Fuel-Flexible Gasification-Combustion Technology for Production of H_2 and Sequestration-Ready CO_2

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ABSTRACT

It is expected that in the 21st century the Nation will continue to rely on fossil fuels for electricity, transportation, and chemicals. It will be necessary to improve both the process efficiency and environmental impact performance of fossil fuel utilization. GE Global Research has developed an innovative fuel-flexible Unmixed Fuel Processor (UFP) technology to produce H_2, power, and sequestration-ready CO_2 from coal and other solid fuels. The UFP module offers the potential for reduced cost, increased process efficiency relative to conventional gasification and combustion systems, and near-zero pollutant emissions including NO_x. GE Global Research (prime contractor) was awarded a contract from U.S. DOE NETL to develop the UFP technology. Work on this Phase I program started on October 1, 2000. The project team includes GE Global Research, Southern Illinois University at Carbondale (SIU-C), California Energy Commission (CEC), and T. R. Miles, Technical Consultants, Inc.

In the UFP technology, coal and air are simultaneously converted into separate streams of (1) high-purity hydrogen that can be utilized in fuel cells or turbines, (2) sequestration-ready CO_2, and (3) high temperature/pressure vitiated air to produce electricity in a gas turbine. The process produces near-zero emissions and, based on ASPEN Plus process modeling, has an estimated process efficiency of 6 percentage points higher than IGCC with conventional CO_2 separation. The current R&D program has determined the feasibility of the integrated UFP technology through pilot-scale testing, and investigated operating conditions that maximize separation of CO_2 and pollutants from the vent gas, while simultaneously maximizing coal conversion efficiency and hydrogen production. The program integrated experimental testing, modeling and economic studies to demonstrate the UFP technology.

This is the fifteenth quarterly technical progress report for the UFP program, which is supported by U.S. DOE NETL (Contract No. DE-FC26-00FT40974) and GE. This report summarizes program accomplishments for the period starting April 1, 2004 and ending June 30, 2004. The report includes an introduction summarizing the UFP technology, main program tasks, and program objectives; it also provides a summary of program activities and accomplishments covering progress in tasks including lab-scale experimental testing, pilot-scale testing, kinetic modeling, program management and technology transfer.

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EXECUTIVE SUMMARY

This is the fifteenth quarterly technical progress report for the UFP program, which is supported by U.S. DOE NETL (Contract No. DE-FC26-00FT40974) and GE. This report summarizes program accomplishments for the period starting April 1, 2004 and ending June 30, 2004. The report provides a description of the technology concept and a summary of program activities and accomplishments in lab-scale experimental testing, pilot-scale testing, program management and technology transfer.

In the UFP technology, coal/opportunity fuels and air are simultaneously converted into separate streams of (1) pure hydrogen that can be utilized in fuel cells, (2) sequestration-ready CO_2, and (3) high temperature/pressure oxygen-depleted air to produce electricity in a gas turbine. The process is highly efficient relative to conventional electricity-producing technologies and produces near-zero emissions. This R&D program has investigated operating conditions that maximize separation of CO_2 and pollutants from the vent gas, while simultaneously maximizing coal conversion to electricity efficiency and hydrogen production. The program integrates lab-, bench- and pilot-scale studies to demonstrate the UFP technology.

Work conducted in the fifteenth quarter of this program has focused on conducting additional experimental analysis of lab-scale systems, the performance evaluation of the pilot plant, kinetic modeling, management and technology transfer.

The lab-scale effort in this quarter has included experimental investigations into CAM performance and lifetime using different CAM preparation methods. Lab-scale experiments provided insight into the impact of preparation method on CAM performance and lifetime and identified methods that result in improved CO_2 capture/release cycling capabilities.

UFP pilot plant performance testing was conducted in this quarter to validate the performance and operability of the UFP system at pilot scale. Results of the pilot plant testing confirmed the feasibility of the UFP technology. The key chemical processes were tested and demonstrated the production of high-purity H_2, the absorption and desorption of CO_2, and the oxidation and reduction of OTM.

Kinetic modeling efforts made use of lab- and bench-scale data to validate process models and derive kinetic parameters that were used to predict behavior at larger scales and in complex systems where measurements of individual reactions are not possible.

The results obtained to date confirm the viability of the UFP process, and provide support for the need for further experimentation to reduce the technical risks associated with this novel approach to coal utilization for H_2 and electricity production.

INTRODUCTION

Electricity produced from hydrogen in fuel cells can be highly efficient relative to competing technologies and has the potential to be virtually pollution free. Thus, fuel cells may become the ideal solution to many of this nation's energy needs if a satisfactory process for producing hydrogen from available energy resources such as coal and low-cost alternative feedstocks such as biomass is developed.

This UFP program addresses a novel, energy-efficient, and near-zero pollution concept for converting coal into separate streams of hydrogen, vitiated air, and sequestration-ready CO_2. The technology module comprising this concept is referred to as the *Unmixed Fuel Processor (UFP)* throughout this report. When commercialized, the UFP technology may become one of the cornerstone technologies to meet the DOE's future energy plant objectives of efficiently and economically producing energy and hydrogen from coal with utilization of opportunity feedstocks.

The UFP technology is energy efficient because a large portion of the energy in the coal feed leaves the UFP module as hydrogen and the rest as high-pressure, high-temperature gas that can power a gas turbine. The combination of producing hydrogen and electricity via a gas turbine is highly efficient, meets all objectives of DOE future energy plants, and makes the process product-flexible. That is, the UFP module will be able to adjust the ratio at which it produces hydrogen and electricity in order to match changing demand.

General Electric Global Research is the primary contractor for the UFP program under a contract from U.S. DOE NETL (Contract No. DE-FC26-00FT40974). Other project team members include Southern Illinois University at Carbondale (SIU-C), California Energy Commission (CEC), and T. R. Miles, Technical Consultants, Inc. The UFP project integrates lab, bench and pilot-scale studies to demonstrate the UFP technology. Engineering studies and analytical modeling are being performed in conjunction with the experimental program to develop the design tools necessary for scaling up the UFP technology to the demonstration phase. The remainder of this section presents the objectives, concept, and main tasks of the UFP program.

PROGRAM OBJECTIVES

The primary objectives of the UFP program are to:

- Demonstrate and establish the chemistry of the UFP technology, measure kinetic parameters of individual process steps, and identify fundamental processes affecting process economics.
- Design and develop bench- and pilot-scale systems to test the UFP technology under dynamic conditions and estimate the overall system efficiency for the design.
- Develop kinetic and dynamic computational models of the individual process steps.
- Investigate operating conditions that maximize separation of CO_2 and pollutants from vent gas, while simultaneously maximizing coal/opportunity fuels conversion and H_2 production.
- Integrate the UFP module into Vision 21 plant design and optimize work cycle efficiency.
- Determine extent of technical/economical viability & commercial potential of UFP module.

UFP TECHNOLOGY

The conceptual design of the UFP technology is depicted in Figure 1. The UFP technology makes use of three circulating fluidized bed reactors containing CO_2 absorbing material (CAM) and oxygen transfer material (OTM), as shown in Figure 1. Coal is partially gasified with steam in the first reactor, producing H_2, CO and CO_2. As CO_2 is absorbed by the CAM, CO is also depleted from the gas phase via the water-gas shift reaction. Thus, the first reactor produces a H_2-rich product stream suitable for use in liquefaction, fuel cells, or turbines.

