DOE/NETL ADVANCED COMBUSTION SYSTEMS: CHEMICAL LOOPING SUMMARY

JULY 2013

DISCLAIMER

EXECUTIVE SUMMARY

Combusting fossil fuels for power generation in nearly pure oxygen, rather than air, presents an opportunity to simplify CO_2 capture for storage or use. In a chemical looping system, oxygen for combustion is produced internal to the process via oxidation-reduction cycling of an oxygen carrier, which eliminates the need for an expensive oxygen separation system as used in other oxy-combustion systems. The concept of chemical looping can be applied to both coal combustion and gasification. Chemical looping has a number of technical advantages (e.g., CO_2 and H_2O kept separate from the rest of the flue gases, expensive air separation unit not required, CO_2 separation takes place during combustion) and challenges (e.g., reliable solids transport system, efficient heat integration, efficient ash separation, attrition-resistant metal oxide carriers) relative to other power systems. These technologies are still conceptual and are being researched around the globe at bench and small pilot scale to prove system design and operation concepts and to reduce capital and operating costs. Three chemical looping projects supported by NETL were completed in 2012. Eight projects, including projects funded by American Recovery and Reinvestment Act of 2009 (ARRA) and Advanced Research Projects Agency-Energy (ARPA-E), are currently being supported with industry, academia, and NETL's Office of Research and Development.

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CHEMICAL LOOPING PRINCIPLES

The combustion of fossil fuels in nearly pure oxygen, rather than air, presents an opportunity to simplify CO_2 capture in power plant applications. Oxy-combustion power production provides oxygen to the combustion process by separating oxygen from air using a cryogenic air separation unit (ASU) or an advanced technology under development, such as an ion transport membrane (ITM). However, chemical looping systems produce oxygen internal to the process via oxidation-reduction cycling of an oxygen carrier, which eliminates large capital, operating, and energy costs associated with oxygen generation. Chemical looping is considered a "transformational" technology with the potential to meet program cost and performance goals and be ready for demonstration-scale testing after 2030. The concept of chemical looping can be applied to coal combustion, where it is known as chemical looping combustion (CLC), or to coal gasification, where it is known as chemical looping gasification (CLG). Additional details on CLC and CLG are provided in the following sections. Table 1 provides a summary of the main technical advantages and challenges for chemical looping technologies..

TABLE 1. TECHNICAL ADVANTAGES AND CHALLENGES FOR CHEMICAL LOOPING TECHNOLOGIES

Advantages	Challenges
• CO_2 and H_2O kept separate from the rest of the flue gases • ASU is not required • CO_2 separation takes place during combustion	• Technology still conceptual and at bench scale • Reliable solids transport system • Efficient heat integration • Efficient ash separation • Attrition-resistant metal oxide carriers

CHEMICAL LOOPING COMBUSTION

Chemical looping combustion (CLC) uses an oxygen carrier to transfer oxygen from the combustion air to the fuel. Figure 1 presents a simplified process schematic for chemical looping combustion, where the process is carried out in multiple separate reactors. The products of combustion (CO_2 and H_2O) are kept separate from the rest of the flue gases, simplifying CO_2 capture for eventual storage or use.

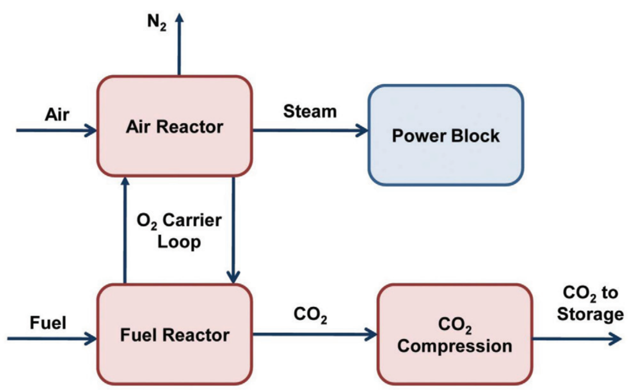

Figure 1: Chemical Looping Process

Figure 2 is a schematic diagram of a typical two-reactor CLC process, where combustion is split into separate oxidation and reduction reactions. The oxygen carrier is usually a solid, metal-based compound with chemical composition of M_xO_{y-1}. It may be in the form of a single metal oxide, such as an oxide of copper, nickel, or iron, or a metal oxide supported on a high-surface-area substrate (e.g., alumina or silica) that does not take part in the reactions. Using a supported metal oxide carrier allows separate optimization of oxygen-carrying capacity and mechanical strength.

The carrier is further oxidized by oxygen in the air reactor, which operates at elevated temperatures (typically 800–1000ºC) to produce a compound with a composition M_xO_y and hot flue gas. The hot flue gas can be used to produce steam that drives a turbine, generating power. The metal oxide from the oxidizer enters the fuel reactor, also operated at elevated temperature, and is reduced to its initial state by the fuel. The reaction in the fuel reactor can be exothermic or endothermic, depending on the fuel and the oxygen carrier. The combustion product from the fuel reactor is a highly concentrated CO_2 and H_2O stream that can be purified, compressed, and sent to storage or for beneficial use.

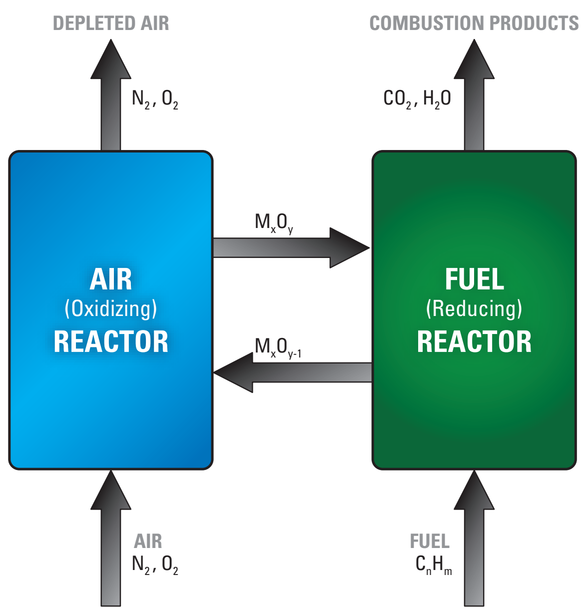

Figure 2: Two Reactor CLC Process

The overall chemical reactions in the two reactors can be expressed as:

Oxidizer: $M_xO_{y-1} + 1/2\ O_2 \rightarrow M_xO_y$
Reducer: $CnH_{2m} + (2n+m)\ M_xO_y \rightarrow n\ CO_2 + m\ H_2O + (2n+m)\ M_xO_{y-1}$
Net reaction: $C_nH_m + ½\ (2n+m)\ O_2 \rightarrow n\ CO_2 + m\ H_2O + heat$

Process equipment must be designed and configured to accommodate the cyclic nature of chemical looping and enable the desired reactions to proceed sufficiently far for efficient fuel utilization and purity of the CO_2 stream. Interconnected fluidized bed systems can provide the necessary residence time and good solids/gas contacting for oxygen uptake and release, as well as enable efficient segregation of the solids from the gas streams using cyclones. The system design must also accomodate effective separation of ash for disposal. Operating conditions will be optimized to maximize fuel and heat utilization, as well as the economic life of the oxygen carrier, while minimizing excess air supply and other factors.

CHEMICAL LOOPING GASIFICATION

Chemical looping processes can also be used to produce hydrogen in combination with CO_2 capture. One form of a chemical looping gasification (CLG) system – a parallel transformational approach – integrates coal gasification and the water gas shift (WGS) reaction in two solid particle loops. The first loop is used to gasify the coal and produce syngas (H_2 and CO). A second solid loop is used in a WGS reactor. In this reactor, steam reacts with CO and converts it to H_2 and CO_2. The circulating solid absorbs the CO_2, thereby providing a greater driving force for the WGS reaction. The CO_2 is then released in a calcination step that produces nearly pure CO_2 for further compression and storage or use. Figure 3 provides a schematic diagram illustrating a two-loop CLG process.

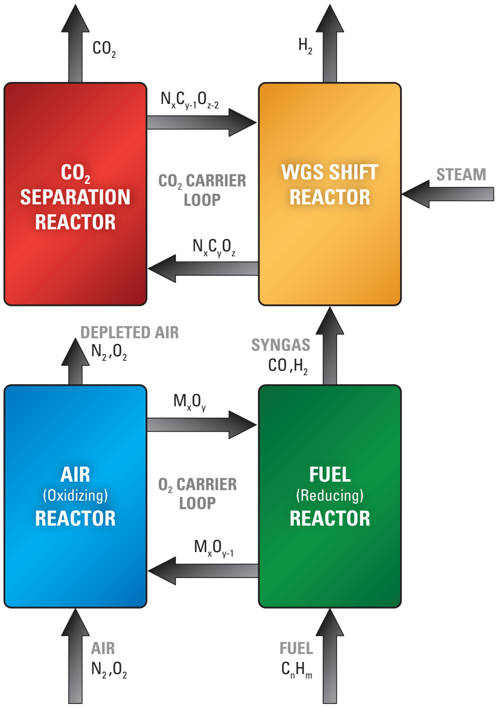

Figure 3: Two-Loop CLG Process

Chemical looping can also be used to enhance the production of hydrogen and CO_2 as part of a conventional gasifier system. With this type of configuration, a gasifier produces syngas that is then fed to a chemical looping process to convert the CO in syngas to CO_2 for removal and to produce additional hydrogen for power production or use as a chemical feedstock. R&D efforts are underway that consider various operating conditions, reactor configurations, looping characteristics, and feeds in CLG systems depending on the application. Because the oxygen carrier is a solid (not energy intensive to pressurize) and the gaseous fuel (i.e., syngas, natural gas) is usually already under pressure, it could be advantageous to operate the fuel reactor under pressure to increase the overall thermodynamic efficiency of the process.

Figure 4 illustrates the approach being taken by Ohio State University's (OSU) to develop a syngas chemical looping process. As indicated, iron is used as the oxygen carrier in this three-reactor process.

