amount of energy. Second, this process has a tendency to corrode equipment. Third, over a short period of time, the amine solution loses viability through amine degradation and loss.

Three advanced solvents were tested and compared with the baseline case of 30 wt% solution of monoethanolamine (MEA) for CO_2 capture. All tests used subbituminous coal for combustion in the identical pulverized coal boiler. The system reached at least 90% CO_2 capture for all solvents tested. Data from the advanced solvents and MEA tests conducted show that for similar test conditions, MEA required about 10%–40% more regeneration energy input to achieve 90% CO_2 capture than the advanced amine-based solvents ranging from the lowest heat input, ~1475 Btu/lb CO_2, to ~1600 Btu/lb CO_2. The regeneration energy required for MEA is 1934 Btu per lb of CO_2. The MEA base case required a 30%–50% higher solvent flow to attain 90% CO_2 capture for a given amount of treated flue gas compared to one advanced amine, indicating use for a large-scale process could lead to significant economic benefits over MEA. Conversely, tests on advanced amine showed a solvent usage about 135% higher than MEA to reach 90% capture. Solvent samples from each test run were analyzed for corrosion and degradation product concentrations. MEA had the highest amounts of sulfate and thiosulfate; all advanced amines had less of these salts. The main organic salts found in the samples were formate, acetate, and oxalate, which are oxidative degradation products of amine-based solvents. Organic ion concentration was higher in MEA samples than advanced amines, some of which did not indicate any organic ions present. The extent of corrosion of process equipment was also monitored during testing by analyzing the samples for trace metals. Results indicate that one advanced solvent solution had the highest amounts of corrosion products, particularly Cr, Ni, and Fe, with concentrations in the 3 to 35 ppm range. However, in another advanced solution, the amount of all five trace metals analyzed was below 5 ppm. Overall, corrosion product concentrations were very low; long-term testing is needed to make firm conclusions on specific solvent corrosion rates (Pavlish et al., 2010).

Based on the literature reviewed, results from combustion pilot testing, and simulation models, the following conclusions can be made regarding the use of advanced amines and process changes for natural gas sweetening (Ebenezer, 2005):

- The loading capacity of the amine solvent can be increased to increase acid gas (CO_2) loading in the solvent.

- Since the CO_2 emission and amine chemical loss is directly proportional to the amine circulation rate, advanced amines can be used to lower the lean amine circulation rate while allowing amine circulation at lower temperatures to minimize the solvent evaporation rate and increase the loading capacity.

- The absorber should be operated at high pressure and low temperature to enhance amine loading capacity, therefore minimizing CO_2 emissions and chemical loss.

- The amine solvent residence time in the stripper should be minimized to reduce its degradation tendency.

- The stripper operating pressure should be near or at atmospheric pressure, while the reboiler temperature should be within the solvent stability conditions.

Use of advanced amines in gas-sweetening applications can be retrofit to reduce costs ($/lb CO_2 captured) required to control acid gases. Increasing the capacity of natural gas (sweetening) treatment plants will require an increase in solvent circulation, fired energy duty, and cooling proportional to the total increase in the feed gas CO_2 partial pressure. Process plant modifications required to accommodate these changes may be significant. Conversion to advanced amines may be the least expensive option, especially when equipment modification or shutdown of equipment is required (Pavlish et al., 2010).

Activity 2.11 – Investigation of Vapor-Phase Emissions from Amine-Based CO_2 Capture

Period of Performance: March–September 2012

Final Report: Appendix B of July–September 2012 Quarterly Report

Author: Steven Schlasner

Brief Summary: A literature and patent review (LPR) was performed to investigate the hazards of vapor-phase emissions from amine-based CO_2 capture technologies. These hazards are a function not only of the amine emitted and its concentration but also degradation products formed and their concentrations as well as the transport of these compounds in the environment (products form from degradation reactions of the amine within the capture process before release and in the environment after release). The LPR identified only a single, comprehensive investigation of these factors; the investigation was performed as part of a program that was underwritten by the Norwegian government and two petroleum companies to provide input to an environmental impact assessment associated with construction of a 1-million-tonne/year carbon dioxide capture facility in Norway's Mongstad industrial center. While the program initially investigated the behavior of four amine solvents and four classes of degradation products (i.e., aldehydes, amides, nitramines, and nitrosamines), as it progressed, focus was narrowed to only the three solvents that had been selected for pilot-scale testing (ammonia, methyldiethanolamine [MDEA], and a proprietary solvent by Aker Solutions) and to the two most hazardous classes of degradation products (i.e., nitramine and nitrosamine). For purposes of preparing a worst-case assessment, the program further narrowed focus by representing hazardous products by their most carcinogenic member, N-nitrosodimethylamine. The conclusion of the worst-case study was that hazardous emissions in the Mongstad scenario would be factors of 20 and 2 less than guidelines for air and drinking water, respectively. The LPR acquired descriptions of the thermal and oxidative reaction pathways and degradation products for four popular solvents (MEA, MDEA, piperazine, and diethanolamine), as well as prepared overviews of 1) results from the Mongstad program's study of relevant sampling and analytical methodology, 2) methods and technologies capable of mitigating and controlling amines and their degradation product emissions, and 3) relevant government regulations. Additionally, the LPR identified the nature of potential hazards and their likelihood, assuming the Mongstad scenario. Although comprehensive, Mongstad's studies have knowledge gaps in several areas (e.g., human health effects and environmental fate of many degradation compounds and relevant sampling and analytical methodologies) as well as issues related to the accuracy of assumptions (e.g., estimation of CO_2 capture unit performance based on average and steady-state conditions, and quality of vendor long-term emission estimates) that leave uncertain the accuracy of the assessment. Additionally, the results are specific to Mongstad's location. Despite this, Mongstad's program is promoting its methodologies as a "toolbox" to establish a standard for conducting risk assessments of emissions from amine technologies and will be basing regulatory requirements for the large-scale Mongstad facility on them.

The Technical Centre Mongstad studies, for the most part, at this stage have concluded that worst-case concentrations of the most hazardous degradation products are factors of 20 and 2 less than National Institute of Public Health guidelines for air and drinking water, respectively. To reach this stage—given the complexity of the assessment and the large number of solvent systems, degradation products, and environmental and other factors—a reduction in scope and adoption of a multitude of assumptions were required to make the assessment more tractable:

- The number of solvents were reduced to three (i.e., ammonia, MEA, and a proprietary amine system).

- The myriad of potentially hazardous products were essentially reduced to one (i.e., N-nitrosodimethylamine).

- Among a multitude of other assumptions, average environmental conditions were assumed as well as the extrapolation of rat test results to humans (Låg et al., 2011; Klein et al., 1991; Peto et al., 1991a,b).