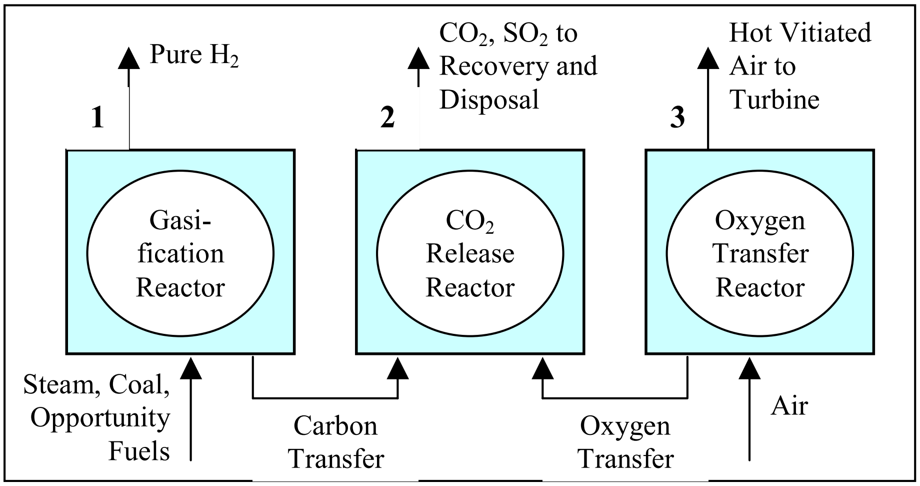


Figure 1. Conceptual design of the UFP technology.

Gasification of the char, transferred from the first reactor, is completed with steam fluidization in the second reactor. The oxygen transfer material is reduced as it provides the oxygen needed to oxidize CO to CO_2 and H_2 to H_2O. The CO_2 sorbent is regenerated as the hot moving material from the third reactor enters the second reactor. This increases the bed temperature forcing the release of CO_2 from the sorbent, generating a CO_2-rich product stream suitable for sequestration.

Air fed to the third reactor re-oxidizes the oxygen transfer material via a highly exothermic reaction that consumes the oxygen in the air fed. Thus, Reactor 3 produces oxygen-depleted air for a gas turbine as well as generating heat that is transferred to the first and second reactors via solids transfer.

Solids transfer occurs between all three reactors, allowing for the regeneration and recirculation of both the CO_2 sorbent and the oxygen transfer material. Periodically, ash and bed materials will be removed from the system and replaced with fresh bed materials to reduce the amount of ash in the system and increase the effectiveness of the bed materials.

PROJECT PLAN

Work on tasks planned for the UFP project (Table 1) was initiated in October 2000. The project was originally scheduled for completion in three years, but a nine-month no-cost extension that was granted by the DOE in August 2003 extended the completion date until June 2004. This extension was necessary due to delays in obtaining a South Coast AQMD permit to construct the pilot plant. The success of the UFP program depends on the efficient execution of the various research tasks outlined in Table 1 and on meeting the program objectives summarized above.

MANAGEMENT AND TECHNOLOGY TRANSFER

Program planning activities have focused on meeting the objectives of the program as stated previously. GE Global Research has made use of several GE methodologies to obtain desired results and systematically conduct program design, construction and testing activities. Methodologies utilized in this program include New Technology Introduction (NTI) and Design For Six Sigma (DFSS). The NTI program is a detailed and systematic methodology used by GE to identify market drivers, and continually ensure that the program will meet both current and future market needs. The NTI program is also strongly coupled with the DFSS and other quality programs, providing structure to the design process and ensuring that the design meets program objectives. This is accomplished through the use of regular program reviews, detailed design reviews, market assessments, planning and decision tools, and specific quality projects aimed at identifying system features and attributes that are critical to quality (CTQ) for customers.

Table 1. Main tasks of the UFP program.

Task	Task Description
Lab-Scale Experiments – Fundamentals *Task 1*	Design & assembly Demonstration of chemical processes Sulfur chemistry
Bench-Scale Test Facility & Testing *Tasks 2 & 3*	Bench test facility design Subsystems procurement& assembly Bench test facility shakedown Reactor design testing Parametric evaluation Fuel-flexibility evaluation Pilot operation support
Engineering & Modeling Studies *Task 4*	Opportunity fuels resource assessment Preliminary economic assessment Kinetic & process modeling Integration into Vision 21 plant Pilot plant control development
Pilot Plant Design, Assembly & Demonstration *Tasks 5, 6, & 7*	Process design Subsystems specification/procurement Reactor design & review Reactors manufacture Components testing Pilot plant assembly Operational shakedown modifications Operational evaluation Fuel-flexibility evaluation Performance testing
Vision 21 Plant Systems Analysis *Task 8*	Preliminary Vision 21 module design Vision 21 plant integration Economic & market assessment
Project Management *Task 9*	Management, reporting, & technology transfer

The project team continues to meet periodically to assess progress, distribute workload, and identify and remove potential roadblocks. An expanded NTI project team that includes senior management and other expert personnel meets monthly to gauge progress and ensure that adequate company resources are allocated and technical issues resolved to allow steady progress toward program objectives.

Program management activities also include the continuous oversight of program expenditures. This includes a monthly review of actual expenditures and monthly projections of labor, equipment, contractor costs, and materials costs.

Technology transfer and networking with experts in the advanced power generation field is an important and ongoing part of project management. Team members continue to seek out opportunities to present the UFP technology and progress at technical conferences. During the last quarter, the following technical papers were presented:

- A. Frydman, G. Rizeq, J. West, R. Subia, P. Kulkarni, and V. Zamansky, "Modeling of Unmixed Fuel Processor for Production of Hydrogen from Coal," *National Hydrogen Association 15th Annual U.S. Hydrogen Conference*, Los Angeles, CA, April 26-29, 2004.
- George Rizeq, Arnaldo Frydman, Raul Subia, Janice West, Vladimir Zamansky and Kamalendu Das, "Unmixed Fuel Processor: Pilot-Scale System Design and Initial Experimental Results," *The 29th International Technical Conference on Coal Utilization & Fuel Systems (Clearwater 2004)*, Clearwater, FL, April 18-22, 2004

EXPERIMENTAL

During the last quarter, testing was conducted on the pilot plant, and additional lab-scale experiments investigated different CAM materials. Laboratory-scale activities are being conducted by SIU in Carbondale, IL, while the pilot-scale system is located at the GE Global Research test site in Irvine, CA.

LABORATORY-SCALE TESTING

The primary objective of Task 1 is to perform a laboratory-scale demonstration of the individual chemical and physical processes involved in GE's fuel-flexible UFP technology. Specific objectives of Task 1 include:

- Support bench- and pilot-scale studies,
- Assist in process optimization and engineering analysis,
- Identify key kinetic and thermodynamic limitations of the process, and
- Verify the process parameters at laboratory scale.

Work conducted in this quarter included an investigation of the properties and lifetime of CAM materials. A new preparation method was developed that utilized CAM precipitation and also made use of anionic surfactants to modify the surface properties of the CAM. Three different surfactants were tested. The performance and lifetime of three CAM samples (each prepared with a different surfactant) were characterized and compared with a CAM sample prepared with no surfactants.