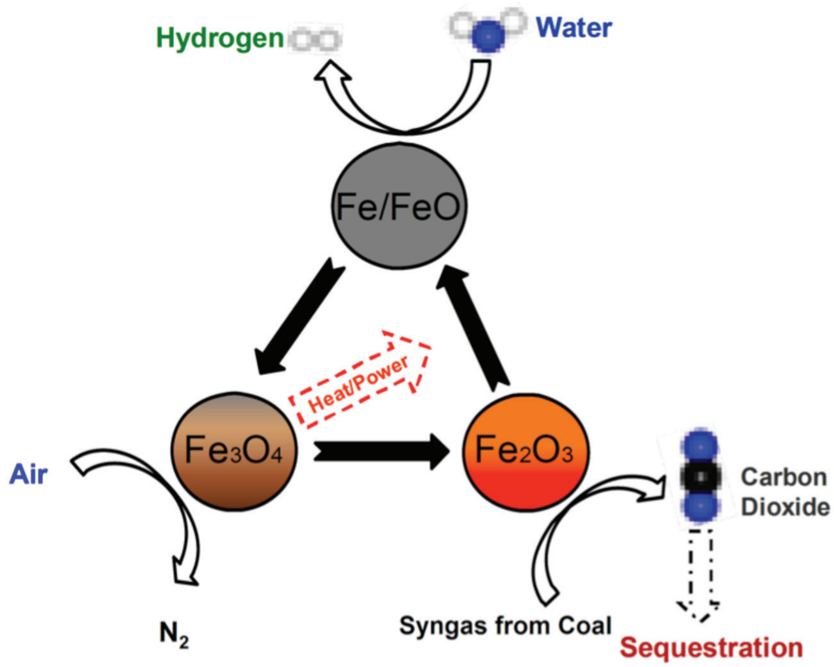

Figure 4: Schematic Diagram of OSU's Syngas Chemical Looping Process

CHEMICAL LOOPING R&D

Chemical looping is in the early stages of process development, and additional efforts are needed to foster the understanding required to prepare the technology for demonstration-scale testing. Bench- and laboratory-scale experimentation is being conducted. R&D is needed in four general areas: oxygen carrier characteristics, solids circulation strategy, reactor design, and overall system and process design, as shown in Table 2.

TABLE 2. R&D AREAS FOR CHEMICAL LOOPING

Oxygen Carrier	Solids Circulation	Reactor Design	System/Process Design
• Composition • Density • Reaction kinetics • Oxygen-carrying capacity • Fluidization properties • Attrition • Agglomeration • Sintering • Chemical, thermal, contaminant degradation	• Dilute pneumatic • Dense pneumatic • Mechanical • Flow control • Mechanical valves • Non-mechanical valves • Uncontrolled	• Gas cleaning • Process optimization • Thermal integration	• Gas cleaning • Process optimization • Thermal integration • Heat transfer strategy

Table 3 summarizes both completed and ongoing NETL/DOE chemical looping R&D projects. In addition, technology sheets with more detailed descriptions of each of these projects are provided in the Appendix.

TABLE 3. COMPLETED AND ONGOING DOE/NETL CHEMICAL LOOPING R&D PROJECTS

Project Focus	Participant	Status	Performance Period	Funding (Program)	Summary Description
FE/NETL Funding					
Calcium-Based Chemical Looping Combustion Technology	Alstom	Active	10/01/2012 - 09/30/2013	$1,249,989 Total $999,991 DOE (Adv. Comb.)	Techno-economic and gap analysis of advanced calcium-based CLC system that was successfully tested previously at 65 kW_{th}. Candidate for down selection under Advanced Combustion FOA.
Solid-Fueled Pressurized Chemical Looping	University of Kentucky	Active	10/01/2012 - 09/30/2013	$755,300 Total $599,687 DOE (Adv. Comb.)	Techno-economic and gap analysis of pressurized chemical looping combustor (PCLC) using iron-based oxygen carriers and combined cycle power production. Candidate for down selection under Advanced Combustion FOA.
Iron-Based-Coal Direct Chemical Looping	Babcock & Wilcox	Active	10/01/2012 - 09/30/2013	$1,400,000 Total $761,600 DOE (Adv. Comb.)	Techno-economic and gap analysis of iron-based coal-direct chemical looping (CDCL) process that was tested previously at 25 kWe. Candidate for down selection under Advanced Combustion FOA.
Coal-Direct Chemical Looping for Retrofits	Ohio State University	Active	01/01/2009 - 09/30/2013	$3,974,200 Total $2,855,052 DOE (Adv. Comb.)	Development of iron oxide (Fe_2O_3)-based CDCL process. Sub-pilot-scale (25 kWe) testing for 200 hours.
Magnetically Fluidized Chemical Looping	University of Florida	Active	10/01/2009 - 09/30/2013	$1,249,900 Total $999,920 DOE (Fuels)	Development of fluidized bed and magnetically stabilized bed reactor systems using chemical looping to separate hydrogen (H_2) and carbon dioxide (CO_2) from coal-derived syngas. Demonstrated high yields of H_2 and CO_2 over several looping cycles.
Simulation and Modeling for Oxy-Combustion and Chemical Looping	University of Utah	Active	09/10/2008 - 08/31/2013	$12,382,153 Total $9,905,726 DOE (Cong. Directed)	Development of Cu-based CLC system and simulation tools to predict performance with uncertainty. Completed extensive model validation and Cu attrition study.
Chemical Looping Combustion Technology	Alstom	Complete	09/30/2003 - 09/30/2012	$15,738,183 Total $12,590,547 DOE (Adv. Comb.)	Development of advanced calcium-based CLC system. Preliminary analysis shows less than 20% increase in cost of electricity. Successful testing conducted at 65 kW_{th}, with 12 hours of autothermal operation at 3-MW_{th}.
Chemical Looping Simulation and Control	Alstom	Complete	07/12/2007 - 07/31/2012	$2,068,281 Total $1,654,625 DOE (Adv. Comb.)	Development of computational models and optimizing control systems for chemical looping processes completed.
FE ARRA Funding					
ICMI – Chemical Looping	NETL-ORD	Active	11/15/2010 - 11/14/2014	$12.0M DOE (FE ARRA)	Construct and test lab-scale integrated CLC reactor system, characterize oxygen carriers, model development, and techno-economic studies. Reactor systems, numeric simulations, and techno-economic studies in progress.
Novel CLC Oxygen Carriers	Western Kentucky University	Complete	12/01/2009 - 11/30/2012	$300,000 DOE (FE ARRA)	Development of Cu-based oxygen carriers using aluminum oxide (Al_2O_3) and titanium oxide (TiO_2) as the substrate. Tested in 10-kW hot-model CLC facility.
ARPA-E Funding					
Syngas Chemical Looping (SCL) – ARPA-E	Ohio State University	Active	04/01/2010 - 09/30/2014	$7,800,000 Total $7,100,000 DOE (APRA-E)	Development of Syngas Chemical Looping for coal and biomass gasification using ferric oxygen carrier and high-pressure reactor. Design of 250-kWth pilot-scale unit, with testing at NCCC.

APPENDIX:
CHEMICAL LOOPING PROJECTS

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ALSTOM'S CHEMICAL LOOPING COMBUSTION TECHNOLOGY WITH CO_2 CAPTURE FOR NEW AND EXISTING COAL-FIRED POWER PLANTS

primary project goals

Progression of the development of an advanced chemical looping combustion (CLC) system for coal-fired power generation that removes greater than 90 percent of the carbon dioxide (CO_2) with a less than 20 percent increase in the cost of electricity (COE).

technical goals

- Advance the development of the chemical looping technology using economic and engineering studies as a screening tool for process and equipment improvements.
- Perform engineering and economic analysis on the effects of operating pressure on the COE to determine the most practical, cost-effective configuration.
- Perform engineering analysis to determine practical methods and limitations of achieving pressurized operations.
- Perform engineering analysis and bench-scale testing to investigate possible process improvements.

technical content

Alstom Power will investigate improvements to a unique CLC system previously developed for CO_2 capture and separation. Alstom's Limestone Chemical Looping Combustion (LCL-CTM) technology has progressed though research conducted in the past 10 years under previous projects (DE-NT0005286, NT41866). The LCL-C technology is applicable for use in new plants or retrofit to existing pulverized coal (PC)-fired and circulating fluidized bed (CFB) power plants.

CLC utilizes a metal oxide or other compound, in this case limestone ($CaSO_4$), as an oxygen carrier to transfer oxygen from the combustion air to the fuel. Since direct contact between fuel and combustion air is avoided, the products of combustion (CO_2 and water) are kept separate from the rest of the flue gases (primarily nitrogen). CLC splits combustion into separate oxidation and reduction reactions. The carrier releases oxygen in a reducing atmosphere to react with the fuel. The carrier is then recycled back to the oxidation chamber to be regenerated by contact with air. Calcination of hot solids produced in the oxidation reactor produce a concentrated stream of CO_2 in lieu of the dilute CO_2 stream typically found in flue gas from coal-fired power plants.

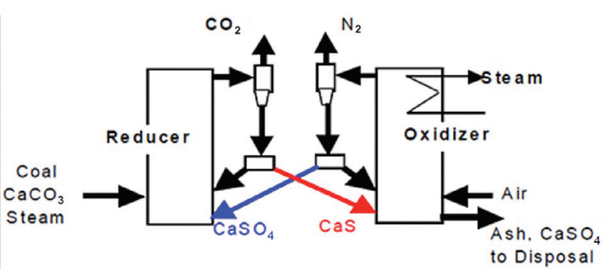

Figure 1: Limestone-Based CLC Process

technology maturity:

Bench-Scale

project focus:

Chemical Looping Combustion Technology

participant:

Alstom Power

project number:

FE0009484

NETL project manager:

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partners:

N/A

performance period:

10/1/12 – 9/30/13

Prior R&D (in DOE project DE-NT0005286), Alstom scaled-up the limestone-based CLC process from a 65-kWth pilot, which was successfully demonstrated in an earlier project (DOE project NT41866), to a 3-MWth prototype facility that was operational in 2010 and 2011. Alstom was able to operate the 3-MWth prototype for 12 hours under autothermal conditions, using only coal as fuel, achieving 96% capture of CO_2.

The current R&D effort, Phase I work for project DE-FE0009484, will include economic evaluations of four LCL-C plant configurations. The base case for the study will be a previously developed CLC plant that will be updated to a current U.S. Department of Energy (DOE) economic basis. It will be used for comparison against other alternatives for the techno-economic studies in this project. A second case will determine the effect of designing the reducer reactor using standard CFB gas velocities. A third case will investigate the effect of using a pressurized reduction reactor, which reduces the reactor size and the amount of compression required for the CO_2 outlet gas stream. A fourth case will investigate the use of an advanced ultra-supercritical (USC) steam cycle for the chemical looping system. The advanced USC steam cycle should increase overall plant efficiency and lower the COE. Mass and energy balances will be performed for each case. The four LCL-C cases will be compared against a base case study of a supercritical PC plant without CO_2 capture.

In conjunction with the economic evaluations, Alstom will conduct a series of engineering studies focusing on equipment performance and selection for pressurized reducer operation, as well as investigating several potential areas for process improvement. Specific systems targeted include solids and fuel management with a pressurized reactor, and methods for accommodating a high-pressure differential between two connected reactors under steady state and load change conditions. Areas of study for process improvement include the sensitivity of the plant efficiency to reducer pressure, the effect of reducer pressure on reaction kinetics, impact and methods for maximizing carbon retention in the reducer, and enhanced oxygen carrier performance.

technology advantages

- Air separation unit (ASU) is not required for oxygen production.
- CO_2 separation takes place during combustion.

R&D challenges

- Scale-up issues.
- Solids handling and transport.
- Oxygen carrying and reactivity.

results to date/accomplishments

Project DE-FE0009484
- Engineering on LCL-C™ Case 1 was completed.
- Material and energy balances for the LCL-C Islands have been completed for the other three cases.