Throughout these studies, when researchers were forced to make assumptions, they tended to adopt the most conservative alternatives and apply large safety margins to compensate for the potentially large estimation errors being introduced. However, in light of the simplifications, assumptions, and substantial knowledge gaps, it is very possible that something important was missed and might not be seen until large plants begin operating. Such important information could include the following:

- Accurate vendor long-term emission estimates
- Accurate, site-specific geographic and atmospheric information
- Knowledge of potential accumulation of lesser hazardous compounds in hazardous quantities
- Environmental and operational dynamics
- Operational malfunctions
- The cumulative effect of potentially hundreds of large amine units operating

Their assumptions are idealized compared to the real world in which vendor specifications can be a challenge to maintain in day-to-day operations and process upsets can occur. For example, in 1994, a California refinery operating a Catacarb (hot potassium carbonate with amine-type activator) CO_2 capture unit released 80–225 tons of solvent to the air over 16 days (Taugher, 2011).

The bottom line is that the studies have established only limited confidence that they can forecast what the most hazardous compounds will be and at what concentrations and what their effects will be and where they will appear in the long term. While Mongstad’s investigation represents a prudent attempt to perform due diligence, it is likely that such knowledge will not be available until substantial operating experience has been acquired, and it first may appear as a change in nature.

Activity 2.12 – Optimization of Technology Development in the Context of Industrial CO_2 Sources

Period of Performance: March–September 2012

Final Report: Appendix C of July–September 2012 Quarterly Report

Author: Steven Schlasner

Brief Summary: In an effort to reduce global warming, governments are seeking means to reduce greenhouse gas (GHG) emissions. Such reductions almost universally have negative economic implications that create two challenges for governments: how to reduce the magnitude of any unfavorable impact and how to equitably distribute that impact among industries and individuals. This activity examined the relationship between and development needs of technologies that implement one approach to GHG reduction, i.e., CO_2 capture, and industrial CO_2 sources. It accomplishes this by 1) identifying major U.S. CO_2-emitting industries, the processes that are the sources of their emissions, and their capture-related requirements; 2) identifying and characterizing relevant CO_2 capture technologies; 3) identifying capture technology development needs; and 4) constructing appropriate matches between capture technologies and applications.

A literature survey was performed to identify and characterize major and high-potential carbon dioxide capture technologies, U.S. industries and associated processes that are the largest carbon dioxide emitters, and carbon dioxide transmission and storage quality specifications. Capture technologies were organized into six categories, including absorption, adsorption, membrane, cryogenic, oxy-fired, and precombustion, and were rated against 22 processes used by the 11 largest CO_2-emitting industries in the United States, including fossil fuel electric power generation, petroleum refining, iron and steel production, cement manufacture, petrochemical production, pulp and paper manufacture, food processing, hydrogen production, lime manufacture, ammonia production, and glass manufacture. While the capture technologies share many developmental needs such as improved materials, realistic demonstration at relevant scale, reduced equipment space and footprint requirements, and reduced cost, their adoption will be dependent on the application and specific circumstance. Circumstantial factors will be most influential in retrofit situations in which integration advantages will determine the competitiveness of alternative capture technologies. First-order ratings of technical appropriateness of capture technologies by category with industries by process are provided.

Carbon dioxide capture will add significant cost to the manufacture of any product and increased complexity to any process that will be required to control its CO_2 emissions. Numerous capture technologies are under development that vary substantially in terms of cost, reliability, demonstrated scale, and characteristics of the feed stream that they can process. While all of these capture technologies claim to offer substantial advantages compared to conventional capture technologies, very few have been demonstrated at a scale and under conditions representative of commercial production. This places some manufacturers who need to procure and install these technologies to comply with evolving government regulations in the awkward position of deciding whether to acquire the most appropriate conventional technology today or consider alternatives such as state-run carbon credit programs or waiting to procure a potentially better technology tomorrow. The risk is that a poor choice will result in an inability to comply with future regulations or will place the manufacturer at a competitive disadvantage.

This report summarizes the findings of surveys performed by the EERC that identified and characterized major and high-potential CO_2 capture technologies, the industries and associated processes that are the largest CO_2 emitters in the United States, and CO_2 transmission and storage specifications. Capture technologies were organized into six categories, including absorption, adsorption, membrane, cryogenic, oxy-fired, and precombustion and were rated

against 22 processes used by industries, such as fossil fuel electric power generation, petroleum refining, iron and steel production, cement manufacture, petrochemical production, pulp and paper manufacture, food processing, hydrogen production, lime manufacture, ammonia production, and glass manufacture. Finally, first-order ratings of technical appropriateness of capture technologies by category with industries by process were performed.

Carbon dioxide capture technologies share many developmental needs such as improved materials, realistic demonstration at relevant scale, reduced equipment space and footprint requirements, and reduced cost; the extent to which these are disadvantageous varies by technology. Capture technologies also are differentiated by other important inherent characteristics, such as reliability and the capacity to integrate with other processes in terms of energy, space, and feedstock, which is especially significant for retrofit situations. Circumstantial factors, such as available space on off-shore platforms, can become overriding determinants in specific situations. For this reason, and because important factors such as the quality of most cost and reliability estimates is questionable, only a high-level evaluation of the technical appropriateness of individual categories of capture technologies with individual processes was performed. The evaluation produced qualitative ratings regarding the appropriateness of nine capture technologies with respect to 22 of the largest CO_2-producing industrial processes. Exceptions to these ratings exist on a case-by-case basis, i.e., applicability of a specific technology (versus class of technologies) to a specific process. For example, peculiarities of a new adsorbent might be particularly compatible with a specific process in a specific plant.

Activity 2.14 – Modification of Amine Solvent Stripping Process to Reduce Energy Input of CO_2 Capture

Period of Performance: April–September 2012

Final Report: July–September 2012 Quarterly Report

Author: John Kay

Brief Summary: This activity explored the idea of reducing the parasitic energy load of solvent-based CO_2 capture technologies by more efficiently stripping CO_2 from the rich solvent in a stripping column. The idea is that the increased stripping efficiency would permit a given solvent to operate at a greater working capacity and/or lower regeneration temperature, decreasing the cost of CO_2 capture. The concept has the potential to decrease the energy penalty associated with all absorption-based CO_2 capture technologies.

A model was built in Aspen Plus® to test the feasibility of the concept. Calculations were performed for a stripper fed rich 30% MEA solution loaded to approximately 0.35 mol CO_2/mol MEA. Both equilibrium-based and rate-based models were developed. The equilibrium-based model showed good results, while the rate-based model hinted at some challenges.