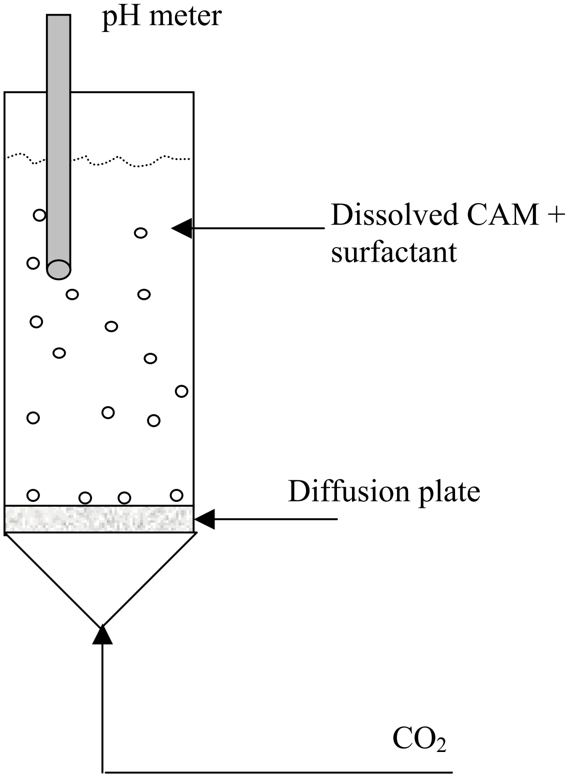


Figure 2. Schematic of the reactor system for CAM precipitation.

The CAM samples were prepared by precipitation from an aquatic solution with a concentration approximately 16 times the saturation concentration. The mixture was placed in a column reactor (Figure 2), and CO_2 was bubbled through the solution. A glass frit was used as a diffusion plate in order to obtain a uniform CO_2 distribution. The solids were observed to start precipitating almost immediately. The pH was monitored for the duration of the precipitation reaction since as the alkaline CAM precipitated out of solution, the measured pH was dominated by the slightly acidic dissolved CO_2. Ten minutes were required for the complete precipitation of the CAM, which was indicated by a significant decrease in pH.

A Quantachrome Nova 2000 BET analyzer was used to obtain multipoint surface areas. A Microtrac S3500 was used for particle size distribution determination. Thermogravimetric analysis was employed to obtain the weight change data during CO_2 capture/release cycles.

TGA experiments were conducted isothermally at 800°C. During CO_2 capture, each CAM sample was exposed to a continuous feed of CO_2; the CO_2 absorbed by the CAM caused an increase in sample weight. Each CO_2 capture step was conducted for 15 minutes. CO_2 release was conducted under a nitrogen atmosphere; as CO_2 was released the sample weight decreased. Each CO_2 release step continued until no changes in weight were observed. Samples were subjected to multiple CO_2 capture/release cycles. A scanning electron microscope was used to assess CAM morphology both before and after cycling.

RESULTS AND DISCUSSION

LABORATORY-SCALE TESTING RESULTS

A commercially-prepared CAM sample obtained from Aldrich Chemical was tested for comparison with the CAM samples prepared by precipitation. The four precipitated CAM samples were tested to characterize specific surface area and particle size distribution. The results of BET analysis and particle size analysis are provided in Table 2, and show that the use of surfactants increased the specific surface area. CAM-S1 showed an increased mean particle size, while CAM-S2 and S3 had decreased particle sizes. All of the precipitated CAM samples had higher specific surface areas than the commercially-prepared Aldrich CAM. Thus, the new precipitation preparation method had a positive impact on surface area.

Table 2. Characteristics of the CAM sorbents prepared with different surfactants.

Sample	Specific Surface Area (m^2/g)	Mean Size (μm)	Median Size (μm)
CAM -no surfactant	588	9.24	9.99
CAM -surfactant 1	663	10.43	10.43
CA M -surfactant 2	634	6.38	6.38
CAM -surfactant 3	614	4.93	5.31
Aldrich CAM	495		

The results of TGA experiments provide insight into the CO_2 capture and release through their measurement of sample weight changes during the capture/release cycle. The weight % measured is an indicator of the state of the CAM, and the rate of change in weight is proportional to the rate of desorption. Figure 3 shows the TGA results starting after a preliminary 15-minute CO_2 capture step. CAM-S1 shows superior performance, as it more completely releases the CO_2 (as evidenced by a reduction in weight %) at a much faster rate than any of the other sorbents tested. All of the precipitated sorbents showed more complete CO_2 release than the Aldrich CAM. The CO_2 release step was continued until no changes in weight were observed; thus, the subsequent CO_2 capture step began at a different time for each CAM sample. CAM-S3 demonstrated a particularly slow CO_2 release step as well as a significant performance degradation in the subsequent CO_2 capture step, as the weight increase due to CO_2 capture was significantly lower than the 100% measured prior to the first CO_2 release step.

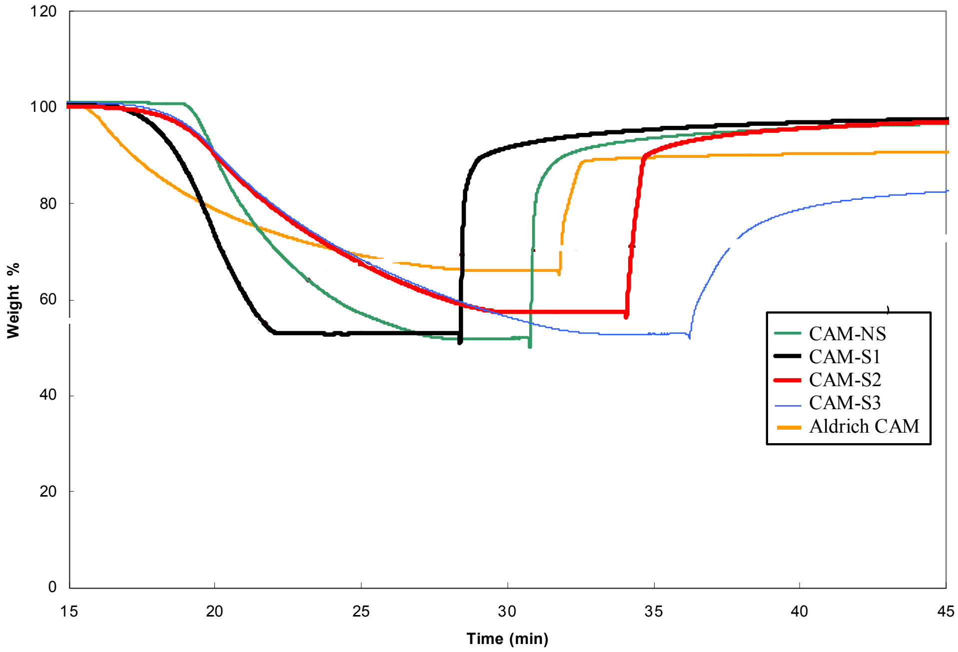


Figure 3. Comparison of the TGA response of a CO_2 capture/release cycle for different CAM materials.

The CO_2 capture results during TGA testing are summarized in Figure 4 and show the change in %CO_2 uptake after multiple cycles. All of the precipitated CAM samples showed improved performance relative to the Aldrich CAM, and the use of surfactants generally improved CO_2 capture, particularly after 6 cycles. The performance of the precipitated CAM prepared without any surfactant (CAM-NS) decreased markedly after each of the first six cycles, then increased to 70% uptake after ten cycles. The performance of CAM-S1 showed a similar trend, but increased to 80% uptake after ten cycles. CAM-S2 decreased gradually with each additional cycle, while CAM-S3 exhibited a steep decline over the first two cycles, then a steady increase over the next five cycles, leveling out at approximately 70% uptake after six cycles. These results, coupled with the rate of weight change results discussed previously, suggest that CAM-S1 is the most promising of the CAM materials tested.