Project DE-NT0005286
- Detailed preliminary engineering completed.
- Installation of prototype unit completed.
- Shakedown and testing of prototype unit complete.

next steps

- Thermoflow (thermal engineering software) models will be developed for each LCL-C plant configuration and used to produce detailed mass and energy balances along with predicted performances.
- Engineering studies will be conducted to focus on equipment performance and selection for pressurized reducer operation, as well as to investigate several potential areas for process improvement.
- A technology gap analysis will be conducted for the five cases investigated.

available reports/technical papers/presentations

Abdullaly, I., et.al, "Alstom's Calcium Oxide Chemical Looping Combustion Prototype for CO_2 Capture from Existing Pulverized Coal Fired Power Plants," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012. *http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/3-Wednesday/I%20Abdulally-Alstom-CLC%20Prototype.pdf*.

Andrus, H., "Alstom's Calcium Oxide Chemical Looping Combustion Prototype Development," presented at the 2010 CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. *http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/wednesday/Herb%20Andrus-NT0005286.pdf*.

Andrus, H., "Chemical Looping Combustion Coal Power Technology Development Prototype," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/5286%20Alstom%20chemical%20looping%20%28Andrus%29%20mar09.pdf*.

Nsakala, N. Y. and Liljedahl, G. N., Greenhouse Gas Emissions Control by Oxygen Firing in Circulating Fluidized Bed Boilers, Alstom Power – U.S. DOE Report, PPL Report No, PPL-03-CT-09, 15 May 2003.

Andrus, H. E., Jr., et. al., Hybrid Combustion-Gasification Chemical Looping Coal Power Technology Development – Phase 1 Final Report, U.S. DOE, December 29, 2004.

Andrus, H. E., Jr., et. al., Hybrid Combustion-Gasification Chemical Looping Coal Power Technology Development – Phase II Final Report, U.S. DOE, June 9, 2006.

SOLID-FUELED PRESSURIZED CHEMICAL LOOPING WITH FLUE GAS TURBINE COMBINED CYCLE FOR IMPROVED PLANT EFFICIENCY AND CO_2 CAPTURE

primary project goals

The University of Kentucky Center for Applied Energy Research (UK-CAER) will investigate a heat-integrated, coal-based combined cycle for power generation using a pressurized chemical looping combustor (PCLC). The PCLC system aims to produce high-temperature flue gas for electricity generation through a gas turbine and a heat recovery unit combined with a conventional steam cycle. The cost-effectiveness and efficiency of the process using iron-based oxygen carriers (OCs) will be examined.

technical goals

- Validate the PCLC process application for power generation through engineering system and economic analysis.
- The University of Kentucky will design and cost a 200-kW PCLC pilot plant based on the results of the data analysis and cost estimates from the 550-MW, commercial-scale economic case study.
- Demonstrate an advanced coal-based power generation technology to potentially meet U.S. Department of Energy (DOE) targets for cost of electricity (COE) while capturing at least 90% of the carbon dioxide (CO_2) released during combustion of fossil fuels.

technical content

UK-CAER is developing a heat-integrated, coal-based combined cycle system for highly efficient power generation. This system will use a PCLC to produce high-temperature flue gas for electricity generation through a gas turbine and a heat recovery unit for supercritical steam production to drive a conventional steam cycle. The PCLC consists of two reactors: (1) an Oxidizer, in which oxygen from air is selectively fixed into an oxygen-carrier structure; and (2) a reducer (Redox), in which coal is burned by the OC. The PCLC will generate two gas streams: (1) a high-temperature, high-pressure, alkali-free clean gas from the oxidizer used to drive an aero-turbine (Brayton Cycle) followed by a heat-recovery steam generator (HRSG) for a Rankine Cycle; and (2) a small-volume, CO_2-enriched stream from the Redox for storage or beneficial use. In addition, the system will use a cost-effective, abundant, iron-based OC. With the presence of water vapor in the CLC system, iron-based OCs show moderate reactivity and capacity, as well as a high resistance to water vapor, ash, and attrition.

technology maturity:

Laboratory-Scale

project focus:

Solid-Fueled Pressurized Chemical Looping

participant:

University of Kentucky

project number:

FE0009469

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performance period:

9/25/12 – 9/30/13

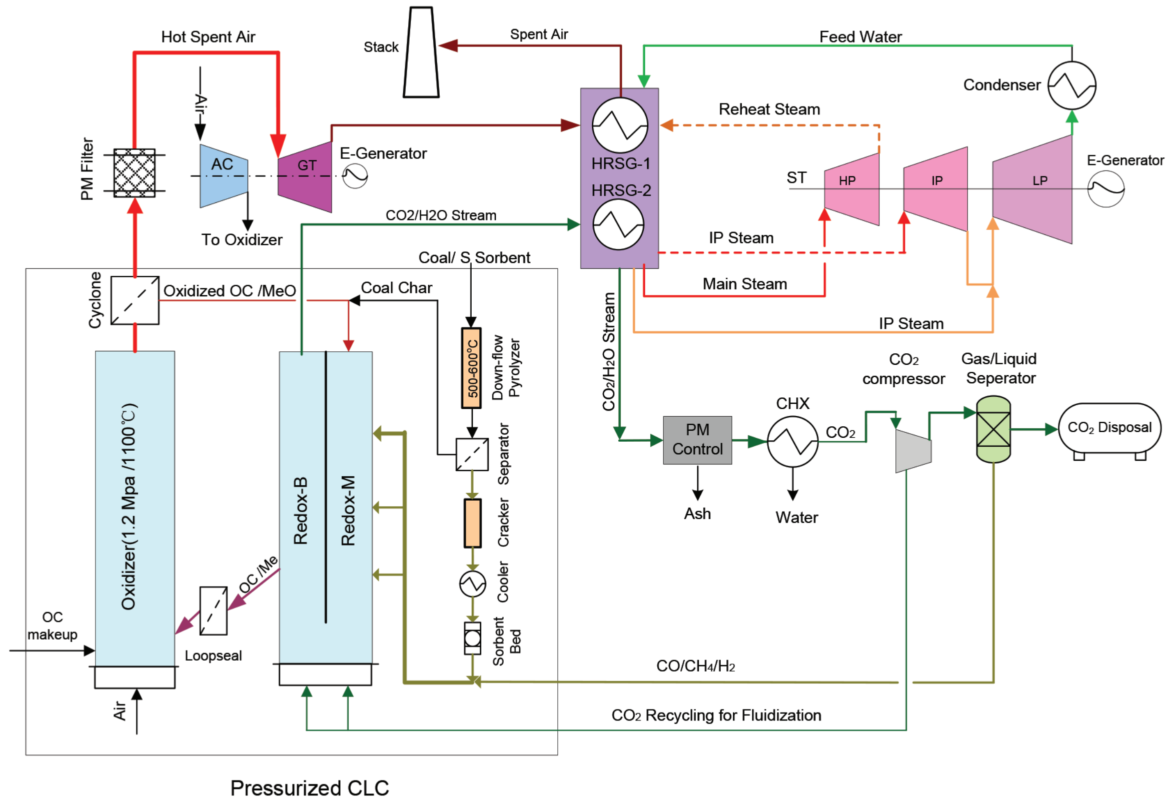

Figure 1: The PCLC Process Under Development

Additionally, the system will address known technical obstacles that impede the application of CLC to solid fuels by including: (1) the use of pulverized coal (PC) to increase reaction kinetics and facilitate separation of the spent OC from the solid coal residues (ash/carbon); (2) the use of a moderate-temperature pyrolyzer to suppress carrier agglomeration and reduce pollutants (≈96% of the mercury [Hg] and portions of the sulfur and alkali); and (3) division of the Redox into two chambers, a down-flow moving bed acting as a gasifier and a partial-reduction reactor for the OC, and a low-velocity bubbling bed serving as a deep-reduction reactor and a device for separating the reduced OC from the solid coal residues on the basis of density and particle size. Flue gas from the Redox (primarily CO_2 and H_2O with a limited quantity of CO and hydrogen [H_2]) will be compressed to the CO_2 critical point at which the H_2O, carbon monoxide (CO), and H_2 are removed, leaving a concentrated CO_2 stream (>95%). Heat transfer units are not needed in the Oxidizer or Redox, thereby avoiding the corrosion and erosion associated with heat-transfer surfaces.

technology advantages

- Simplicity with only one solid recirculation loop (a fast bed as oxidizer and a moving/bubbling bed as reducer and OC/ash separator).
- A relatively small volume of coal impurity-contaminated gas produced in the Redox M/B that is less costly to treat.
- Flue gas turbine combined cycle that eliminates the need to install heat-transfer surfaces inside pressure vessels for temperature control, thereby eliminating their associated corrosion/erosion problems.
- A cost-effective, iron-based OC produced from an industrial waste stream.
- Reduced reactor size and lower power requirements for compression of the enriched-CO_2 stream due to the elevated operation pressure (1.7 MPa).

R&D challenges

- Cost-effective, iron-based OCs to compensate for the large makeup rate due to the OC attrition and de-activation by coal impurities.
- Reaction kinetics improvement for oxidation and reduction of iron-based OC to reduce solid inventory and reactor size.
- High conversion of solid fuel and near-complete combustion of gaseous products from solid fuel in-situ gasification to improve coal conversion (combustion) efficiency and to lower down-stream cost for separation gaseous fuel from the CO_2 stream.
- Effective separation of OC particles from mixtures of OCs and solid fuel ash.
- Systems to control and monitor gas-solid flow, reaction, and energy distribution in the two reactors under elevated pressure.
- Effective pollutant removal in the Redox to avoid sulfur/nitrogen oxides (NO_x)/alkaline metal/mercury accumulation in the system.
- Integration of high-quality energy from CO_2 stream into HRSG-steam turbine system.
- Cost-effective technology to produce appropriate OCs with particle size between 200 to 500 µm.

results to date/accomplishments

- The University of Kentucky developed rate-based reactor models for the PCLC of coal that were integrated into the ASPEN model for the 550-MWe simulation based on the UK-CAER and Southeast University (China) bench- and pilot-scale experimental results.
- The Technology Engineering Design Interim Report for the proposed 550-MWe integrated PCLC combined-cycle process was completed.
- Process and major components designed for pilot scale (200kWth) for proposal to the next research phase.

next steps

- The technical and economic analysis for the proposed combined cycle will be completed.
- Technology gap analysis will be performed.

available reports/technical papers/presentations

Liu, K., "Solid-Fueled Pressurized Chemical Looping with Flue-Gas Turbine Combined Cycle for Improved Plant Efficiency and CO_2 Capture," Kickoff Meeting presentation, Pittsburgh, Pennsylvania, October 2012. *http://www.netl.doe.gov/technologies/coal-power/ewr/co2/oxy-combustion/FE0009469-kickoff-caer.pdf*.