The equilibrium-based model showed a reduction of the reboiler duty by approximately 33%. After the equilibrium model was completed, a rate-based stripper model was built. Its initial results contradicted the equilibrium model. The concept appeared to drop the temperature of the stripper column by 10° to 15°F at the same reboiler heat duty. The CO_2 could not be removed from the solvent as effectively at these lower temperatures, requiring an increase in the reboiler duty. To counter this, side duties were added to each stage to heat the column while reducing the reboiler duty. This approach helped to reduce the overall heat duty so that it was roughly equal to the base case. However, the 33% reduction as predicted by the equilibrium model was not realized for this model.

According to data included in *Cost and Performance Baseline for Fossil Energy Plants Volume 3b: Low-Rank Coal to Electricity: Combustion Cases,* it can be calculated that the reboiler duty of amine-based CO_2 capture at pulverized coal power plants firing low-rank coal represents 27.7% to 29.5% of the thermal input to the power plant (Chou et al., 2011). This can be thought of as the parasitic load of the reboiler. The reduction in the reboiler parasitic load if the reboiler heat duty could be reduced through the use of the EERC's concept was calculated. For a 20% reduction in reboiler heat duty, the reboiler parasitic load drops to 22.2% to 23.6%. If the reboiler heat duty is reduced by 33%, as was indicated to be possible by the equilibrium model, the reboiler parasitic load would be reduced to 19.6% to 24.7% (the values vary depending on the plant type and assumed electrical generation efficiency as well as whether the plant fires lignite or subbituminous coal).

This concept is a unique idea that could have a significant and wide-ranging impact on CO_2 capture technologies because of its applicability to all absorption-based CO_2 capture technologies, whether they operate by chemical or physical absorption and whether they are aqueous or nonaqueous in nature. Key technical issues that should be explored are process design and the selection and sizing of equipment needed for implementation. The EERC's concept, including the results of the Aspen Plus models, was submitted to the Advanced Research Projects Agency – Energy (ARPA-E) but was not selected for funding. Opportunities for development of the concept will continue to be sought.

Activity 2.15 – CO_2 Capture Using Treated Activated Carbon and Electrically Driven Thermal Swing Adsorption (ETSA) Regeneration

Period of Performance: June–September 2012

Final Report: Appendix E of July–September 2012 Quarterly Report

Authors: John Hurley and Dustin McNally

Brief Summary: The electrically driven thermal swing adsorption (ETSA) process was evaluated in initial proof-of-concept tests for use at near-atmospheric pressure conditions to capture and separate CO_2 from a simulated flue gas. ETSA is similar to the thermal swing adsorption gas separation process except that in ETSA, the adsorber bed is directly and evenly heated resistively by applying an electric current to just the bed during regeneration. AC that was treated using a new EERC process to reduce its electrical resistivity by a factor of 10 was used as the adsorber to separate the CO_2 from the N_2 at ambient pressure. The adsorber bed was regenerated using the ETSA process by passing an electrical current directly through the treated AC to evenly and rapidly heat it, driving off the CO_2, followed by backflushing with nitrogen. The simulated flue gas was 15% CO_2 and 85% N_2 at a flow rate of 20 scfh. The results of the testing show that the ETSA process is able to remove greater than 99% of the CO_2 from the simulated flue gas. During regeneration, approximately one-half of the CO_2 produced was above 90% purity in these small-scale tests. However, we believe that with simple system alterations and upscaling, ETSA should be able to recover 90% of the CO_2 at a purity of 90% or above.

An economic analysis was performed based on these results, comparing the cost of regeneration energy per ton of CO_2 produced at 90% purity in an ETSA system versus regeneration using heating with steam and regeneration of aqueous MEA. Steam heating and ETSA regeneration costs are equal at loaded steam costs of $36/ton and $0.07/kWh electricity or $26/ton of steam at $0.05/kWh. Energy costs for a MEA-based adsorber are estimated to be lower than for the ETSA system at atmospheric pressure because of the low adsorptivity of the AC under ambient conditions, but at pressures above 5 bar the adsorptivity increases sufficiently that the ETSA energy cost should be comparable to or lower than for MEA.

In these initial proof-of-concept tests, ETSA has been shown to be effective at removing more than 99% of the CO_2 from a simulated flue gas stream in laboratory testing. Approximately 50% of the CO_2 was recovered at a purity of over 90% in those tests, but we believe that in larger systems and with minor design changes, 90% of the CO_2 should be recovered at a purity of 90% or above. A comparison of the cost of regenerating the AC bed using electricity versus steam indicates breakeven prices between the two methods if the loaded cost of the steam and its condensation is $36/ton for electricity at $0.07/kWh or $26/ton at $0.05/kWh. In addition, regeneration of aqueous MEA is also likely to have a lower energy cost at atmospheric pressure because the AC can only adsorb 2% of its weight in CO_2 under ambient conditions. However, at pressures over 5 bar, the amount of CO_2 that can be adsorbed by the AC is predicted to rise to 5%, making the cost of energy for ETSA regeneration approximately the same as for MEA regeneration, and at higher pressures the energy cost for ETSA regeneration should be less than that for MEA regeneration.

Activity 2.17 – Review and Modeling of Precombustion Capture of CO_2 from Natural Gas-Fired Plants

Period of Performance: January 2013 – March 2014

Final Report: Appendix A of January–March 2014 Quarterly Report

Authors: Josh Stanislowski, Nikhil Patel, Denny Laudal, and Michael Holmes

Brief Summary: Technologies are currently available for postcombustion capture of carbon dioxide from natural gas (NG)-fired power plants. One concept that has not been evaluated in significant detail is precombustion capture of CO_2 from NG. NG would be reformed and shifted to hydrogen, and the H_2 would be fired in a combined-cycle power generation scheme. The relatively pure stream of CO_2 would be purified with an assumed lower cost and lower energy penalty than a postcombustion approach. In this ministudy, the EERC reviewed current technologies available for precombustion capture of CO_2 from NG-fired power production to provide information as to their limitations and to identify needs to facilitate commercial application. Two modeling options were identified and evaluated using Aspen Plus to determine the plant efficiency of a precombustion system with conventional and advanced technologies. This efficiency was compared to a baseline system using NG combustion. This initial study was limited in scope and, therefore, provides a high-level analysis to determine if further study is warranted.

The results of this modeling study suggested that the precombustion capture concept has the potential to improve the efficiency of CO_2 capture if advanced technologies are utilized such as H_2 separation membranes. The present data indicate that it would be difficult to justify using a physical solvent technology in a precombustion capture scheme unless further study is performed to optimize the integration of the solvent technology or advanced physical solvents are employed. Overall, the results of the study indicate that there is promise for precombustion capture technologies in a NG conversion system, and a full technoeconomic analysis of the concept is warranted for future study.