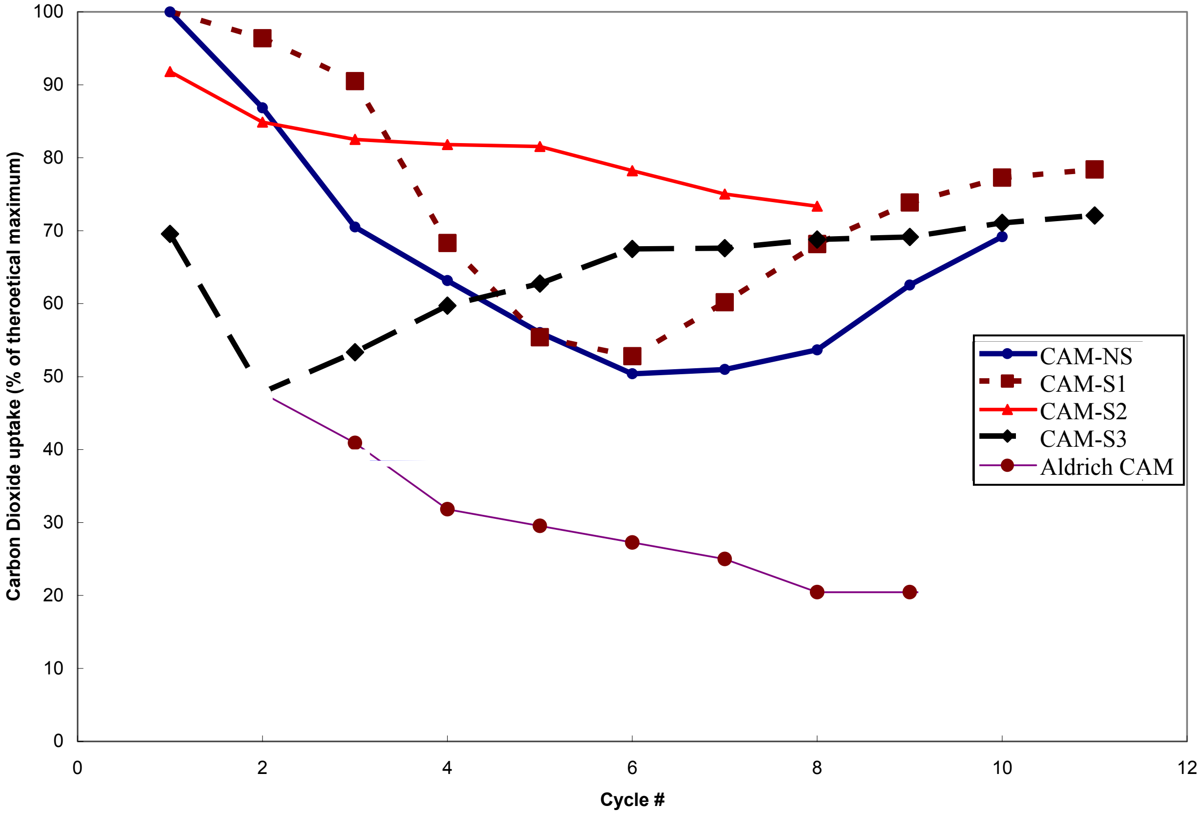
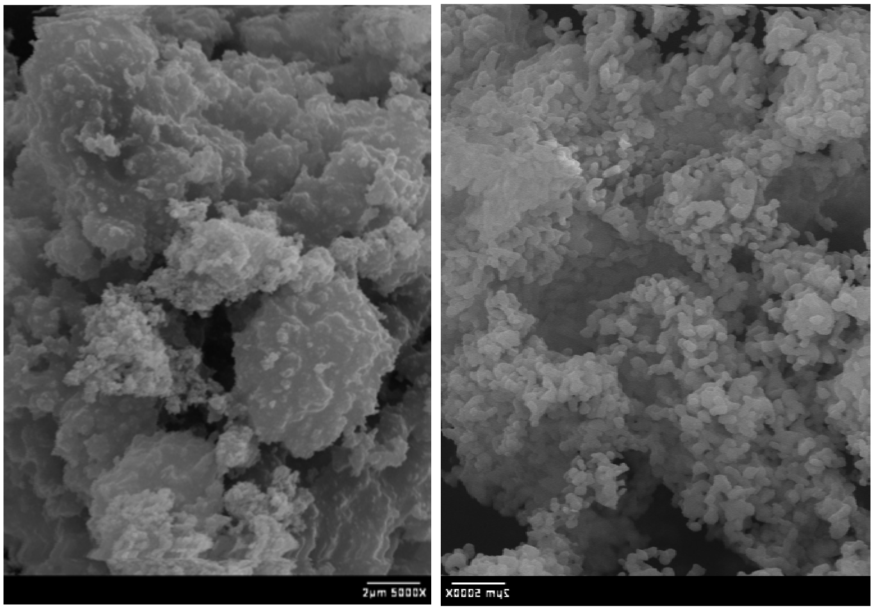


Figure 4. Change in CO_2 uptake after multiple CO_2 capture/release cycles for the four precipitated CAM sorbents and the commercially-prepared Aldrich CAM sorbent.

The changes in CAM performance after several cycles were investigated using a variety of techniques. SEM microscopy was used to characterize the morphology of CAM samples both before and after cycling. Figure 5 is a comparison of the morphology of CAM-NS both before and after four CO_2 capture/release cycles. The micrographs show that a physical change in the samples had occurred, with the surface becoming less rough. This



a) CAM -NS: before b) CAM-NS: after 4 cycles

Figure 5. SEM micrographs showing the morphology of CAM-NS a) before and b) after 4 CO_2 capture/release cycles.

change was associated with the degradation in performance previously illustrated in Figure 4, which showed CO_2 uptake decrease from 100% to 65% after four cycles.

The results of the CAM testing showed that use of the precipitation method for CAM preparation yielded higher specific surface areas, and that surfactant 1 improved the rate of CO_2 release and CO_2 absorption, as well as the performance over time. The demonstrated ability to manipulate CAM properties and performance via preparation method suggests that CAM materials can be further optimized for high performance and long lifetime.

PILOT PLANT TESTING RESULTS

The objective of the pilot plant testing task is to evaluate the performance and operability of the UFP system at pilot scale. Shakedown testing was completed in the previous quarter, demonstrating the capabilities of the solids transfer system and the major auxiliary systems. Testing began this quarter with the high-temperature curing of the reactor refractory and the release of CO_2 from the bed materials. Coal slurry was then fed to the system and coal gasification performance was characterized, as well as CO_2 capture/release and OTM oxidation/reduction.

Reactor Heat-Up

The heat-up of the reactors was complicated by the need to cure the refractory at high temperature in air. The second-stage superheaters were limited in their ability to provide heat to the system since they were primarily designed to operate for preheating to prevent condensation after switching to steam. During refractory curing, a large amount of water was driven off the refractory, but this occurred very slowly at the second-stage superheater's heat input rate. Thus, R1 was retrofitted with propane feed to provide auxiliary heat particularly for start up to increase the reactor temperature to pre-gasification condition. Since the retrofit did not include an ignition system, it was necessary to increase the reactor temperature (using the second-stage superheater) above the ignition temperature of propane to ensure auto ignition. This technique had previously been used for reactor heat-up in a different project, and worked well in this application as well.

Release of CO_2 from Bed Material

Before coal slurry could be fed into the pilot-scale reactor for coal gasification testing, the CAM was prepared by releasing any CO_2 present from the CAM. CO_2 release takes place at high temperatures (~900°C). These temperatures were reached by extending the heat-up of the fluidized bed to reach temperatures above 900°C using the retrofitted propane heat-up system described above.