COMMERCIALIZATION OF THE IRON-BASED COAL-DIRECT CHEMICAL LOOPING PROCESS FOR POWER PRODUCTION

primary project goals

The Babcock and Wilcox Power Generation Group, Inc. (B&W) will validate the iron-based coal-direct chemical looping (CDCL) process and evaluate its potential as a cost-effective carbon dioxide (CO_2) capture technology for electric power generation.

technical goals

- Develop a commercial plant design concept.
- Perform a techno-economic evaluation of the commercial design.
- Identify technology gaps.
- Develop a preliminary design and budget estimate for a suitable pilot facility that will address the technology gaps and provide additional information to advance its technology readiness level.

technical content

B&W, in collaboration with Ohio State University (OSU) and Clear Skies Consulting, is developing an advanced, iron-based CDCL process. Over the past 10 years, OSU has developed a proprietary iron oxide (Fe_2O_3)-based composite oxygen carrier particle that is 10 times more reactive than pure Fe_2O_3 and is recyclable for more than 100 reduction-oxidation cycles without loss in reactivity. The CDCL process developed at OSU evolved from a novel concept to an integrated sub-pilot (25 kilowatt thermal [kWth])-scale system with more than 200 hours of successful continuous operation studying various kinds of coal.

The CDCL process consists of a unique moving bed reduction reactor where coal reacts with the iron-based oxygen carrier particles to form normal combustion products, predominantly CO_2 and H_2O, while reducing the oxygen carrier particles from iron (III) oxide (Fe_2O_3) to a mixture of iron (II) oxide (FeO) and iron (Fe). The reduced oxygen carrier particles are then sent to a combustor where they are regenerated with air. The oxygen carrier particle oxidation reaction (particle regeneration) releases large amounts of heat to generate steam for power generation. The CO_2 produced in the reducer is cooled, cleaned, and compressed for sequestration or to be used for enhanced oil recovery (EOR). The unique reactor design and reaction pathway of the CDCL process allows for repowering or greenfield installation. A preliminary techno-economic analysis indicated the CDCL process has the potential to achieve greater than 96% CO_2 capture with an increase in the cost of electricity (COE) of approximately 33%.

In Phase I, the project will validate the advanced CDCL process for power generation through a techno-economic analysis and development of a commercial-scale plant design. By leveraging laboratory and previous sub-pilot work, the project team will collect data regarding oxygen carrier particle and process performance.

technology maturity:

Sub-Pilot 25 kWth-Scale Demonstration

project focus:

Iron-Based Coal Direct Chemical Looping

participant:

Babcock & Wilcox

project number:

FE0009761

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partners:

The Ohio State University
Clear Skies Consulting

performance period:

10/1/12 – 9/30/13

A conceptual 550-megawatt electric (MWe) plant design will be developed. A previously developed Aspen Plus® process model will be updated to incorporate the commercial CDCL process parameters. Based on the process simulation results and the detailed plant cost estimate, a comprehensive economic analysis of the commercial CDCL plant will be conducted and the COE will be determined. A sensitivity analysis will be performed to evaluate the effects of changes to key process parameters on the project economics. A detailed process analysis will identify and quantify critical technology gaps requiring closure to establish the viability of the commercial CDCL plant.

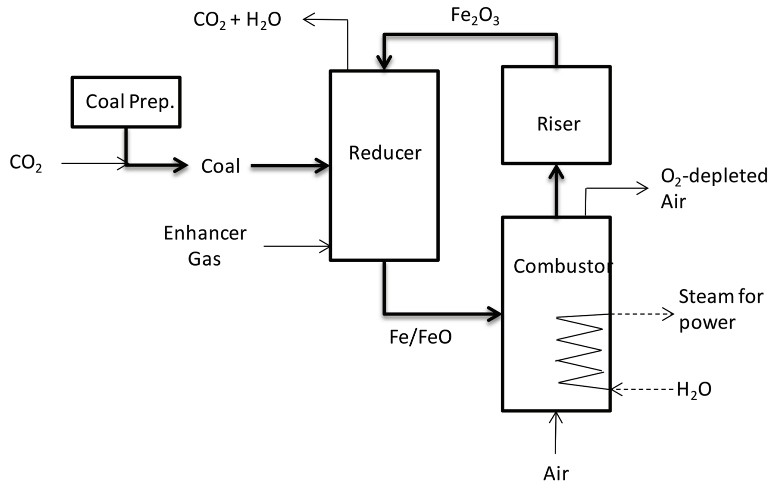

Figure 1: Simplified Schematic of the Coal Direct Chemical Looping Combustion Process

technology advantages

- Need for the air separation unit (ASU) is eliminated.
- The CDCL technology is applicable to both new and existing power plants.
- The process can be applied for repowering of existing plants, as the CDCL process requires no modification of the existing steam turbine cycle.

R&D challenges

- Reducer, combustor, and riser design and performance.
- Oxygen carrier particle formulation and performance.

results to date/accomplishments

- Completed the detail mass and energy balances.
- Completed conceptual 550-MWe commercial plant design.

next steps

- Develop a proposal-level cost for the commercial CDCL plant design and complete a comprehensive economic analysis of the plant.
- Determine the technical gaps separating the current CDCL technology and a commercial product that meets U.S. Department of Energy (DOE) goals.

available reports/technical papers/presentations

General project information is available on DOE National Energy Technology Laboratory (NETL) website at: *http://www.netl.doe.gov/technologies/coalpower/ewr/co2/oxy-combustion/cdcl-bw.html*.

COAL-DIRECT CHEMICAL LOOPING RETROFIT TO PULVERIZED COAL POWER PLANTS FOR IN-SITU CO_2 CAPTURE

primary project goals

Ohio State University (OSU) is developing an iron oxide (Fe_2O_3)-based chemical looping process for retrofit on existing coal-fired power plants.

technical goals

- Select optimum iron-based oxygen (O_2) carrier. Evaluate the reactivity, recyclability, and physical strength of different Fe_2O_3-based O_2 carrier particle compositions.
- Demonstrate bench-scale (2.5 kWth) coal-direct chemical looping (CDCL) system including fuel reactor demonstration and coal char and volatile conversion. Determine optimum fuel reactor operating conditions to gasify coal char using O_2 carrier particle.
- Demonstrate sub-pilot-scale (25 kWth) CDCL system including integration of fuel reactor and combustor with continuous solid circulation at reaction temperature. Operate integrated sub-pilot system for a minimum of 50 continuous hours with the optimal O_2 carrier. Determine the fate of nitrogen oxide (NO_x) and sulfur via integrated system testing.
- Conduct ASPEN simulation based on the CDCL test results.
- Conduct techno-economic study.

technical content

Researchers at OSU are developing a one-step CDCL process to produce electric power and high-purity carbon dioxide (CO_2) in retrofit power plant applications. While preliminary tests with the bench-scale reactor have shown 90 to 95% coal char conversion and >99% volatile conversion, the primary focus of this project is to identify the optimal O_2 carrier chemical composition and conduct integrated, continuous CDCL testing at the sub-pilot (25 kWth) scale.

As shown in Figure 1, the CDCL system consists of a fuel reactor and a combustor. The moving-bed fuel reactor utilizes a countercurrent gas-solid contacting pattern to maximize the conversion of the Fe_2O_3-based O_2 carrier, as it transfers O_2 to facilitate coal combustion. The combustor, an entrained-flow reactor, uses air to pneumatically transport the O_2 carrier back to the fuel reactor, while re-oxidizing the O_2 carrier and generating a significant amount of heat. A portion of the heat generated in the combustor is used for steam generation via the high-temperature exhaust gas, while the remainder is carried to the fuel reactor by the hot regenerated particles to supply the heat required for coal combustion.

The O_2 carrier consists primarily of Fe_2O_3 based on earlier tests that showed an acceptable O_2 capacity and no loss of activity during more than 100 redox cycles in a thermogravimetric analyzer (TGA) test. To optimize the reactivity, recyclability, and physical strength of the Fe_2O_3-based O_2 carrier for the CDCL process, OSU researchers evaluated the perfor-

technology maturity:
Laboratory-Scale

project focus:
Coal-Direct Chemical Looping for Retrofits

participant:
Ohio State University

project number:
NT0005289

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Clear Skies Consulting
CONSOL Energy Inc.
Shell/CRI/Criterion Inc.
Air Products and Chemicals Inc.

performance period:
1/1/09 – 9/30/13

mance of different support materials and promoters using a TGA and a fixed-bed reactor. These initial screening experiments were used to select the 10 most reactive and recyclable particle compositions, which were subjected to additional reactivity and physical strength tests. These 10 particles were tested to measure their reactivity with coal char in an inert environment and their tolerance to carbon deposition using a TGA. The particles were then pelletized for further evaluations, such as pellet strength and reactivity, using a fixed-bed. After eliminating pellets with unacceptable strength and reactivity, the five most promising Fe_2O_3-based composite O_2 carrier particles were identified.

Bench-scale (2.5 kWth) testing of the five most promising O_2 carrier particle compositions in a moving-bed reactor will be used to determine the optimal O_2 carrier particle composition for the CDCL process. A series of bench-scale tests have been conducted for more than 100 hours.

Using the sub-pilot-scale (25 kWth) testing unit shown in Figure 2, the integrated CDCL process will be evaluated during a minimum of 50 hours of continuous operation with the optimal O_2 carrier particle composition. During testing, OSU researchers will monitor the composition of outlet gases (including CO_2, sulfur dioxide [SO_2], and NO_x), attrition of the O_2 carrier, and the ash separation effectiveness of the cyclone system.

To quantify the performance and potential benefits of the CDCL process, detailed modeling and a techno-economic analysis of the system will be conducted by CONSOL Energy.

technology advantages

- An air separation unit is not required for O_2 production.
- CO_2 separation simultaneously takes place with the coal conversion.
- The CDCL process is a versatile technology that can produce power, synthesis gas (syngas), or hydrogen (H_2), while offering fuel flexibility.

R&D challenges

- Scale-up issues.
- Solids handling and transport.
- O_2 carrier capacity, reactivity, and attrition.
- Slow reaction rates between the O_2 carrier and coal char.
- Ash management.

results to date/accomplishments

- Completed analyses for selection of optimum O_2 carrier and support particle. Identified five Fe_2O_3-based O_2 carrier particles. Testing of the O_2 carrier particles included evaluation of recyclability, carbon deposition tolerance, reaction with coal char, and pellet strength and reactivity.
- Demonstrated coal conversion by O_2 carrier using a TGA for solids analysis and a fixed-bed experiment for gas analysis.
- Conducted bench-scale testing (2.5 kWth) of coal char conversion. Studied the effects of H_2O (steam) and CO_2 as gasification enhancers on metallurgical coke char with the goal to determine the optimum O_2 carrier. Achieved 97% char conversion with H_2O (steam) as the gasification enhancer and 88% char conversion with CO_2 as the gasification enhancer.
  - The conditions that produce the highest conversion are the use of steam as an enhancer gas, higher temperatures, higher char residence times, and higher O_2 carrier to char ratios. However, all of these factors need to be optimized, since a high residence time will result in a larger, more capital-intensive setup, and a higher temperature will result in possible sintering of particles. Furthermore, the use of steam is a parasitic energy requirement, so conversion using steam needs to be controlled.
- Conducted solid handling and gas sealing study for sub-pilot-scale demonstration using the cold model reactor. Demonstrated the robustness of the 25-kWth sub-pilot unit for coal conversion for more than 830 hours of operation, which includes a 200-hour continuous operation. Results show nearly 100% CO_2 purity with a steady fuel conversion greater than 95%.