- The precombustion capture processes requires reforming of the NG as a first step and subsequent removal of the CO_2 from the reformate gases prior to its combustion in the power generation cycle.

- The reformer configuration and optimized operating condition allowed about 16.6% CH_4 to remain unconverted, which was later oxidized in the gas turbine combustor. The CO_2 in the combustor exhaust contributed to uncaptured CO_2.

- On a molar basis, approximately 98% CO conversion is achieved in water–gas shift reforming. The unconverted CO was oxidized in the gas turbine combustor contributing to postcombustion CO_2 emissions.

The outcome of the effort demonstrated that the membrane-based precapture process can offer a competitive edge over the solvent-based CO_2 capture process. The caveat is that the steam utilized for sweeping H_2 from the membrane is injected in the gas turbine section. The auxiliary power consumed in water recovery from the exhaust is not included in the current calculations. Considering water recovery is a critical process requirement, modeling studies of different water recovery technologies and their integration with precombustion CO_2 capture processes should be performed. The energy losses were found to be severe in the case of solvent-based CO_2 precapture. It may be presently difficult to justify the process efficiency penalty for using the solvent capture process. It should be noted that the efforts to optimize the solvent were limited to the scope of this study, and that further modeling efforts could reveal more efficient process schemes that could be competitive with membranes and postcombustion capture. This sets a stage for conducting process improvement studies aimed at increasing efficiencies and reducing heat losses by thermally integrating exhaust recycling and optimizing individual processes associated with the solvent capture process. Future studies should be aimed at exploring these aspects and also reexamining postcombustion capture processes with identical configurations in order to arrive at a direct process comparison.

Activity 2.18 – Assessment of the Operational Integration of CO_2 Capture at a Coal-Fired Utility

Period of Performance: January–September 2013

Final Report: Appendix A of July–September 2013 Quarterly Report

Author: John Kay

Brief Summary: Current economics and technology are not favorable for capture of carbon dioxide from combustion sources such as electric power plants for EOR. The cost of capture is severalfold larger than the value of CO_2 in EOR applications. Even if economics become more favorable as a result of factors such as regulatory controls and improvements in technology or oil prices, an incompatibility exists between the inherently variable nature of the power generation rate and the need for reasonably constant CO_2 feed rates by oil fields. The conventional approach to addressing mismatch between production and demand is introduction of temporary storage. This study examined various facets of introducing temporary storage into planned or existing CO_2 capture, compression, and transportation systems.

Alternative approaches were reviewed. The approaches included cycling pipeline pressure (also called packing), storage of partially processed CO_2 by removing and temporarily storing CO_2 offline from the capture process while still attached to the separation chemical, fabricated vessels and piping, and underground temporary storage. The least expensive alternatives, in terms of construction cost, appeared to be underground storage in depleted reservoirs, aquifers, and salt caverns. Cost, performance, and acceptable operating conditions varied significantly among the different formations. Superficially, it appears unlikely that temporary storage could be incorporated and justified on an economic basis for shorter pipelines (i.e., lengths of less than a few hundred miles) in situations other than the most optimistic. However, it is not unreasonable to envision modest oversizing of pipelines to enable short-term storage by packing, especially if additional CO_2 sources are expected to be integrated in the future. It is also not unreasonable to envision addition of temporary storage to pipelines that are periodically constrained.

The opportunity to beneficially deploy storage to attenuate variation of captured CO_2 emissions from a variable source, such as a power plant, depends upon many factors which include the value of the CO_2, regulatory requirements, performance of the power plant or plants being considered, existing infrastructure, operation strategy, total costs, and location.

The relative benefit of storage, then, is very much a function of pipeline length and operating strategy. The opportunity to beneficially deploy storage to attenuate variation of captured CO_2 emissions from a variable source, such as a power plant, depends upon many factors:

- The value of CO_2. With estimates of the cost of CO_2 capture from combustion sources being roughly $80 a metric ton depending on location, but its value to EOR being less than one-half of that, some other factor must appear, such as environmental regulation of CO_2, to improve the value of a CO_2 capture scenario. The relatively larger magnitude of this factor compared to CO_2 value in EOR will give priority to its specifications for a capture scenario design.

- Regulatory requirements, flexibility, and cost of CO_2 emissions. Regulatory requirements can have a profound effect on the value of storage. Inexpensive penalties and fees, low capture requirements, extended averaging periods and flexibility could minimize the need for storage while the opposite could justify its construction. The extent of any effect is situation-dependent and is evaluated on the magnitude and extent of the regulatory requirements and the position, condition, resources, and other requirements of the generating facility.

- Power plant performance. In the absence of variation, attenuation and storage is unnecessary; thus capture at a level below variation or establishment of true baseload performance would eliminate the need for storage except to back up generation or capture process interruptions and upsets.

- Existing CO_2 capture, transportation, and utilization. The amount, size, type, and location of existing components can significantly impact the type, utility, size, preferred operating strategy, value, and cost of storage. As noted previously, it appears unlikely that temporary storage could be justified on an economic basis for shorter pipelines. However, it is not unreasonable to envision modest oversizing of pipelines to enable short-term storage by packing, especially if additional CO_2 sources are expected to be integrated in the future. It is also not unreasonable to envision addition of temporary storage to pipelines that are periodically constrained, since storage is less expensive than construction of new pipelines that would be required to attenuate flow rate variation. Conditions and capabilities of the existing CO_2 systems will constrain storage design. For example, a capture system that is sized to process less than the maximum CO_2 flow rate could hamper implementation of an emit excess strategy.

- Operating strategy. Operating strategy has major impacts, not only on storage requirements, but also on CO_2 capture equipment sizing and operation. The emit excess strategy has the smallest storage requirement but potentially the largest capture capacity requirement. The capture constant percent strategy has the largest storage requirement and intermediate capture capacity requirement. The threshold limited capture strategy has an intermediate storage requirement and potentially the smallest capture capacity requirement. Thus the capture constant percent strategy is the least attractive of the three strategies, with the emit excess and threshold limited capture strategy advantages being dependent upon the specific demand profile, relative component costs, and other situation-dependent factors.

- Relative capture, compression, storage, and pipeline total costs.

- Location, type, and quality of available underground storage.

Novel Carbon Storage Studies

Activity 2.10 – Investigation of North Dakota Clays for Making Ceramic Proppants

Period of Performance: January–September 2012

Final Report: Appendix A of July–September 2012 Quarterly Report

Authors: John Hurley and Bethany Kurz

Brief Summary: Small ceramic beads called proppants are often used during hydraulic fracturing operations to prop open the fractures created in a tight hydrocarbon-bearing formation in order to allow NG and oil to flow out of the formation during production or allow carbon dioxide to penetrate into the formation during combined EOR and carbon dioxide storage operations. North Dakota has several clay deposits located in the western part of the state that may be suitable for ceramic proppant development because of their high concentrations of kaolinite. High-alumina kaolinite is one of the key ingredients used to manufacture ceramic proppants (Murphy, 2012).