Figure 6 shows the CO_2 concentration and bed temperature during CO_2 release. Although CO_2 is expected as a propane combustion product, the CO_2 levels measured were high and somewhat transient due to the CO_2 generated during the release process. The slow increase in temperature is an indication that significant heat was required to release CO_2 from the CAM. CO_2 concentration peaks were followed by a decrease in bed temperature, which immediately reduced CO_2 release. After 210 minutes, CO_2 release was complete, as indicated by the subsequent sharp increase in bed temperature and decrease in CO_2 concentration.

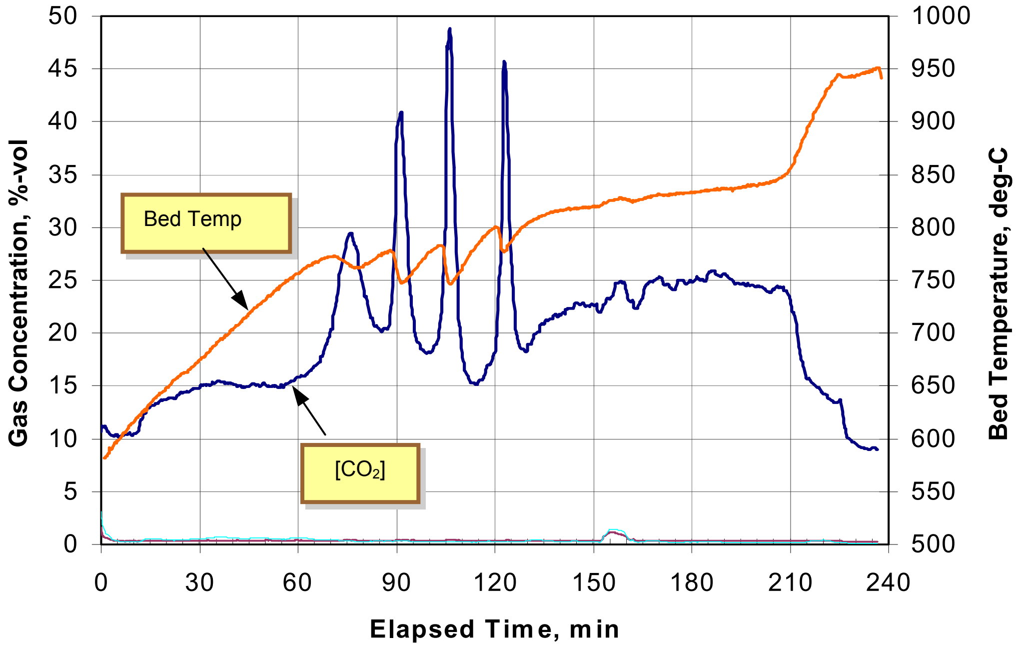


Figure 6. Curing refractory and releasing CO_2 from CAM during initial reactor heat-up with propane fired at 40,000 Btu/hr.

Coal Test Results

Testing conducted with coal, both at bench scale and pilot scale, confirmed the basic principles of the UFP technology. Although additional testing is needed to identify operating limits and optimize performance, the data generated to date support the projections of UFP performance and did not identify any showstoppers.

Since the shakedown test data demonstrated the ability of the pilot plant to circulate solids between three reactors with reasonable control, the initial coal test was conducted in a single reactor to validate the coal-slurry feeding mechanism and the main chemical processes one step at a time. The plan was to also conduct coal tests with the three reactors circulating, but those tests were deferred to the next stage of this program due to the timing constraints associated with the May 14 deadline for vacating the Irvine Test Site and relocating the pilot plant to a new GE test site in Santa Ana, CA (12 miles north of the main GE Global Research office in Irvine.)

As discussed above, coal testing was conducted in a single reactor operated in semi-batch mode with a mixed CAM-OTM bed (1:1 by weight) and operating at approximately 20 psig. The semi-batch operation required the use of two operating modes: gasification and oxidation. During the gasification mode, the bed was fluidized with steam, and coal slurry was fed for a period of several minutes. Steam fluidization continued after the coal slurry was stopped, and gasification products were monitored. Coal gasification; CO_2 absorption by CAM; and OTM reduction by H_2 and CO are the key process that took place during the gasification stage. During the oxidation mode, the bed was fluidized with air. The consumption of O_2 by OTM and related bed temperature increase; as well as the release of CO_2 at elevated temperatures are the key processes that took place during the oxidation stage.

Coal Gasification

Figure 7 shows the temperature profiles in the reactor during the coal gasification stage. Superheated steam entered the reactor at ~920°C for the duration of the gasification test. The temperatures of both the lower and upper sections of the bed were initially at 800°C, while the freeboard region near the top of the reactor was at ~550°C. The coal slurry (approximately a 50/50 water/slurry mixture) was fed into the fluidized bed near the top of the bed. The water content of the slurry had a significant effect on bed temperature, as illustrated by the upper bed's steep temperature drop during the first six minutes of testing. However, the temperature in the lower section of the bed remained ~800°C due to the steam feed inlet temperature of ~ 900°C; The temporary increase in the temperature of the freeboard region suggests that the coal slurry feed may have disturbed the fluidized bed causing temporary bed agglomerates and allowing the fluidizing steam to channel through the bed to the freeboard.

During the coal gasification test, it was decided to stop feeding the coal slurry when the upper bed temperature decreased to 600°C. However, steam fluidization continued. As seen in Figure 7, at the time coal slurry feed stopped, both the upper and lower bed temperatures began to approach 700°C, an indication of improved bed fluidization and mixing.

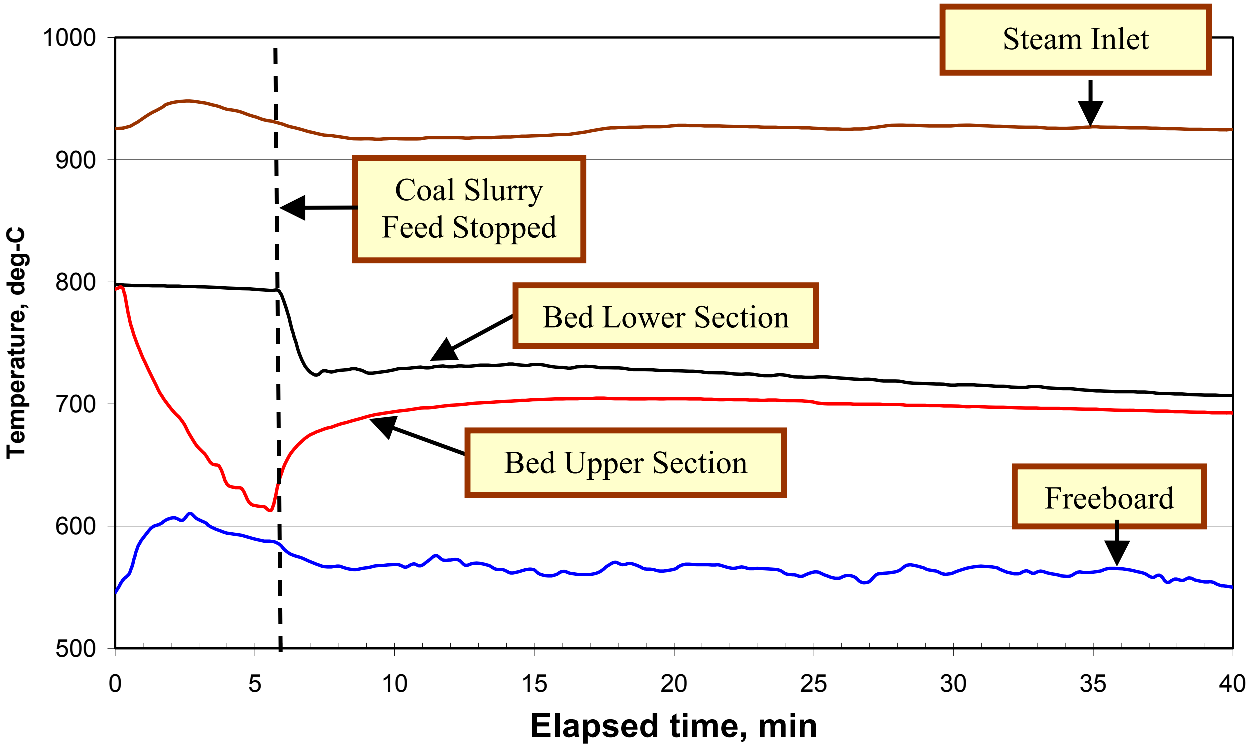


Figure 7. Temperature profiles during coal gasification test.