- Results indicate the ability to capture carbon without the need for a carbon-stripping step for incomplete carbon conversion or an oxygen-polishing step for the CO_2 stream. Performance of carbon capture in the CDCL system was determined using three fuels (metallurgical coke, sub-bituminous coal, lignite coal).
- Determination of the fate of sulfur and nitrogen pollutants for low-rank fuels such as sub-bituminous and lignite coals reveal the pollutants exit the system in the CO_2 stream and not in the spent air stream for lower-ranked coals (sub-bituminous and lignite).

next steps

- Continued integrated 25-kWth sub-pilot demonstration with varied operating parameters.
- Conduct ASPEN simulation studies.
- Complete a techno-economic analysis.

available reports/technical papers/presentations

Kim, H.R.; Wang, D.; Zeng, L.; Bayham, S.; Tong, A.; Chung, E.; Kathe, M. V.; Luo, S.; McGiveron, O.; Wang, A.; Sun, Z.; Chen, D.; Fan, L.-S., "Coal direct chemical looping combustion process: Design and operation of a 25-kWth sub-pilot unit," Fuel 108 (2013) 370–384.

Bayham, S. C.; Kim, H. R.; Wang, D.; Tong, A.; Zeng, L.; McGiveron, O.; Kathe, M. V.; Chung, E.; Wang, W.; Wang, A.; Majumder, A.; Fan. L.-S., "Iron-Based Coal Direct Chemical Looping Combustion Process: 200-h Continuous Operation of a 25-kWth Subpilot Unit," Energy Fuels 27 (2013) 1347-1356.

Tong, A.-S., "Coal Direct Chemical Looping Retrofit to Pulverized Coal Power Plants for In-situ CO_2 Capture," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012. *http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/3-Wednesday/LS%20Fan-OSU-CDCL.pdf*.

Fan, L.-S., "Coal Direct Chemical Looping Retrofit to Pulverized Coal Power Plants for In-situ CO_2 Capture," presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, August 2011. *http://www.netl.doe.gov/publications/proceedings/11/co2capture/presentations/3-Wednesday/24Aug11-Fan-OSU-Coal%20Direct%20Chem%20Looping.pdf*.

Fan, L.-S., "Chemical Looping Systems for Fossil Energy Conversions," John Wiley & Sons, Inc., Hoboken, NJ, USA, October 2010. *http://www.wiley.com/WileyCDA/WileyTitle/productCd-0470872527.html*.

Kim, R., "Coal Direct Chemical Looping (CDCL) Retrofit to Pulverized Coal Power Plants for In-Situ CO_2 Capture," presented at 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. *http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/wednesday/Ray%20Kim-NT0005289.pdf*.

Kim, R., "Coal Direct Chemical Looping Retrofit for Pulverized Coal-fired Power Plants with In-Situ CO_2 Capture," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/wednesday/Ray%20Kim-NT0005289.pdf*.

MAGNETICALLY FLUIDIZED BED REACTOR DEVELOPMENT FOR THE LOOPING PROCESS: COAL TO HYDROGEN PRODUCTION R&D

primary project goals

The University of Florida (UF) is developing novel fluidized bed and magnetically stabilized bed reactor systems that use a chemical looping process with metal oxide sorbents to separate hydrogen (H_2) and carbon dioxide (CO_2) from coal-derived synthesis gas (syngas).

technical goals

- Conduct laboratory-scale testing to investigate chemical, heat, and mass transfer in the fluidized and magnetically stabilized bed reactors, and develop modeling/simulation tools.
  - Determine optimal reaction pathways and operation conditions for iron (Fe)- and alloyed Fe-metal oxide powders in both reducing and oxidizing environments.
  - Evaluate the chemical kinetics for reaction pathways.
  - Characterize chemical, thermal, and fluid transport properties of fluidized bed and magnetically stabilized bed reactors.
  - Investigate reactivity and durability of Fe, Fe/zirconia (Zr), and Fe/magnesium oxide (MgO).
  - Conduct a techno-economic analysis.
- Design, construct, and operate a bench-scale system to further evaluate the viability of the process upon successful completion of the laboratory-scale testing

technical content

The metal oxide looping process is a two-step process; in its simplest form, steam is injected into a reactor containing a reduced metal oxide (e.g., iron oxide [FeO]). The steam oxidizes the FeO to produce magnetite (Fe_3O_4), and high-purity H_2 is liberated. The H_2 is captured by condensing the water vapor from the steam and H_2 mixture. In the second step, the Fe_3O_4 must be reduced so that water splitting can proceed in a cyclic manner. The looping process uses carbon monoxide (CO) produced from the gasification of coal to reduce the Fe_3O_4. The advantages of the chemical looping process are that the H_2 produced via water splitting is highly pure, and the reduction step can be accomplished at sufficiently low temperature (400 to 850°K) to enable a commercially viable reactor. The highly concentrated CO_2, produced during the reduction step, is suitable for sequestration.

Research efforts focus on detailed thermal management throughout the process to enable efficient recuperation of heat; advanced reactor design that enables rapid kinetics; Fe or other metal powders that are stable and highly reactive over thousands of cycles; and operation in thermodynamically favorable regimes to maximize H_2 production and minimize the formation of Fe-carbide compounds. The successful design of an efficient and cost-effective chemical reactor will ensure rapid kinetics, a homogenized thermal field, a high production rate, uniform solids distribution, completed reaction pathways, and low-pressure drop with minimal energy consumption.

technology maturity:
Laboratory-Scale

project focus:
Magnetically Fluidized Chemical Looping

participant:
University of Florida

project number:
FE0001321

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partners:
N/A

performance period:
10/1/09 – 9/30/13

The fluidization of magnetic powders has received considerable attention in the literature. The majority of the fluidization approaches utilize magnetically assisted fluidization. In this process, a uniform steady magnetic field is applied to a conventional fluidized bed to stabilize it. The advantage of operating in this regime is that sintering, which occurs during the oxidation step, creates a fixed structure reactor that maintains a high porosity, surface area, favorable chemical kinetics, and low-pressure drop. The application of the magnetic field eliminates bubbling and serves to stabilize the fluidized bed to promote bed uniformity with favorable chemical kinetics. Magnetically stabilized fluidized beds provide enhanced uniformity of void fraction, enhanced heat transfer, and enhanced reactivity. In addition, a conventional fluidized bed reactor is studied for comparison with the magnetically stabilized bed. A blend of Fe and low-cost silica (SiO_2) powder is used to suppress particle sintering and sustain fluidization.

Figure 1 shows the process flow diagram for the chemical looping process. Coal is the input to the system, and the outputs consist of highly pure H_2 and highly concentrated CO_2 that is suitable for sequestration. The energy content of gasifier products and heat released during the oxidation step drives the complete chemical looping process. Steam at the desired temperature is obtained by using the high-temperature syngas. Treated syngas is reheated to the required reduction temperature using the raw syngas. Two identical reactors are used in the process in order to maintain a continuous stream of products. While one reactor operates in the oxidation mode producing H_2, the other reactor operates in the reduction mode regenerating the Fe bed.

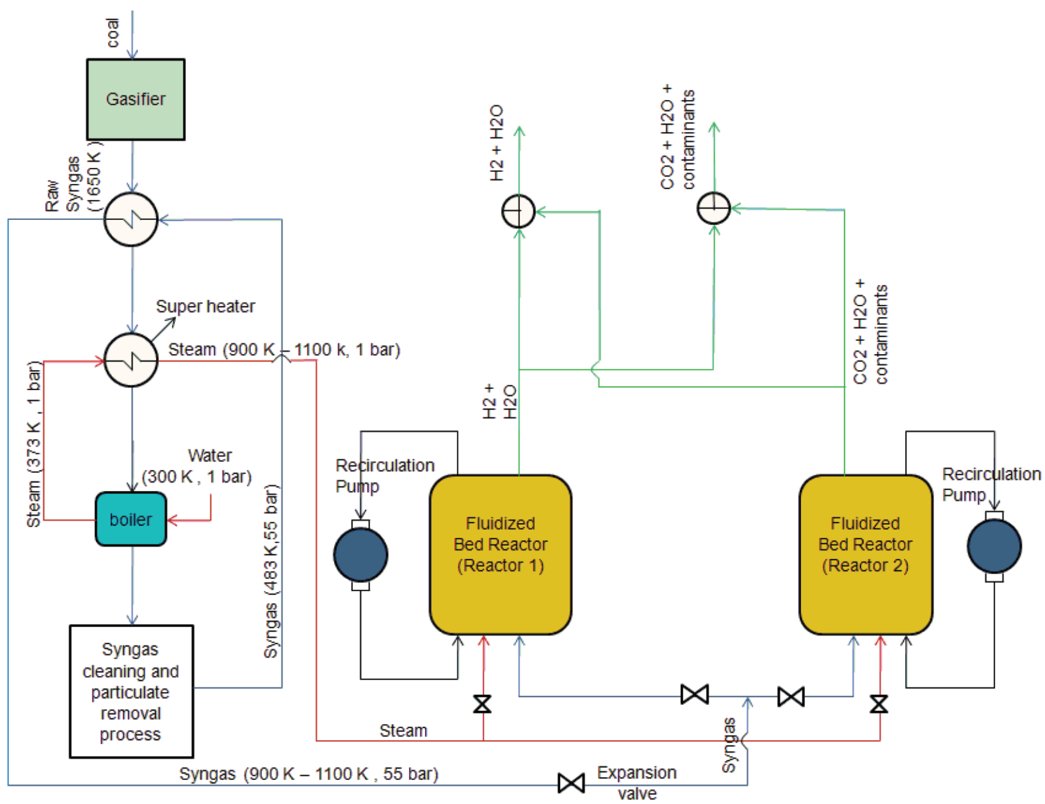

Figure 1: Process Flow Diagram of the Chemical Looping Process Using Cleansed Syngas for the Oxidation Step

A laboratory-scale, magnetically stabilized reactor has been fabricated, and its performance is being characterized. The cylindrical reactor shown in Figure 2 is fabricated with a quartz wall and can accommodate the upper operating temperature limit of the reactor (800°C). A porous ceramic frit is positioned at the entrance of the reactor in order to evenly distribute the flow. Two magnetic poles produce a transverse magnetic field and create magnetic chains of Fe particles within the bed. The magnetic chains repel each other, because of their polarity, and form a naturally porous structure. The reactants enter the reactor from the bottom and exit through the top. The reactor is insulated with high-temperature ceramic fiber insulation.