The work performed in this ministudy showed that additives can have an effect on the types of crystalline material present in the finished proppants but did not have a strong effect on strength under the heating schedule used. The proppants had a high amorphous glass content and were only one-third as strong as smaller-sized commercial proppants made from kaolin clay. However, tests with different heating schedules showed that sintering times have a very large effect on strength and also that holding at lower temperatures to allow recrystallization can dramatically reduce the amount of amorphous material remaining in the proppants; therefore, further refining the heating schedule could possibly dramatically increase the strength of the particles by maximizing sintering while minimizing amorphous glass content. Also, testing of different size ranges of proppants indicates only around 10% of the difference in strength between the larger EERC proppants and the smaller commercial proppants is due to size difference.

Based on the results of this work, it is recommended that in future work the process for creating the green proppant particles should be modified to produce a higher concentration of particles in the smaller size ranges usually used in hydraulic fracturing operations. Also, the heating schedule used to sinter the green particles into hardened proppant particles should be refined to increase the density of the particles and also increase the crystalline content of the particles. We believe that heated-stage x-ray diffraction analysis should be used to determine the changes in crystallinity of the particles with time and temperature in order to significantly speed the process of determining the best heating schedule to achieve these goals.

Activity 2.13 – Evaluation of Clay-Based Cenospheres for Use in Hydraulic Fracturing

Period of Performance: March–September 2012

Final Report: Appendix D of July–September 2012 Quarterly Report

Authors: Donald McCollor, Jason Laumb, and Bethany Kurz

Brief Summary: Advances in horizontal drilling and hydraulic fracturing technologies and practices have led to increased development of oil and gas from tight shale formations across the United States. Hydraulic fracturing includes the injection of a mixture of water, proppant, biocide, and various other compounds into the subsurface at high pressure to create and/or expand fractures within a reservoir to more efficiently recover oil and/or gas. Proppants are a key component of the process and allow the fractures to remain open after the fracture fluid returns to the surface and pressure within the formation is reduced. Commonly used proppants throughout the nation include sand, resin-coated sand, and ceramic beads; however, there is currently a shortage of high-strength proppants, particularly those made from ceramics. Most common ceramic proppants are made from bauxite or high-purity kaolin clay that has been sintered to a high density. However, high-quality deposits of these minerals can be very far from the fields of oil and gas production, leading to high shipping costs to transport the proppants to the production site. For example, many of the high-strength ceramic proppants are manufactured using bauxite deposits from China.

As producers increasingly consider CO_2 EOR and, hence, CO_2 storage in tight oil-and-gas plays, high-performance proppants, such as lightweight ceramics, will likely play a key role in helping to sustain the fracture network and allow for CO_2 transport within the reservoir. Given that proppants are a critical component of hydraulic fracturing, research that helps improve and understand proppant performance is a key factor in helping to increase oil and gas production and efficiency in unconventional reservoirs.

While many proppant manufacturers have focused on high-Al-containing materials, past coal combustion studies completed by EERC personnel lend evidence to suggest that low-Al-containing materials, fired under the appropriate conditions, could make a suitable proppant (Zygarlicke et al., 1992; Laumb et al., 2008; Benson et al., 2008a,b). These studies provide vast amounts of information on the transformation of inorganic materials under high-temperature oxidizing and reducing conditions. Examples of highly crystalline, high-strength materials have been observed in both fly ash and slag produced from combustion processes that involve low-Al-containing clays. These experiences by EERC personnel have led to the hypothesis that low-density, high-sphericity proppants of suitable strength can be made from widely available, low-Al-containing materials.

One way to increase the strength of the glassy material is to promote crystal growth. Growth of crystals (mullite, for example) in the material is a function of chemistry, atmosphere, temperature, and time during the firing process. One way to control and optimize these conditions is through the use of an atmospheric drop-tube furnace, which is a laboratory-scale, entrained-flow tube furnace with the ability to combust coal, produce ash, and create glass particles under closely controlled conditions. Parameters such as initial hot-zone temperature, residence time, and gas-cooling rate can be closely controlled and monitored.

Proppant formulations were developed using low-Al-containing North Dakota clays. Three base recipes were developed, with the goal of creating a low-density proppant material. The promotion of crystal growth is likely important to form proppants from the low-Al-containing materials. Mullite, anorthite, and iron spinel chemistries were identified as the most promising crystalline species to target. Initial tests indicate that it is possible to form low-density, spherical materials with low-Al-containing clays. However, the strength of the material needs to be increased for use as a suitable proppant material. The iron spinel and mullite formulations show the most promise and likely need more time at temperature to increase sintering, melting, and the formation of crystals from the resulting melt. Because CO_2 EOR is a very effective means of secondary or tertiary oil recovery, industry is increasingly contemplating the use of CO_2 for EOR in unconventional oil and gas formations like the Bakken and Three Forks reservoirs. A secondary benefit of CO_2 EOR is permanent CO_2 sequestration. However, the success of CO_2 EOR and CO_2 sequestration in unconventional oil and gas plays will likely be dependent on proppant performance, since propped fractures will be necessary for transport of CO_2 and extraction of oil and gas within the reservoir. This project helped advance our knowledge of how to develop high-performance proppants using materials widely available within North Dakota and throughout the country. Further work should be performed to optimize their utilization for EOR and CO_2 sequestration.

Activity 2.16 – Electrical Thermal Swing Adsorption (ETSA) Testing to Enhance CO_2 Flood Efficiency and Natural Gas Liquids (NGLs) Separation

Period of Performance: November 2012 – December 2013

Final Report: Appendix A of October–December 2013 Quarterly Report

Authors: John Hurley and Dustin McNally

Brief Summary: The EERC tested the ETSA technology to determine if it can be used to increase the storage efficiency of carbon dioxide used in a combined CO_2 EOR and CO_2 storage operation as well as to remove NGLs from the produced gas in a single process. The efficient use of CO_2 is very important because the current demand for CO_2 outweighs the limited supply available to the oil industry for hydrocarbon production that also results in long-term CO_2 storage in the reservoir rock.

During the CO_2 flood of an oil reservoir for combined CO_2 EOR and CO_2 storage, a portion of the CO_2 used can emerge with the produced oil and gas, thereby reducing the amount stored underground. For commercial purposes and in order to increase the efficiency of the sequestration process, the CO_2 must be collected from the output of a producing well, processed, and recycled for further use in an injection well. In addition to CO_2, the produced gas can include NGLs such as propane that have high intrinsic value and are usually separated from the NG by expansion or condensation. However, the remaining methane or CO_2 must then be recompressed for pipeline transport.