The product gas concentrations during the first twenty minutes of the test are shown in Figure 8. Since the OTM was in its oxidized state at the start of testing, a portion of the H_2 produced during gasification reacted to reduce the OTM (H_2 + OTM-O → H_2O + 2OTM). The extent of H_2 participation in OTM reduction was calculated based on the amount of OTM that was oxidized in the subsequent test described below. This was used to calculate the actual peak H_2 concentration, which was estimated at approximately 80% during this test. Thus, the measured peak H_2 concentration (~60%) shown in Figure 8 is lower than the actual H_2 concentration (~80%) due to the consumption of H_2 by the OTM. The estimated peak H_2 concentration is consistent with bench-scale gasification testing results.

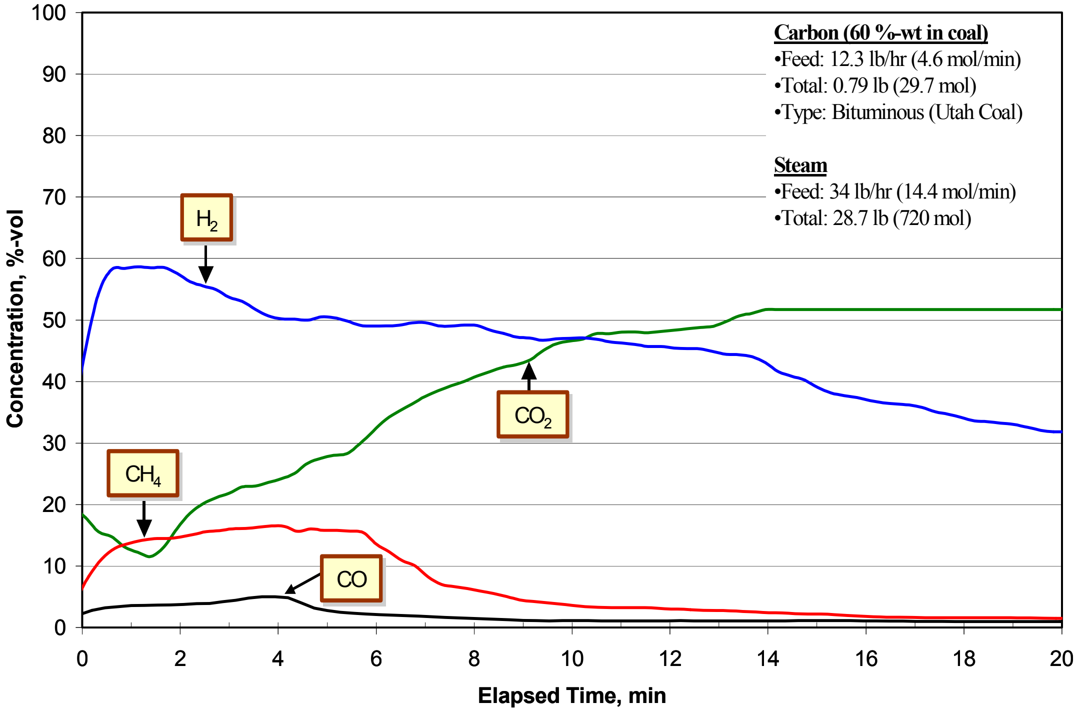


Figure 8. Product gas concentrations during gasification test.

The reduction of OTM and the gasification of coal are separated in the integrated UFP system (when operating the three reactors in circulating mode), occurring in R2 and R1, respectively, and would lead to measured H_2 yields closer to 80% in R1. However, the above-described gasification test provides confirmation of both processes concurrently. The measured CH_4 concentration markedly decreased after the coal slurry feed was stopped. This is because methane is a product of coal devolatilization, which takes place quickly when the coal is initially fed into the reactor.

The CO_2 concentration was low initially, then increased rather steadily. This performance is consistent with the limited amount of bed material and the fact that it was not being regenerated as the case would be when the system is operating in a circulating mode. Since the test was conducted in semi-batch mode, the product gas volume decreased as the test continued, and thus, the high concentrations of CO_2 were not necessarily present in large amounts as coal gasification was reaching equilibrium. In addition, as gasification products declined, it is possible that CO_2 absorbed by the CAM may have been stripped by the steam fluidization gas, shifting the absorption equilibrium toward desorption, even at the low gasification temperatures. In steady-state operation, a continuous supply of fresh CAM would be circulated to the gasification reactor, allowing a low CO_2 concentration to be maintained during gasification.

OTM Oxidation

Air was fed to the reactor during the oxidation stage, which immediately caused an increase in temperature from 700 to 820°C. Figure 9 shows the temperature profile as well as the O_2 consumed, calculated as the difference between the O_2 concentration in air and the measured O_2 concentration in the product stream. During the first ten minutes of the test, 13.3 moles of O_2 were consumed, which corresponds to reduction of 23% of the OTM. Ultimately, 22.5 moles of O_2 were consumed, corresponding to 40% OTM reduction. This OTM performance is significantly better than the 20% reduction predicted by the bench-scale studies. The higher H_2 concentrations present may have contributed to the improved performance. The reduction of OTM by coal combustion products (unmixed combustion) is one of the unique features of the UFP technology that is not as well characterized, and the good performance illustrated provides further confirmation of the viability of this technology

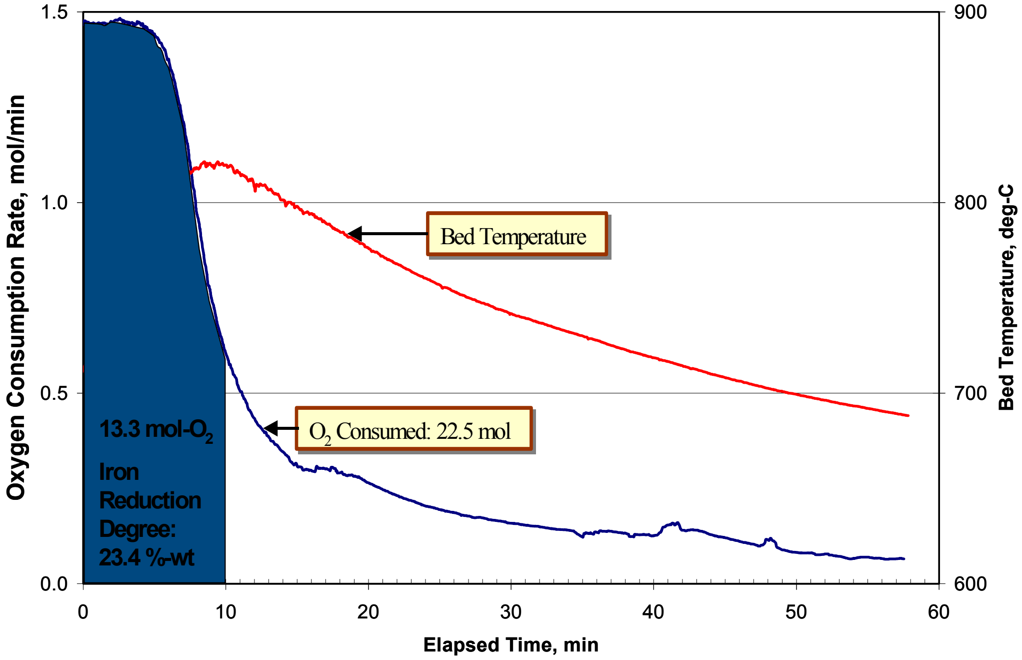


Figure 9. Oxygen consumption rate during pilot-scale oxidation test.