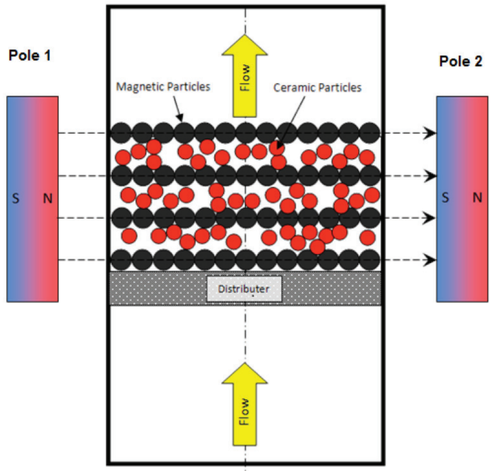

Figure 2: Magnetically Stabilized Bed Reactor [2]

This novel reactor has inherent advantages. It exploits the particle sintering during the oxidation step to form a stable porous structure. The high porosity favors chemical reaction and low-pressure drop through the bed. A first principle-based model has been developed that takes fluid momentum, thermal, and species transport into consideration. The model has been validated with the experimental measurements in the lab- and bench-scale reactors over a wide range of operating conditions. The computational results from the model provide reliable predictions for the large-scale throughput in a scaled-up design.

technology advantages

- Chemical looping enables extraction of high-purity H_2 and sequestration-ready CO_2 from syngas near gasification operating conditions to obtain improved thermal efficiency over more traditional gas separation methods that operate at low temperatures and pressures.
- Metal oxide sorbents with magnetic properties significantly reduces pressure drop, provides more uniform solids distribution, and aid in solids transport within the magnetically stabilized bed reactors.
  - A uniform stabilized bed with no large voids can be sustained, thus more uniform flow through the bed is established.
  - Uniform porosity results in uniform temperature field within the reactor bed.
  - Large surface area available to enhance reaction rate per unit volume.
  - The bed stabilization characteristics can be controlled through the magnetic input field configuration and strength.
  - High-velocity vapor flow can be sustained without the risk of caring the particles out of the reactor and damaging the structure.
  - Stoichiometric flow can be sustained.

R&D challenges

- Iron powders have a tendency to sinter at high temperature, which inhibits chemical reactions.
- Maintaining stability of powder reactivity over many cycles.
- Multi-scale, multi-physics modeling effort is required.

results to date/accomplishments

- Completed a comprehensive parametric chemical equilibrium study for the chemical looping cycle based on Fe and Fe oxides. A thermodynamic investigation of the H_2 production step indicates that H_2 is favored at low temperatures with steam to H_2 conversion exceeding 90% at reaction temperatures below 700°K. The H_2 yield is independent of pressure.
- Constructed and tested a laboratory-scale experimental system to evaluate H_2 and CO_2 productions performance in the magnetically stabilized bed reactor. Investigated the optimum conditions for providing the best reaction results using magnetically stabilized porous matrix of Fe-SiO_2.

- Devised three distinct plant layouts for reaction temperature ranges of 500 to 900°K, 900 to 1,100°K, and 1,100 to 1,200°K, respectively. Results from a thermal management study for the proposed chemical looping process indicate that no external energy is needed for looping cycle based H_2 production, but system configurations vary with temperature. Simulation of multiple cycles indicates that temperatures in the 900 to 1,000°K range will maximize H_2 yield.
- Demonstrated a high yield of H_2 and CO_2 productions within the magnetically stabilized bed reactor over several looping cycles.
- The fluidization regimes, bed expansion, and pressure drop were measured over a range of mass flux, mixture concentration, and magnetic field strength.
- Hydrogen production, as well as the reduction kinetic rate, has been measured over many redox cycles.
- Fundamental kinetic studies were completed, and a reaction rate law that is consistent with observation has been constructed.
- A Fortran-based multi-physics simulation code was developed to model reactive flows during oxidation and reduction in magnetically stabilized beds.
- Economical analysis on the operation cost is performed, and the hydrogen production cost is determined to be less than \$1.6/kg_{H2}.

next steps

Large-scale reactor design and system control.

available reports/technical papers/presentations

Mehdizadeh, A.; Klausner, J. F.; Mei, R.; and Barde, A., "Enhancement of thermochemical hydrogen production using an iron-silica magnetically stabilized porous structure." International Journal of Hydrogen Energy, 37:8954-8963, 2012. *http://www.sciencedirect.com/science/article/pii/S036031991200554X*.

Mehdizadeh, A.M., et.al, "Investigation of hydrogen production reaction kinetics for an iron-silica magnetically stabilized porous structure," International Journal of Hydrogen Energy, 37(18): 13263-13271, 2012. *http://www.sciencedirect.com/science/article/pii/S0360319912016126*.

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Allen, K.; Mehdizadeh, A. M.; Klausner, J. F.; and Coker, E. N., "Study of a Magnetically Stabilized Porous Structure for Thermochemical Water Splitting via TGA," High-Temperature-XRD, and SEM Analyses, Industrial & Engineering Chemistry Research, 52 (10): 3683-3692, 2013. *http://pubs.acs.org/doi/abs/10.1021/ie302691e*.

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DEVELOPMENT OF COMPUTATIONAL APPROACHES FOR SIMULATION AND ADVANCED CONTROLS FOR HYBRID COMBUSTION-GASIFICATION CHEMICAL LOOPING

primary project goals

Alstom set out to develop advanced computational models and optimizing control systems for chemical looping processes.

technical goals

- Identify sensor and control needs for chemical looping processes.
- Develop process simulation models with dynamic capability to evaluate control methods.
- Incorporate advanced process controls into the chemical looping plant design process.
- Investigate advanced process controls for complex solids flow and gas pressure control.
- Develop a control system design concept for the chemical looping prototype facility.

technical content

Alstom set out to develop advanced computational models and optimizing control systems for chemical looping processes, such as the hybrid combustion-gasification process shown in Figure 1. Chemical looping is a two-step process which first separates oxygen (O_2) from nitrogen (N_2) in an air stream in an air reactor. The O_2 is transferred to a solid oxygen carrier. The oxygen is carried by the solid oxide and is then used to gasify or combust solid fuel in a separate fuel reactor. As shown in Figure 1, a metal or calcium material (oxygen carrier) is burned in air forming a hot oxide (MeOx or CaOx) in the air reactor (oxidizer). The oxygen in the hot metal oxide is used to gasify coal in the fuel reactor (reducer), thereby reducing the oxide for continuous reuse in the chemical looping cycle.

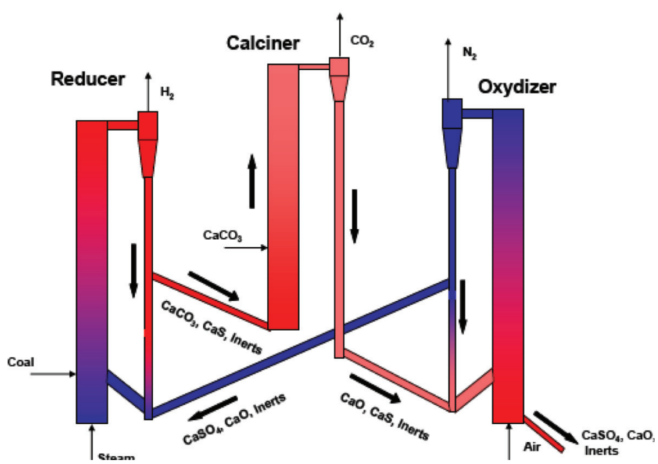

Figure 1: Alstom's Hybrid Combustion-Gasification Process

technology maturity:
Laboratory-Scale

project focus:
Chemical Looping Simulation and Control

participant:
Alstom Power

project number:
FC26-07NT43095

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partners:
Taft Engineering, Inc.
University of Illinois Urbana-Champaign (UIUC)

performance period:
7/12/07 – 7/31/12

Chemical looping is applicable to both new and retrofit plants and has the flexibility to be designed in a number of configurations. The reactor can be operated in a partial combustion mode, to generate a carbon monoxide (CO)-rich synthesis gas (syngas) which in another variant can be shifted to produce hydrogen (H_2). Alternately, it can operate in full combustion mode, resulting in exhaust of carbon dioxide (CO_2) and water. The three main configurations are: Option 1, chemical looping combustion with CO_2 capture; Option 2, chemical looping gasification with downstream CO_2 capture; and Option 3, chemical looping gasification to produce H_2 with inherent CO_2 capture.

Chemical looping is a process with multiple material and energy streams inter-connected between the multiple reactors. In order to obtain and maintain optimal conditions for operation with reduced waste stream volume and minimum required energy, advanced optimizing control systems are required. As such, process control development is needed to operate the system in a safe, integrated, and optimized fashion and is viewed as critical for enhancing the performance of the chemical looping system. This project worked to develop model-based controls that can be used to operate the system. Approaches to model development and control algorithms were developed by researchers at Alstom and the University of Illinois Urbana-Champaign (UIUC).

Alstom worked to develop computational models to gain a better understanding of the chemical looping process behavior and to develop control strategies, including: a two-loop, cold flow model; a dual-loop, hot flow model (without reactions); and a real-time, dual-loop simulator. The dual-loop simulation platforms are configured to test conceptual control designs. For example, it was used to investigate both linear and non-linear control concepts and evaluate control strategies with different sensors and actuators. In addition to working to develop process models and advanced controls applications, Alstom also worked on advanced sensors, such as the ultrasonic-time of flight and the image-based, laser-light spot and triangulation prototype level sensors.

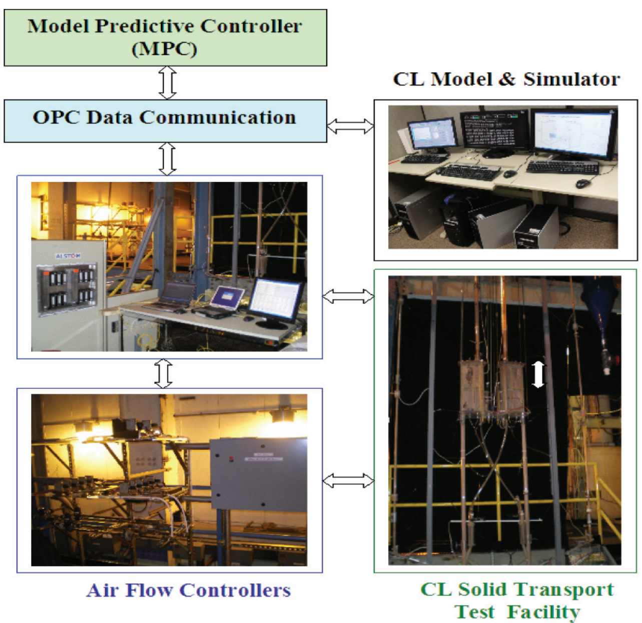

Figure 2: Experimental Facility Control Testing

Figure 3: Sensor Testing

technology advantages

Power plants using conventional circulating fluidized bed or transport reactor technology do not require sophisticated control since there is only a single, uncontrolled recycle loop. However, it is anticipated that power plants using a chemical looping process that has more complex multi-loop controlled solids circulating and transfer loops will require more sophisticated and demanding process control systems to optimize operations and reliability. The overall advantage is to develop advanced multivariable optimizing controls integrated early into the process development cycle to ensure a plant level design that is more controllable and reliable.

Advanced control systems for chemical looping will provide for more stable and continuous operation of the process, thus enabling high efficiency, high reliability, low environmental impact, and reduced costs. Project investigations have shown that traditional controls are more subject to interactions and disturbances, and hence less robust to maintaining stable loop control when compared to model-based control of the same system, suggesting that this approach may be essential for reliably operating multiple cross-flowing loops together in a continuous manner.