The EERC developed a process to separate gases based on their adsorption on AC in a process similar to pressure swing adsorption, except that during the regeneration step, the AC bed is heated by passing an electrical current directly to the absorber bed. This process, ETSA, can remove both CO_2 and NGLs from the methane in one operation, which was tested to determine if it is effective for use in separating produced gases from an EOR operation in order to recover methane, NGLs, and CO_2 for separate uses. A benefit of the process is that it separates the gas at the pipeline pressure such that the methane does not need to be recompressed after the gases are separated.

Testing was performed to simulate separation of a produced gas consisting of methane/CO_2 and methane/propane/CO_2 at pipeline pressures. It was determined that the ETSA process does separate the gases from the mixture, but it requires too much energy and flush gas in the regeneration step to be effective. The process was capable of effectively separating propane from the CO_2 and methane mixtures but was found to be a purity of only about 65%, much lower than would be expected from a traditional process.

This testing was performed by scaling up the ETSA process to a six-times larger bed using treated AC for adsorbing contaminant CO_2 and propane from methane gas. It was learned during this testing that by purifying a highly adsorbed gas, such as methane, the adsorptivity of the bed during flow tests is about 40% less than that seen during purification of less adsorbed gases (N_2). This provides a significant disadvantage for the ETSA process for use on oil field recovery and purification (and, ultimately, CO_2 storage) as the reduced adsorption times do not allow for a net production of purified methane and limit the amount of contaminant adsorbed before needing to regenerate.

The AC bed was capable of separating a mix of propane and CO_2 from methane, and the propane was much more highly adsorbed and likely became a liquid when it was separated as a result of the operating pressure of 450 psi. The propane liquid desorbs during regeneration at about 65% purity, while the CO_2 desorbs at about 10%–35% purity during the ETSA regeneration. Both of these purities could be increased by using multiple beds to upgrade the mixed gas into a more usable purity, but this would require further investigation.

The ETSA process was shown to require about 100 Joule/liter of produced propane (at 65% purity), whereas a simple compression calculation shows that propane can be separated by using about 700 Joule/liter of propane when compressing and condensing a 15% propane mixture. Although the energy required is less for ETSA, it is not a significant difference given the issues with a reduced adsorption time when separating contaminants from a similarly adsorbed gas (such as for CO_2 and methane) and considering that the purity of the captured contaminant would require multiple beds to upgrade to a more desirable purity.

The ETSA process, while more efficient than a traditional pressure swing regeneration, will require much more processing to supply purified gases effectively on the given gas mixtures, especially considering the reduced adsorption when purifying CO_2 and propane from methane. The process of separating liquids (propane) worked well, but the purity was not as high as compression/condensation methods, likely due to the solubility of the contaminants in the liquid propane. One aspect not investigated would be to use the ETSA method to reduce the amount of energy required in a compression/condensation process by removing a portion of the gases as a preprocessor before compressing, but because of the negative amount of methane produced, this would not be likely to offset the capital costs.

Activity 2.19 – Measurement of CO_2 Adsorption Isotherms for Clays

Period of Performance: December 2014 – March 2015

Final Report: Appendix A of January–March 2015 Quarterly Report

Authors: Blaise Mibeck, Christopher Beddoe, Alexander Azenkeng, Kurt Eylands, John Hurley, and Steven Smith

Brief Summary: This effort focused on the development of a procedure using a quartz crystal microbalance (QCM) to measure mass changes in clay samples that were exposed to CO_2 at 50°C and up to 2200 psi. QCM is a relatively low cost, easy to operate gravimetric technique that uses the piezoelectric effect of quartz crystals to detect mass changes in a sample on the order of ng/cm^2.

The purpose of this study was to develop the apparatus and procedures to determine CO_2 adsorption curves using a QCM at pressures and temperatures relevant to geologic CO_2 storage in the deep subsurface. For this effort, testing focused on measuring the adsorption of CO_2 onto the common clay mineral, kaolinite, since clays are often present in the matrix and fracture pathways of formations that are considered good targets for geologic storage of CO_2. The QCM technique helps to improve our understanding of CO_2 adsorption onto clays in the subsurface and allows for improved storage capacity estimation and dynamic simulation of CO_2 plume extent.

CO_2 adsorption isotherms were collected for five samples of kaolinite at 50-psi pressure increments up to 2200 psi. The results of this effort appear consistent with a study in which CO_2 showed simple Langmuir Type 1 adsorption curves. A change in the kaolinite film roughness pre- and post-CO_2 was observed. This phenomenon could be responsible for porosity changes in flow-through experiments and has implications for CO_2 storage.

The ratio of CO_2 adsorbed to kaolinite mass ranged from 0.013 to 0.033 pg/µg. In all cases except one, the amount of CO_2 adsorbed to the samples increased steadily and then began to stabilize, as would be expected, because CO_2 adsorption is limited by the amount of sample present and contributing free sites for molecules to join. The one exception was that the sample with the highest mass continued to adsorb CO_2, indicating that a longer test duration may be needed for samples with a higher mass.

This study demonstrates the ability to quantify the amount of CO_2 adsorbed onto kaolinite clay. Over the course of the evaluation, the QCM was developed, methods and procedures were tested, and CO_2 was adsorbed on multiple samples. The ability to operate a QCM at high pressures will provide insight regarding the role clay minerals play in the long-term storage of CO_2. Ultimately, this work can be utilized to inform CO_2 storage capacity estimations and dynamic simulation of CO_2 injection scenarios, aid in the determination of lateral areal extent of injection plumes, and provide a mechanism for determining invasion into cap rocks formerly considered impenetrable.

Activity 2.20 – Development of an Analytical Approach to Differentiate Between Different Corrosion and Scale-Forming Mechanisms

Period of Performance: February–September 2014

Final Report: Appendix A of July–September 2014 Quarterly Report

Authors: Alexander Azenkeng, Kurt Eylands, and Bethany Kurz

Brief Summary: A strategic ministudy to investigate the different types of corrosion and scale-forming mechanisms associated with carbon sequestration practices and carbon dioxide-based EOR was conducted by the EERC. This effort was primarily a literature survey to identify the various types of corrosion, scale, causal mechanisms, and options for prevention. There is an abundance of literature and information on corrosion and scale-forming mechanisms that commonly occur in the oil and gas industry, especially during production operations and pipeline transport. As such, this information was reviewed and used to determine the corrosion and scale-forming mechanisms likely to be encountered during geologic carbon sequestration and CO_2 EOR. The results of this study indicate that corrosion problems during the deployment of carbon sequestration and CO_2 EOR practices can be highly variable, complicated, and fairly widespread throughout many facets of the process from surface transportation and storage equipment to downhole pipes/casings and associated accessories.

