Coal Energy Conversion with Aquifer-Based Carbon Sequestration:
An Approach to Electric Power Generation with
Zero Matter Release to the Atmosphere

Investigators
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Introduction

The goal of this project is to provide fundamental information needed to develop a novel coal-based electrical power generation process that includes capturing and storing CO_2 in inherently stable forms. The process involves the conversion of the chemical energy in coal to thermal energy and electricity with permanent storage of conversion products in saline aquifers. The process produces no NO_x, SO_x, particulate matter, mercury, greenhouse gas, or any other air emissions. Carbon dioxide-laden water and fly ash/saline solid residues are the only process effluents. Such a system eliminates the need for costly gas cleanup equipment as well as reduces the costs associated with years of monitoring stack-gas emissions. In addition, it provides a carbon dioxide sequestration option that may be more acceptable to the public because it is easy to understand and is potentially a walk-away approach to sequestration.

Coal-fired power plants, owing to the nature of their fuel, have the potential to emit undesirable substances into the environment such as nitrogen and sulfur oxides, particulate matter, mercury, arsenic, lead, and uranium. Clean coal technologies that have been developed to remove these substances from flue gases before they are emitted into the atmosphere have significantly increased the cost of coal-derived energy, reducing the economic attractiveness of an otherwise inexpensive fuel. The economic benefit is further reduced when CO_2 must be removed from the flue gases and sequestered because of its potential impact on climate change. Constructing power plants that release no combustion products to the atmosphere at all but instead, that sequester the entire effluent stream would end the expensive cycle of continually identifying and managing the next-most-harmful coal combustion product.

Deep saline aquifers have been recognized as suitable locations for the storage of CO_2. Sufficient sites have been identified in the United States to store over 3,500 billion tons of CO_2. This is enough capacity to store about 86 years of CO_2 generated in coal-fired power plants at the rate of coal consumption for electric power generation in 2005. Preliminary estimates indicate that injection and extraction aquifers separated by about 22.5 km with 5-km long well lengths should store the effluent of a nominal 500 MW_e power plant over its nominal 40-year operation (key assumptions include 30-m thick aquifer, 1-Darcy permeability, and 20% porosity). The scheme for electrical power generation under investigation produces CO_2 that is in equilibrium with the aquifer environment, eliminating the possibility of it migrating back to the surface through fissures or well bores once injected into the aquifer. The stream that will be returned to the aquifer will be in thermal and mechanical and close to chemical equilibrium with the

water already in the aquifer. This injected stream will be less buoyant than liquid CO_2 at reservoir conditions, allaying any concerns about selective CO_2 release.

The advantages of this aquifer-based coal-fired power plant relative to current and other proposed power generation systems include (i) maximally efficient power production while storing CO_2 products in indefinitely stable forms, (ii) near-zero traditional air pollutant emission and stack elimination, and (iii) size reduction of reactor vessel (compared to pulverized-coal systems). Although the thrust of the project is directed to clean coal utilization, the process being developed applies in general to all stationary thermal processors (gasifiers and combustors) using all types of fuel (coal, natural gas, oil, biomass, waste, *etc*.). Our investigation aims to lay the foundation for an efficient coal energy option with no matter release to the atmosphere and in which all fluid combustion products, particularly carbon dioxide, are pre-equilibrated in aquifer water before injection into the subsurface.

Background

In the coal energy conversion scheme being investigated, water from a deep saline aquifer is employed. The water is desalinated, used in the coal energy conversion process, and returned to the same or nearby aquifer. Pressures in deep saline aquifers range from 75 to 270 bar, and have temperatures from 35 to 103°C. The high aquifer pressures are advantageous, for coal processing is to take place near the critical point of water, at pressures as high as 221 bar. Owing to the solvation properties of supercritical water, nonpolar organic compounds and oxygen are miscible in all proportions and many inorganic salts are insoluble in water above its critical point. Consequently, all the organic coal conversion products will dissolve in the supercritical water; reaction products will be in the same fluid as the aquifer water as soon as they are formed. In this way, all trace species introduced with the coal (such as mercury, arsenic, *etc*.) as well as all coal conversion products are sequestered in the aquifer along with the CO_2. The only matter that will not be directed into the aquifer are ash and some inorganic salts, which will be separated during the reaction process and returned to the lithosphere.

Supercritical water ($T_{c,H2O} = 647$ K, $P_{c,H2O} = 221$ bar) has several properties that make it an attractive medium for power generation. Besides the fact that gases and organic compounds are miscible in supercritical water, it is a dense phase ($\rho_{c,H2O} = 322$ kg/m^3) in which transport rates are high enough that reactions can be completed in several seconds, depending on the reactants and the reactor state.