R&D challenges

Challenges included the development of real-time, fast, and dynamically accurate response models for use in simulation and dynamic control of the chemical looping multi-loops, followed by the inclusion of new measured control variables and reliable instrumentation as input into the model-based control. Additional challenges were to scale-up the computational models and simulation tools and integrate the advanced controls with the scale up of the chemical looping process from the current laboratory scale to a commercial demonstration-size unit. This included consideration of the appropriate process dynamics, chemical reactions, and externalities so the control can account for a large number of variables and the changes in process dynamics at the larger size units that will impact stable loop control.

results to date/accomplishments

- Developed process and control performance benchmarks.
- Completed process characterization by developing an understanding of the dynamic operation and control issues at the cold flow and chemical looping test facilities.
- Completed process modeling and simulation.
- Validated chemical looping process models.
- A two-loop, cold flow model has been validated with extensive test data.
- A real-time, dual-loop cold flow simulator has been developed to test control designs.
- A hot-loop model (without reactions) has been developed and parameterized using data from the chemical looping process development unit (PDU) test facility.
- The dual-loop simulation platform was completed and was used to evaluate different control strategies with various sensors and actuators.
- Conceptual proportional-integral-derivative (PID) control and model predictive control (MPC) designs have been completed and tested with the simulator.
- A real-time linear MPC controller was deployed and tested on the 15-foot, dual-loop facility with stable dual-loop dynamic operations achieved.
- A wavelet model based controller was designed by UIUC and tested on Alstom's 15-foot test facility.
- Partial Differential Equation (PDE)-based control methodology was evaluated by UIUC using dynamic simulations; a linearized PDE-based controller was implemented and tested on Alstom's 15-foot test facility.
- Initiated scale-up modeling and simulation of a larger cold flow solids transport test facility.
- Completed further scale-up to develop dynamic models and multi-loop simulations for the 3-MWth chemical looping prototype test facility developed by Alstom under DOE/NETL project No. DE-NT0005286.
- Evaluated a nonlinear model predictive control (NMPC) design based on the development of an initial reduced order model (ROM) for dual-loop prototype chemical looping controls.
- Completed evaluation of advanced sensors. Both solids level and the two-phase mass flow sensor candidates were evaluated and ranked for chemical looping service. The evaluation confirmed that a direct measurement of both level and mass flow rate was feasible and would significantly aid in the process control. Soft sensing based on the measurement of differential pressures has also been investigated. Microwave-level sensor was installed on pilot-scale system.

next steps

This project ended on July 31, 2012.

available reports/technical papers/presentations

The 33rd International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, Florida, USA, June 1-5, 2008, "Simulation and Advanced Controls for Alstom's Chemical Looping Process," Xinsheng Lou, Carl Neuschaefer, and Hao Lei.

51st ISA Power Industry Division Symposium & 18th Annual Joint ISA POWID/EPRI, Controls & Instrumentation Conference, Scottsdale, Arizona, USA, June 8-13, 2008, "Simulation and Advanced Controls for Hybrid Combustion-Gasification Chemical Looping Process," Xinsheng Lou, Carl Neuschaefer, and Hao Lei.

International Pittsburgh Coal Conference, Pittsburgh, PA, USA, September 21-24, 2009 "Dynamic Simulation and Advanced Controls for Alstom's Chemical Looping Process," Xinsheng Lou, Carl Neuschaefer, Hao Lei, and Abhinaya Joshi.

Modelling, Controller Design, and Computational Tools for the Closed-Loop Control of the Cold Flow Fluidized Bed Rise, submitted to the journal of Nonlinear Phenomena in Complex Systems by UIUC Dong Ye, Shu Zhang, Vivek Natarajan, Bryan Petrus, and Joseph Bentsman.

An invited presentation on this project was given by Carl Neuschaefer at the workshop on advanced controls organized by DOE/NETL aligned with 2008 ISA Power Conference in Scottsdale, Arizona, USA.

2010 International Pittsburgh Coal Conference, Istanbul, Turkey, October 11-14, 2010, "Development of Real-time Dynamic Simulation of Chemical Looping Process for Advanced Controls," Hao Lei, Xinsheng Lou, Abhinaya Joshi, and Carl Neuschaefer.

An invited presentation on this project was given by Dr. Xinsheng Lou at the workshop on advanced sensor and controls organized by DOE/NETL and EPRI aligned with 2012 ISA Power Conference in Austin, Texas, USA.

2011 International Pittsburgh Coal Conference, Pittsburgh, Pennsylvania, September 12-15, 2011.

Modeling, "Simulation and Advanced Controls for 3-MW Prototype Chemical Looping Process," Abhinaya Joshi, Xinsheng Lou, and Carl Neuschaefer.

2011 International Pittsburgh Coal Conference, Pittsburgh, PA, September 12-15, 2011 "Solids Transport Instrumentation Level and Mass Flow Rate," Majid Chauhdry and Joe Quinn.

51st IEEE Conference on Decision and Control, Maui, Hawaii, USA, December 10-13, 2012.

"Wavelet Multi-resolution Model Based Generalized Predictive Control for Hybrid Combustion-Gasification Chemical Looping Process (I)," Shu Zhang, Joseph Bentsman, Xinsheng Lou, Carl Neuschaefer.

NOVEL OXYGEN CARRIERS FOR COAL-FUELED CHEMICAL LOOPING COMBUSTION

primary project goals

Western Kentucky University (WKU) set out to develop a series of advanced oxygen carriers for chemical looping combustion (CLC). The development of the advanced oxygen carriers focused on improving their overall physical and chemical characteristics and testing them in an actual CLC facility.

technical goals

- Develop attrition-resistant and thermally stable oxygen carriers to achieve an autothermal heat balance of the processes for generating high-purity carbon dioxide (CO_2) with favorable kinetics.
- Evaluate the impacts of scale-up methods and application of inexpensive raw materials (copper [Cu]-based minerals and widely available inexpensive clays) for preparation of oxygen carriers on reaction performance in testing within hot-model conditions.
- Prepare multi-metal or free-oxygen-releasing oxygen carriers and explore their optimal formula and reaction mechanisms.
- Evaluate the adaptability of prepared oxygen carriers to diversified coal types in the hot-model tests and investigate methods for eliminating carbon deposits on oxygen carriers.

technical content

WKU set out to develop a series of advanced oxygen carriers for coal-fueled CLC. CLC is a flameless combustion technology where there is no direct contact between air and fuel. The CLC process utilizes oxygen from metal oxide oxygen carriers for fuel combustion. The products of CLC are CO_2 and water vapor (H_2O). Thus, once the steam is condensed, a relatively pure stream of CO_2 is produced ready for storage. The many benefits of this combustion process include minimizing production of oxides of nitrogen (NO_x) and production of a CO_2 stream ready for storage that does not require additional CO_2 separation units; thus, there is no energy penalty or reduction in power plant efficiency.

technology maturity:

Laboratory-Scale

project focus:

Novel CLC Oxygen Carriers

participant:

Western Kentucky University

project number:

FE0001808

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partners:

None

performance period:

12/01/09 – 11/30/12

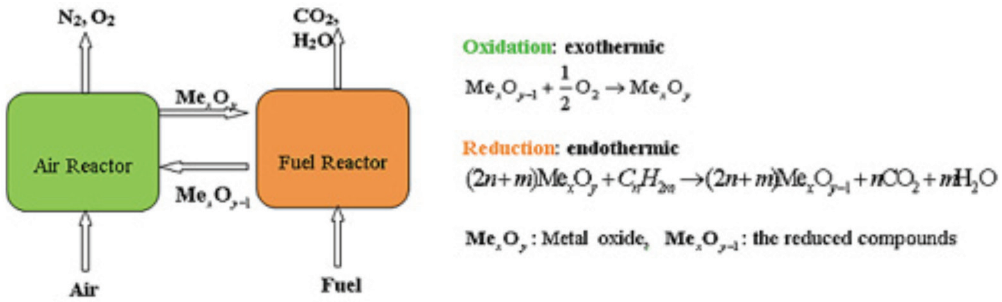

Figure 1: Conceptual Schematic of CLC

Oxygen carriers are composed of two major constituents: the reactive constituents and the supporting materials (substrates). Of the various metal oxides that can potentially be used as the reactive constituents for CLC, Cu-based oxygen carriers are promising, low-cost candidates that were evaluated in this project. WKU investigated four categories of Cu-based oxygen carriers on two different substrates (aluminum oxide [Al_2O_3] and titanium oxide [TiO_2]) by screening chemical formulas, investigating preparation methods, and characterizing the carriers using thermogravimetric analysis (TGA) and temperature program reduction methods.

Various analysis techniques were utilized to evaluate the oxygen carriers. Scanning electron microscopy with energy dispersive X-ray spectroscopy was used for morphology characterization. Phase transformation was identified by X-ray diffraction. The surface area and pore size distribution were evaluated via Brunauer-Emmett-Teller analysis. The temperature-programmed reduction technique provided the loading capacity and kinetics analysis of the oxygen carriers. The strength of the oxygen carriers was evaluated using the American Society for Testing and Materials attrition test.

One Cu-based oxygen carrier, using activated Al_2O_3 as supporting material, was selected for evaluation in a scale-up facility. A CLC process model was developed to optimize the performance of the selected oxygen carrier. The development of the advanced oxygen carrier focused on improving the oxygen-transfer capability, achieving favorable thermodynamics to generate high-purity CO_2, increasing the reactivity, increasing the attrition resistance, improving the thermal stability in reduction-oxidation (redox) cycles, and achieving an auto-thermal heat balance. The final formulation of the selected oxygen carriers was evaluated in a 10 kilowatt (kW) integrated coal-fueled CLC facility.

technology advantages

Copper-based oxygen carrier maintained good reactivity and largely minimized agglomeration.

R&D challenges

- Attrition loss of active ingredient (Cu).
- Oxygen releasing performance and thermal stability of the CuO on Al_2O_3 oxygen carrier.

results to date/accomplishments

- Three categories of Cu-based oxygen carriers were prepared using Al_2O_3 as the substrate. A fourth category of Cu-based oxygen carrier was prepared using TiO_2 as the substrate.
- The oxygen carriers were evaluated to understand morphology, phase transformation, surface area, pore size, loading capacity, conversion rate, kinetics, and strength.
- The chemical formula and preparation method of one Cu-based oxygen carrier, using activated Al_2O_3 as supporting material, was selected for scale-up. This carrier was finalized following TGA testing for more than 864 redox cycles, and successfully passed the durability and kinetics evaluations in a bench-scale, fixed-bed setup.
- The flow dynamics of solid recirculation without gas leakage between the air and fuel reactors were studied in a 10-kW equivalent cold-model CLC facility.
- The selected Cu-based oxygen carrier was tested in a scaled-up, 10-kW coal-fueled CLC facility for eight hours per day for three days.
- The testing demonstrated that the preparation method of the Cu-based oxygen carrier not only helps to maintain its good reactivity, but also largely minimizes its agglomeration tendency.

next steps

This project ended on November 30, 2012.

available reports/technical papers/presentations

Pan, W. P. and Cao, Y. "Recovery Act: Novel Oxygen Carriers for Coal-fueled Chemical Looping," Western Kentucky University Final Technical Report, DOE Project DE-FE0001808, February 2013.