Although corrosion is a natural phenomenon that can occur spontaneously by electrochemical reactions in the presence of oxygen or moisture, it can be exacerbated by operational activities and/or by the use of chemicals at various stages during CO_2 sequestration and CO_2 EOR, such as drilling and completion, CO_2 injection, and product water extraction. The key corrosion mechanisms discussed in this study include sweet corrosion, sour corrosion, oxygen corrosion, galvanic or electrochemical corrosion, crevice corrosion, pitting corrosion, erosion corrosion, microbiologically induced corrosion, stress corrosion cracking (sulfide stress corrosion, chloride stress cracking, corrosion fatigue), stray current corrosion, strong acids corrosion, and dense brines corrosion. Of these mechanisms, CO_2 itself is responsible for a specific type of corrosion known as sweet corrosion, which often occurs in association with, or leads to, other corrosion mechanisms such as pitting or crevice corrosion. While many of the corrosion mechanisms discussed in the report are not directly attributable to CO_2, they are important because they may affect the tubing and piping used to transport or inject CO_2 or used to transport fluids associated with CO_2 EOR.

Because the oil and gas industry has been effectively managing corrosion and scale-related issues for decades, there is an abundance of information on preventive measures that can be applied to carbon sequestration projects. There is far less information available on analytical protocols to effectively and accurately diagnose various corrosion mechanism and causal factors. The results of this ministudy indicate that a comprehensive analytical and diagnostic approach needs to be followed to adequately identify potential corrosion mechanisms and resultant scale-forming conditions, which can be very difficult to diagnose, but the understanding of which is critical to the identification of effective preventive measures. To adequately understand the causal mechanisms responsible for corrosion and scale formation, an integrated analytical strategy is needed that includes scanning electron microscopy, x-ray fluorescence spectroscopy, x-ray diffraction, and microbiological activity testing (e.g., for sulfate-reducing bacteria and iron bacteria). Each of these analyses provides key pieces of information that are related, but unique, and excluding one of the analyses may impede accurate identification of the corrosion and scale-forming mechanisms. In addition, diagnostic data such as injection well history, tubing and casing composition, formation fluid chemistries, dissolved gas concentrations (e.g., for O_2, H_2S), and formation mineralogy are among the critical pieces of information needed to conduct an accurate assessment. Using an integrated and comprehensive approach to identify, diagnose, and effectively address corrosion and scale issues in the field is critical to prevent equipment failures that could lead to unintended leaks and to reduce the financial resources needed to manage and control corrosion-related problems.

The results of this literature review indicate that corrosion problems during the deployment of carbon sequestration and CO_2 EOR practices may be highly variable, complicated, consequential, and widespread throughout many facets of the process from surface storage and transportation equipment to downhole pipes/casings and associated accessories. However, corrosion-related issues have been effectively managed for decades in the oil and gas industry, including CO_2-based EOR, wherein CO_2 transport, injection, and processing have been occurring on a commercial scale for 40 years.

Because of the complexity of various corrosion and scale-forming mechanisms and the variety of conditions under which they occur, it is important to evaluate data from multiple analytical techniques and to gather as much background information about the environmental conditions in which the corroded material existed. For example, various different corrosion mechanisms can result in formation of the same scale by-products; thus it is important to look not only at the chemical and mineralogical makeup of the scale but also at the elemental and mineralogical distributions within the scale, the texture of the scale (which could indicate biotic or abiotic corrosion mechanisms), and the presence or absence of corrosion-enhancing microbes. This document provides a reference upon which more advanced analytical protocols and diagnostic tools can be developed.

Preliminary Engineering Studies

Activity 2.4 – Evaluation of Electric Vehicles and Other Fossil-Based Technologies as Near-Term Solutions to Reducing Foreign Oil Imports

Period of Performance: April–June 2009

Final Report: Appendix C of the July–September 2009 Quarterly Report

Authors: Ben Oster, Steven Wilmoth, and Joshua Strege

Brief Summary: It is likely that domestic fossil energy will play an increased role in fueling our nation's transportation infrastructure during the next decade (U.S. Energy Information Administration, 2009). While the United States has limited supplies of conventional domestic oil, there are several options for using other domestic fossil-based resources in transportation. These include direct coal liquefaction, indirect coal liquefaction, gas-to-liquids technology, compressed gas vehicles, aboveground oil shale retorting, in situ oil shale recovery, increased tar sands production, unconventional oil recovery, hydrogen production from fossil fuels for use in fuel cells, and electric generation for use in electric vehicles.

Although many of these technologies have the potential to replace or reduce oil imports in the long term, the vast research and infrastructure needs for some technologies will likely delay their deployment for many years. If the world is truly facing a coming oil crisis, long-term technologies may not realistically be adopted until some other technology or lifestyle has already achieved widespread acceptance. Some technologies are inherently inefficient and use excessive NG, which may be in tight supply by the time a new technology is developed; some technologies may likewise have excessive GHG emissions. There is a need to identify those fossil-based technologies that can rapidly and sustainably deploy in the event of a lasting oil crisis.

At this time, plug-in hybrid electric vehicles show much potential for near-term commercialization. They represent an efficient use of abundant coal resources, making their impact on energy prices less than for many other options. Plug-in vehicles and their batteries are already near mass production in the United States and elsewhere. They face few if any technological hurdles to be made commercially viable. Unlike other fossil-based transportation options, there is no need for a massive infrastructure change to use plug-in hybrid electric vehicles because they can recharge using the existing electrical infrastructure that already carries most of the energy derived from domestic fossil resources. Moreover, they represent distributed consumer-end products rather than large, centralized producer-end facilities. This means there is no need for bench-, demonstration-, and pilot-scale testing or for plant permitting, construction, and shakedown, needs that create a significant time delay between conception of new technology and market availability. The life cycle GHG emissions from a vehicle running on electric power are significantly lower than for a vehicle running on almost any other fuel. Because electric vehicles use electricity rather than liquid fossil fuel products, they have the potential to lower emissions because pollutants such as CO_2 can be more easily captured at a power plant than at a vehicle tailpipe.

However, plug-in hybrid electric vehicles are not without disadvantages. Unlike processes that generate liquid fuels, converting to electric transportation will require consumers to purchase new vehicles. Large fleets of plug-in vehicles may overload transmission lines unless they are recharged using off-peak electricity (Hadley, 2006). Battery electric vehicles face the same problem and do not appear to be as attractive in the near-term as plug-in hybrids, because current batteries do not offer the same energy density as gasoline or diesel.