The coal testing conducted on the pilot-scale system provided valuable information and encouraging support for the UFP technology. Due to time constraints described previously, additional testing with coal at higher pressures and in steady-state mode has been deferred to the next stage of this program, which will benefit from the lessons learned during this project.

Kinetic Modeling

The behavior of bed materials as they circulate between reactors is strongly influenced by kinetic considerations. Thus, kinetic modeling can provide insight into how to manipulate variables such as solids circulation rate to achieve optimized performance. It is also important to consider kinetics when scaling up a process or planning for system integration. Kinetic models can be used to predict the selectivity and conversion of key UFP reactions at given operating conditions, setting the stage for optimization. A global kinetic process model was developed for the UFP technology using ASPEN Plus software.

Kinetic parameters for various reactions were obtained from the literature and by using Chemkin software for gas phase reactions. These kinetic parameters were validated using bench-scale UFP results. A semi-batch kinetic model was developed to represent the bench-scale experiments. The validated kinetic parameters were used in the integrated kinetic model of the UFP pilot scale reactors. The kinetic parameters used in the integrated model will be further validated using pilot-scale experimental data as the program proceeds to the next stage. The kinetic model will also be used to optimize the operating conditions of the UFP technology and perform scale-up design.

Kinetic Model Setup

ASPEN Plus was used to model the UFP reactors using global kinetic equations. Major assumptions for UFP fluidized bed modeling include: steady state, completely mixed fluidized bed and adiabatic operation (heat loss will be added in a future version). The UFP reactions include both gas-solid reactions that are kinetically limited (e.g. steam gasification of coal) and equilibrium reactions (e.g. water gas shift reaction). The ASPEN kinetic model appropriately considers both kinetically limited and equilibrium reactions.

Table 3 lists the main UFP reactions in the three reactors. The type of the reaction (kinetic or equilibrium) was decided based on the information available in the literature as well as experimental results. Chemkin was used to estimate gas phase reaction rates.

Table 3. Main UFP reactions in the kinetic model.

Reactor	Reactions	Reference/Comments
R1	**C(s) + H2O -> CO + H2**	Kinetic, Van Heek et al., Journal of the Institute of Fuel, (1973) 249
	CO + H2O <--> CO2 + H2	Equilibrium, Mann et al., Fuel 83 (2004)1643
	S + 2H(fuel bound) -> H2S	Kinetic, reducing environment
	Cl + H(fuel bound) -> HCl	Equilibrium, Chemkin, reducing environment
	CO2 + CaO(s) <-> CaCO3(s)	Equilibrium
	NH (fuel bound) + 2H(fuel bound) -> NH3	Kinetic, reducing environment
R2	**C(s) + H2O -> CO + H2**	Kinetic, Van Heek et al., Journal of the Institute of Fuel, (1973) 249
	Fe2O3(s) + H2 <--> 2 FeO(s) + H2O	Kinetic, reversible, bench scale results
	Fe2O3(s) + CO --> 2 FeO(s) + CO2	Kinetic, bench scale results
	CaCO3(s) <--> CaO(s) + CO2	Equilibrium
R3	**2FeO(s) + (1/2) O2 --> Fe2O3(s)**	Equilibrium, bench scale results

The global kinetic rate equation used for each kinetic reaction shown in Table 3 is shown below:

$$r_n = k_{0n}\,(T/T_o)^m e^{-E_n/R(1/T-1/To)}\ \Pi\ C_i^{\alpha_I}$$

Where

r_n = rate of nth reaction
k_{0n} = pre-exponential factor
T_o = reference temperature, K
T = temperature, K
m = temperature exponent
E_n = activation energy for nth reaction
C_i = concentration of ith component
A_i = concentration exponent for ith component

Modeling of Bench-Scale Kinetic Data

The bench-scale UFP experiments were carried out in a semi-batch mode, where the bed was filled with coal and bed materials: CAM and OTM. The reactor bed was fluidized with steam, air or syngas. Only the gaseous products were analyzed during these experiments. An ASPEN semi-batch model was developed to determine the kinetic parameters from the bench scale results.

Figure 10 shows comparison of model predictions and the experimental data for the coal gasification reaction in R1. The percentage of total carbon detected in the gas phase is plotted as a function of time. The model predictions showed good agreement with experimental data. The kinetic parameters for coal gasification obtained from the experimental data were identical to the kinetic parameters reported in the literature (Van Heek 1973).

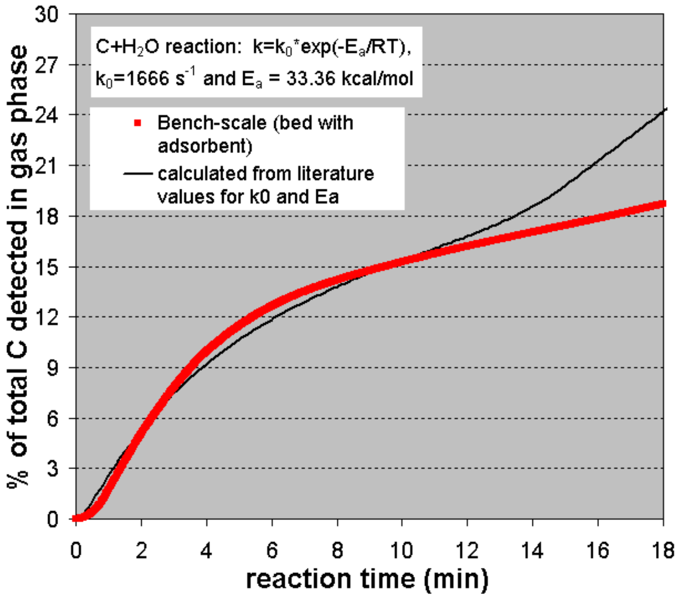


Figure 10. Comparison of coal gasification reaction model with bench-scale results.

Figure 11 shows a comparison of the kinetic model predictions and the bench-scale results for reduction of OTM by CO and H_2 in Reactor 2. The conversion of OTM is plotted as a function of reaction time. The OTM re-oxidation reaction by steam needs to be considered along with the reduction reaction of OTM by CO and H_2 in order to match the model predictions with the experimentally observed results.