NETL

the ENERGY lab

Chemical Looping Combustion at NETL

Background

Chemical Looping Combustion (CLC) is a promising technology for highly-efficient CO_2 capture. A growing body of work indicates attractive cost and performance characteristics compared to other technologies. Utilizing an oxygen carrier material to transfer oxygen from the air to the fuel, CLC facilitates CO_2 recovery because the exhaust stream is just carbon dioxide and water vapor, which is easily purified by condensed the water. Researchers at the National Energy Technology Laboratory (NETL) are investigating CLC technology for CO_2 control applications. Rather than pursue step-wise scale-up tests for a single chemical looping application, the research will accelerate the technology development of CLC using data from a suite of experiments (and literature) to calibrate numeric models for desired industrial applications. This approach will benefit from emerging capabilities at NETL, including the Simulation-based Engineering User Center (SBEUC), the Carbon Capture and Simulation Initiative (CCSI), as well as experimental expertise in fluid beds, material characterization, and thermal science. The CLC research at NETL is part of a larger Industrial Carbon Management Initiative (ICMI) which is exploring methods to both capture and utilize carbon dioxide from industrial sources.

Material Development

CLC technology starts with the selection of the oxygen carrier material. The requirements for a good oxygen carrier are high oxygen transport capacity, high reactivity, high mechanical strength, environmentally friendly, physical/chemical stability, and low production costs. For instance, a low oxygen capacity and low rates will result in a larger amount of solids transfer contributing to a significant increase in CLC reactor size and operating costs. Iron and copper based oxygen carriers are the most promising oxygen carriers reported in the literature. Researchers at NETL have tested various iron and copper oxygen carriers, including natural ores and synthetically made materials.

NETL's Chemical Looping Reactor located in Morgantown, WV

Of the natural ores tested, hematite (Fe_2O_3) showed the best performance at 800-900°C. However, the major challenge with CLC using Fe_2O_3 and natural ores is the release of adequate amounts of oxygen from the oxygen carrier during the CLC reduction cycle, therefore, researchers incorporated dopants into the hematite as promoters to improve the reactivity of the natural ore hematite for methane CLC.

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U.S. DEPARTMENT OF ENERGY

In addition to natural ores, novel synthetic oxygen carriers have also been developed by NETL to obtain high oxygen capacity and reactivity at a wider temperature range (700-900°C). Copper oxide (CuO) possesses higher reactivity than Fe_2O_3, but softens at high temperatures, which limits its application in CLC. However, the composition of the bimetallic Cu-Fe oxygen carriers can withstand the elevated temperatures and have been optimized to achieve the best reactivity, high oxygen transfer capacity, stability, and attrition resistance during multi-cycle methane-CLC reactions.

Experimental Support

After oxygen carrier materials are selected, developed, and manufactured, they are tested in various reactor systems to evaluate system performance in CLC operation. These experimental efforts include:

- The 50 kWth Chemical Looping Reactor (CLR), which is a fully integrated circulating fluidized bed reactor that can circulate 1000 lbs/hr of carrier material at temperatures up to 1000 °C (1830°F) – see photo, Page 1
- A cold flow replica of the CLR, which allows researchers to study the hydrodynamics of the system while measuring key elements like bed height through a clear polycarbonate tubing structure
- A single fluid bed reactor, which allows researchers to isolate and study CLC reactions in a fluid bed setting
- Attrition testing, which evaluates the physical endurance of the carriers after multiple collisions
- Fundamental thermogravimetric and analytic equipment needed to characterize basic carrier properties

The results from these experiments not only evaluate carrier materials in fluid bed environments, it also supports calibration and validation of high and low fidelity models that have been developed to accelerate the development of CLC technology.

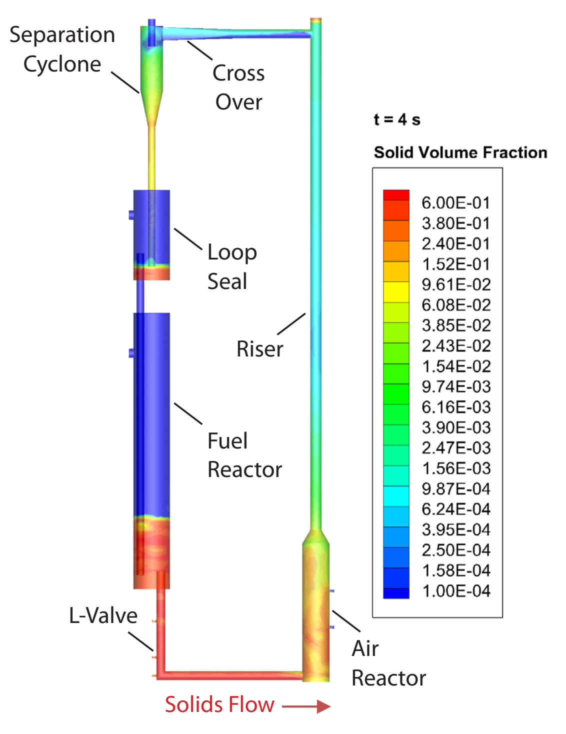
Modeling

Numeric models are applied at different operating regimes and are used to help explain observed phenomena related to the multiphase fluid dynamics and chemistry of the onsite experiments run by the research staff. The developed models range in complexity from spreadsheet-based process models to three-dimensional computational fluid dynamic (CFD) models of specific systems that vary in size from small fixed bed units to the 50 kWth CLR. The models have been used to assist project engineers in the development of test plans for the experiments units. This has been accomplished by conducting a simulation based sensitivity study to identify the importance of operating conditions with respect to fuel utilization and the overall performance of the test units. Model validation is also being conducted to quantify the error between the simulations and experimental results. Throughout the process, information gathered by the simulations is fed back to the experimental group to provide direction for future test plans.

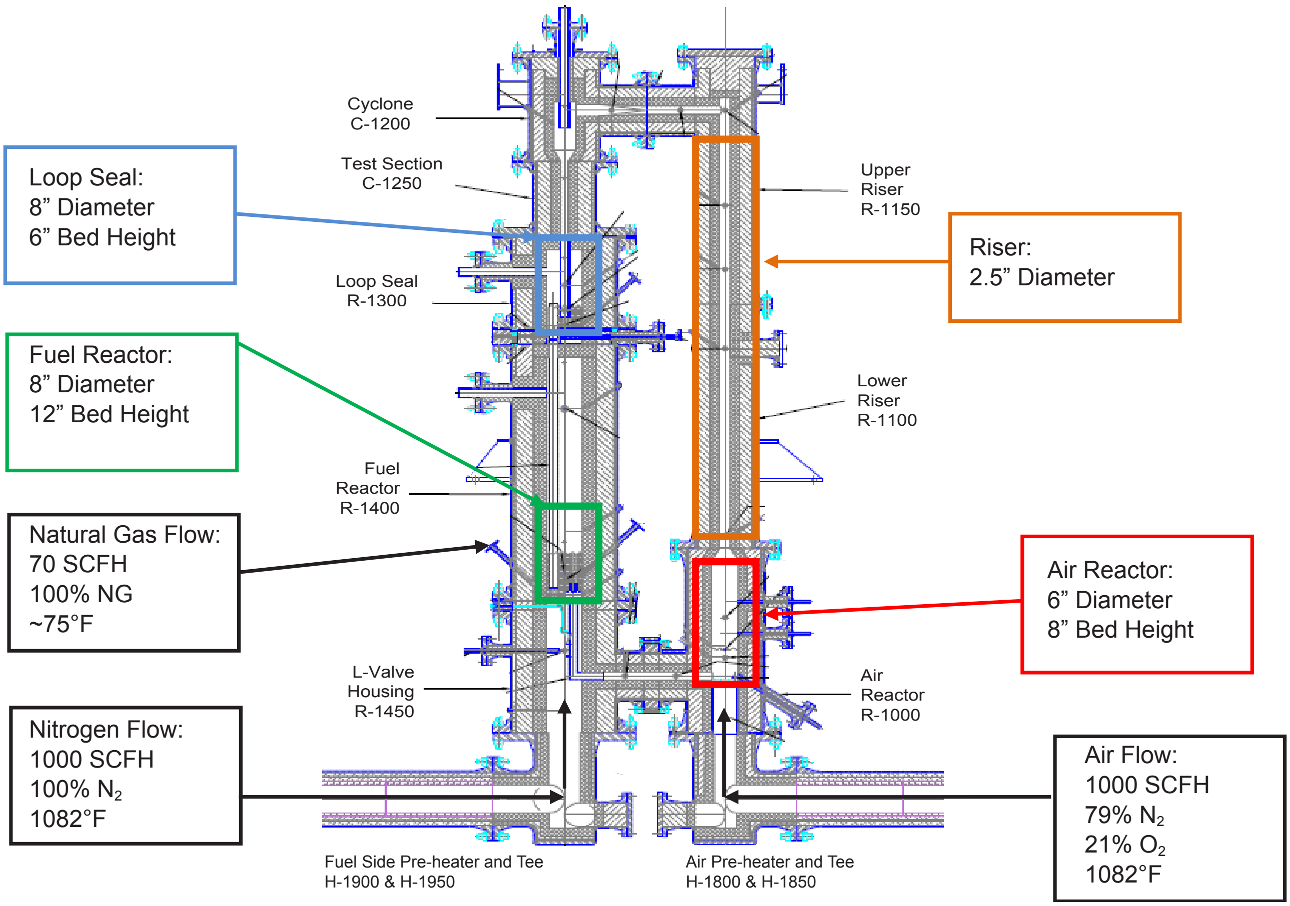
Techno-Economic Analysis

Bridging all of the technology development is a techno-economic analysis. NETL has developed a baseline CLC design concept to evaluate preliminary economic and performance information of a CLC system. The study includes a sensitivity study of key parameters still being developed which provides direction for where future technology development should be focused.

The systems analysis study considered different chemical looping reactor concepts (e.g. circulating bed, bubbling bed, moving bed) and oxygen carriers for the baseline system. A supported Fe_2O_3 oxygen carrier with a circulating bed reactor configuration was selected for this initial study. A natural gas fueled, industrial steam generation application to be operated with carbon capture was selected. The plant design capacity is 275,000 lb/hr of steam at 600 psia, and 586°F. Ninety percent carbon capture is assumed to be required. CLC reactor models were generated for the purpose of identifying and understanding the behavior of key reactor performance parameters. In parallel, process models were developed to understand the overall performance and cost potential of the CLC process in specific applications so that reactor performance and cost goals could be established. Together, reactor models and process models are used in sensitivity studies to help guide the experimental development of the technology. In the future, these models will be used to compare the baseline system with other reactor configurations, system scales, and fuel types, such as coal-fueled power generation.



Numeric model of chemical looping reactor. Colors show the volume fraction of oxygen carrier material



Process schematic of NETL's Chemical Looping Reactor (CLR) is shown with the Fuel Reactor on the left and the Air Reactor on the right. Information includes vessel diameter, bed heights (by operational design), and some process information.

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Chemical Looping Summary
July 2013