Overall, plug-in hybrid electrics present a promising opportunity for permanently reducing oil dependence in the near future while achieving a reduction in GHG emissions. They should be considered a part of any comprehensive energy plan to deal with the threat of peak oil.

Activity 2.5 – Zero-Energy Building Technologies

Period of Performance: July 2009 – June 2010

Final Report: Included in April–June 2010 Quarterly Report

Author: Greg Dvorak

Brief Summary: Buildings are a major consumer of energy in the United States. The energy is primarily produced from nonrenewable resources. The use of nonrenewable resources raises environmental, financial, and national security concerns. Zero-energy buildings (ZEBs) are designed to use energy more efficiently and only use energy from renewable resources. Several ZEBs are in use throughout the world, including in the United States. The major barriers to ZEBs are the high initial cost, resulting in long payback periods, and a lack of data and understanding of the technology types. These and other barriers are being overcome through research, development, and demonstration with government assistance. Several technologies available for designing and constructing ZEBs are discussed in this report.

The ZEB concept addresses an important and growing issue, wasteful energy consumption. In the United States, 40% of the energy used is consumed by buildings (U.S. Department of Energy Office of Energy Efficiency and Renewable Energy, 2008). Energy consumption continues to increase as a result of many factors, including population rise, increased floor space, and the rapid growth in electrical technologies. A large portion of the energy is generated from nonrenewable resources such as coal and oil. Most of the oil in the world is located in unstable regions, affecting the security and stability of our nation. These and other nonrenewable products also release by-products that pollute the planet.

ZEBs reduce nonrenewable energy consumption by using renewable energy resources and energy-efficient technologies and strategies. Energy efficiency is an important aspect since it will reduce the overall energy consumption. This reduction makes renewable energy generation more viable.

Several barriers exist for ZEB technologies, but they are, in part, the result of the people who occupy the buildings. The most obvious and talked about is initial cost. All of these energy-efficient technologies cost more to set up than existing technologies. The increased cost is usually due to the special materials, processes, training, or equipment needed. Payback periods are estimated, with some being several months and others being several years or decades. Government grants, tax incentives, utility rebates, and other incentives help to reduce the cost. It is important to consider not only the reduced energy consumption but other factors such as improved property value and pollution reduction.

New technologies also do not benefit from economy of scale. At the start, costs are high because of the uncertainties of the technologies. Laboratory testing and optimizations help reduce material and manufacturing costs. Early investors test the technologies and provide real-world data. When people begin to demand the product, large-scale manufacturing decreases costs. Several ZEB technologies are in the early investor stage and waiting to reach large-scale production. It is up to consumers to demand ZEB technology options and that ZEBs become the standard.

Another difficulty for ZEB technologies is the competition. New and efficient technologies must not only compete against current designs but must also compete with other new ZEB technologies. This competition occurs on both a financial and resource (such as space) level. While healthy competition facilitates improvements, it can also slow down the deployment of both technologies.

ZEBs and their technologies focus on reducing the world's dependence on nonrenewable, polluting resources. A whole-building design strategy is necessary to reach this goal. Since a whole-building strategy is needed, it is important to address other environmental factors. Water conservation, waste reduction, land conservation, indoor air quality, and thermal comfort are other important factors to think about when designing a building.

Activity 2.7 – Preliminary Evaluation of Non-Pt Alkaline Methanol Fuel

Period of Performance: July–December 2010

Final Report: Appendix A of the October–December 2010 Quarterly Report

Author: Ted Aulich

Brief Summary: Direct methanol fuel cell (DMFC) technology offers a promising approach to utilizing a wide range of fossil fuels more efficiently than today's internal combustion engines because of its higher efficiency and less complex system and established large-scale methanol production from fossil-derived syngas. However, the high cost of Pt-based anode and cathode electrocatalysts is one of the major barriers to the commercialization of DMFCs using proton-conducting membranes. The replacement of proton-conducting membranes with alkaline membranes enables the use of non-Pt base metals as less expensive electrocatalysts for both oxygen reduction and methanol oxidation reactions. However, the activities of base metal electrocatalysts are too low at temperatures relevant to the operation of alkaline membrane-based methanol fuel cells (60°C). Recently, the EERC developed a novel alkaline methanol fuel cell that is operated in the intermediate temperature range of 80° to 200°C and has demonstrated high power density (up to 100 mW cm^{-2}). Moreover, we have found that base metal catalysts show improved activity toward methanol electrooxidation and oxygen electrochemical reduction in the temperature range of interest. Therefore, the use of non-Pt catalysts in place of Pt-based catalysts in methanol fuel cells would be a huge boost to their commercialization because of the much lower cost of non-Pt catalysts.

In this project, we have demonstrated the potential of using non-Pt catalysts to replace Pt-based catalysts in intermediate-temperature methanol fuel cells via the preparation and evaluation of a range of non-Pt catalysts. Silver-based catalysts show high activity to the oxygen reduction at the cathode side of the fuel cell, which is comparable to that of Pt, especially in the intermediate-temperature range. It is expected that the replacement of Pt-based cathode catalysts with silver will simply reduce 50% of the catalyst cost, even with the same traditional anode catalysts.

Further efforts have focused on the evaluation of non-Pt anode catalysts toward methanol oxidation. Both unsupported and supported Ni catalysts show very low activity and are, therefore, not a near-term candidate, although they are stable in alkaline media and have a very attractive low cost. This setback can be offset by the discovery of the high activity of palladium-based catalysts toward methanol oxidation. The activity of palladium-based catalysts is favorably compared to that of the traditional Pt-based anode catalysts. Because Pd is currently three times cheaper than Pt, the use of Pd in place of Pt will considerably decrease catalyst cost. Moreover, it is expected that the loading of Pd at the anode can be further decreased via catalyst development efforts. Therefore, it can be concluded that the use of non-Pt catalysts to replace Pt-based catalysts is highly likely to reduce the total catalyst cost by ten times without sacrificing performance.

CONCLUSIONS

The goal of the Strategic Studies subtask has been to provide data that better define paths forward to address critical questions faced by the fossil energy industry. A wide range of small, focused research topics have been addressed. The resources applied to these efforts were usually between $15,000 and $25,000 of funding, with typical time lines of 6 months or less. The Strategic Studies topics that have been investigated herein have developed key data and information in order to attract the interest of the fossil energy industry. The ultimate goal of these efforts was to address technical issues facing the energy industry by establishing and expanding applied research programs. In the last 4 years, the studies have focused exclusively on carbon capture and storage-related topics. These efforts have helped to form the technical underpinning for significant CCS research programs, including the Plains CO_2 Reduction Partnership, the Partnership for CO_2 Capture, the Bakken CO_2-based enhanced oil recovery program, and several other collaborative efforts related to CCS.

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