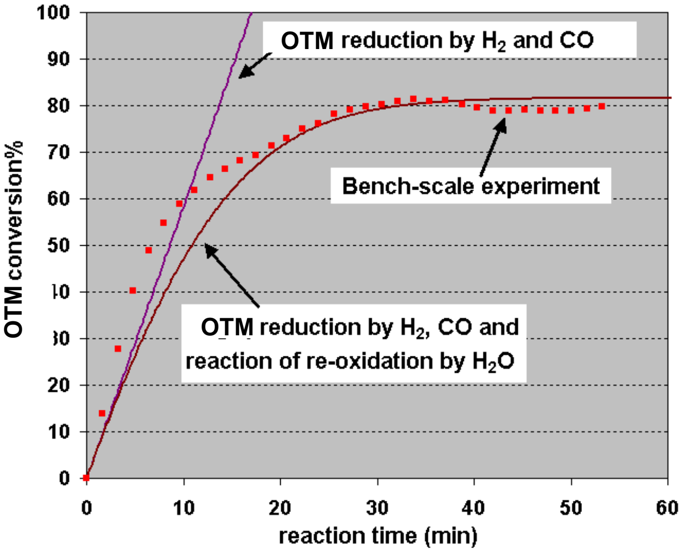


Figure 11. Comparison OTM reduction model with bench-scale results.

It was determined from the experiments carried out by GE and SIU that OTM oxidation in R3 is fast and the reaction approaches equilibrium. Table 4 shows the kinetic parameters obtained from the bench scale data for various reactions.

Table 4. Kinetic parameters obtained from bench-scale data.

Reaction	**k_0, s-1**	**E_a (kcal/mol)**
$C(s) + H_2O \rightarrow CO + H_2$	1,666	33.3
$OTM\text{-}O(s) + H_2 \rightarrow 2\ OTM(s) + H_2O$	1E5	30
$OTM\text{-}O(s) + CO \rightarrow 2\ OTM(s) + CO_2$	5E4	30
$2\ OTM(s) + H_2O \rightarrow OTM\text{-}O(s) + H_2$	90	30

Integrated Three-Reactor Kinetic Model

The kinetic parameters obtained from the bench-scale results and from the literature were used in the integrated three-reactor model. The main difference between the bench-scale kinetic model and the integrated model is that the integrated model is a continuous three reactor model while the bench-scale model is a semi-batch model. The integrated kinetic model will be used to optimize the operating conditions for the UFP technology. Figure 12 shows an example of sensitivity analysis that can be carried out using the integrated kinetic model. The coal conversion in R1 is plotted as a function of two parameters: coal flow rate and % water in slurry. Under the given process conditions, coal conversion decreases as the coal flow rate and % water in slurry increase. Typically ~50% conversion of coal is obtained in the first reactor (gasifier). These results match the equilibrium-based model predictions used to estimate process efficiency.

Figure 13 shows the dry mole fraction of H_2 in R1 predicted by the kinetic model. Typically >85% H_2 (dry basis) will be present in the product stream from R1.

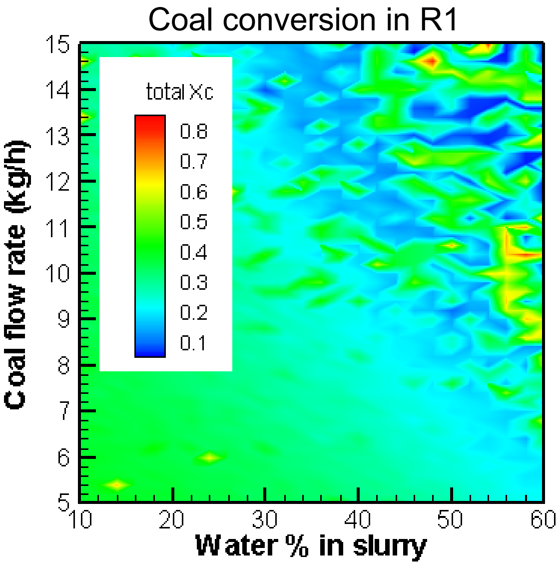


Figure 12. Coal conversion in R1 as a function of coal flow rate and % water in slurry.

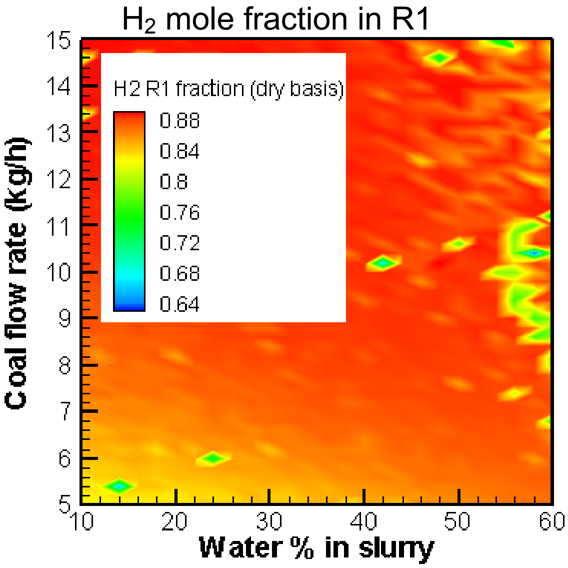


Figure 13. Hydrogen mole fraction in R1 as a function of coal flow rate and % water in slurry.

Additional kinetic modeling is planned, particularly for validation of the kinetic parameters used in the integrated model using pilot plant test results from the next stage of this program. The kinetic parameters for the reactions of impurities present in coal (sulfur, ammonia and chlorine) will be evaluated carefully. This updated model will be used to identify operating conditions that will provide optimized performance.

CONCLUSIONS

Significant progress was made in the fifteenth quarter. Lab-scale experiments provided insight into the impact of preparation method on CAM performance and lifetime and identified methods that result in improved CO_2 capture/release cycling capabilities.

Results of the pilot plant testing confirmed the feasibility of the UFP technology. The key chemical processes were tested and demonstrated the production of high-purity H_2, the absorption and desorption of CO_2, and the oxidation and reduction of OTM. Lab and bench-scale experiments, as well as process modeling efforts have supported the pilot plant design efforts and provided data in support of pilot plant optimization through targeted testing of key UFP processes individually.

Kinetic modeling efforts made use of lab- and bench-scale data to validate process models and derive kinetic parameters that were used to predict behavior at larger scales and in complex systems where measurements of individual reactions are not possible. A global kinetic process model was developed for the UFP technology using ASPEN Plus. Sensitivity analyses were conducted to identify operating conditions that provide improved performance.

The results obtained to date confirm the viability of the UFP process, and provide support for the need for further experimentation to reduce the technical risks associated with this novel approach to coal utilization for H_2 and electricity production.

FUTURE WORK

Future work on UFP technology development will include additional experimental testing of the UFP process at pilot scale. In addition, kinetic and process model development will continue to support pilot-scale system operation and provide a basis for the design of larger-scale experimental systems. The continuing analysis of UFP economics based on experimental and modeling results will provide the data necessary to identify areas that have the most significant impact on the UFP's commercialization potential. These tasks will aid in ensuring that the UFP system will meet the needs of the power generation industry both efficiently and economically.

REFERENCES

K. H. Van Heek, H. Juntgen, W. Peters, "Fundamental studies on coal gasification in the utilization of thermal energy from nuclear high temperature reactors" Journal of the Institute of Fuel, 46 (1973) 249.

LIST OF ACRONYMS AND ABBREVIATIONS

AQMD	Air Quality Management District
CAM	CO_2 Absorber Material
CEC	California Energy Commission
CEMS	Continuous Emissions Monitoring System
CTQ	Critical to Quality
DFSS	Design for Six Sigma
GC	Gas Chromatograph
IGCC	Integrated Gasification Combined Cycle
NETL	National Energy Technology Laboratory
NTI	New Technology Introduction
OTM	Oxygen Transfer Material
R1	Reactor 1
R2	Reactor 2
R3	Reactor 3
SEM	Scanning Electron Microscope
SIU-C	Southern Illinois University – Carbondale
TGA	ThermoGravimetric Analyzer
UFP	Unmixed Fuel Processor
U.S. DOE	United States Department of Energy