System Schematic

A flow diagram that outlines the essential features of the proposed coal-to-electricity scheme, employing oxygen produced in an air-separation unit as the oxidizer, is shown in Fig. 1. The brine from the aquifer is preheated and desalinated before introduction into the system since salts are insoluble in supercritical water at the temperatures anticipated during the coal conversion process. After salt separation the supercritical water from the aquifer is combined with pulverized coal to form a dilute slurry, ~10% solids by mass. The slurry is then combined with a fraction of the preheated oxidizer in a reformer where the coal volatiles and char are converted to compounds miscible in supercritical water. The inorganic solids are removed from the system at this point and any carbonaceous solids are recycled to the reformer inlet. The single-phase, post-reformer, fuel solution is then passed to an oxidation reactor where the remainder of the oxidizer is added and

chemical-to-sensible energy conversion is completed. The hot products from this reactor are used to drive a heat engine that produces work and cools the fluid. The product stream is then further cooled via heat integration with the incoming brine. The previously separated salts can be reintroduced into the cooled solution before it exits the plant to the injection well, if the commercial value of the salts is low. The plant outlet state is a fully equilibrated, single-phase brine solution carbonated to just below CO_2 saturation conditions.

Figure 1: Schematic of coal processing under supercritical conditions using aquifer brine as a solvent. Processing occurs at a near-constant pressure above the critical point of water (pumps not shown) so as to achieve compact, high-efficiency extraction of hydrocarbons from the coal followed by complete oxidation to carbon dioxide and water. A heat engine is used to extract sensible energy from the product gases and to begin the cooling process toward aquifer conditions. After further heat exchange with the incoming brine, the product stream is mixed with excess brine to yield a homogeneous subcritical (in temperature) CO_2-saturated brine for injection back into the aquifer.

The water must be kept at a high pressure for re-injection, therefore it is not feasible to extract energy via expansion work, the efficiency of the process would be too low. Instead, energy is extraction in the form of heat, using a closed helium Brayton cycle with heat input at 1400 K and 250 bar (matching the reformer hot stream pressure) combined with a steam bottoming cycle. Assuming isentropic efficiencies for real turbomachinery of 85%, preliminary thermodynamic analysis indicates an efficiency for the combined cycle of nearly 50%. Making allowances for energy to operate the oxidizer plant, the overall plant efficiency will be in the mid 40s, which places this option on par with sequestered IGCC designs. Although the preliminary analysis indicates that the proposed system and IGCC can achieve similar efficiencies, the proposed system has

some advantages because it operates with no matter release to the atmosphere and it delivers equilibrated (carbonated) brine to the sequestration effort in place of neat CO_2.

Research Objectives and Tasks

The overall objective of this research project is to provide the information needed to design and develop the key process units in the proposed aquifer-based coal-to-electricity scheme with CO_2 capture and sequestration. The project is divided into five task areas: (i) Life Cycle Analysis, (ii) Supercritical Coal Reforming, (iii) Synthesis Fluid Oxidation, (iv) Materials Research, and (v) Aquifer Interactions. The Life Cycle Analysis task will provide fully qualified cycle efficiency and process analyses. These analyses will be used to determine the design choices made in investigating component requirements in the proposed scheme with CO_2 capture and sequestration.

Research efforts in the Supercritical Coal Reforming task are aimed at determining the supercritical water (SCW) conditions that maximize the amount of chemical energy from the coal in the synthesis fluid. Defining the optimum amount of oxygen required to drive the gasification reactions and at the same time yield a high energy-content synthesis fluid as a function of coal composition in the SCW environment is one of the goals of this task. Other goals are to characterize coal extraction and pyrolysis and char gasification and oxidation to the extent that coal conversion rates in supercritical water environments can be correlated with temperature, pressure and properties of the coal. In concert with this is the goal of developing models that can predict accurately coal conversion rates to synthesis fluid under SCW conditions. This requires the development of accurate expressions for the predictions of thermochemical and transport properties of SCW media.

The research efforts concerned with the Synthesis Fluid Oxidation task center around the design of the oxidation reaction. The stream exiting the oxidation reactor, entering the heat exchanger of the heat engine needs to operate as close as possible to material thermal limits to maximize heat engine efficiency. Thus, a primary goal of the oxidation reactor design effort is the distancing of oxidation zones from reactor walls. An additional requirement is control of reducing and oxidizing streams to avoid liner corrosion. Under consideration is the design of a combustor in which hydrodynamics and water injection are used to control reaction, mixing, and wall interactions.

The Materials Research tasks are focused on identifying materials for construction of the process units. Materials represent one of the most critical issues in developing the proposed process. The simultaneous presence of oxygen and ions in the supercritical fluid forms an aggressively corrosive environment. In addition, deposition of ash on reactor surfaces induces corrosion. Very little information is available on materials degradation at the high-pressure, high-temperature conditions that will exists in the process units.

Research activities associated with the Aquifer Interactions task are concerned with characterizing the impact of dissolved constituents in the water being returned to the aquifer on aquifer ecology. Of interests are the fates of contaminants prevalent within coal, such as arsenic, mercury, and lead. Geochemical conditions in the deep subsurface are likely to lead to the partitioning of elements such as As and Hg to the solid phase. These elements are subject to migration should physical isolation be disturbed. Another

concern is the possible oxygenation of the aquifer, potentially destabilizing the sulfidic minerals. A third concern is the potential to develop dramatic fluctuations in pH resulting from variations in CO_2 content, possibly destabilizing aquifer solids and inducing dissolution or colloidal transport. Geochemical constraints are expected to diminish the risk imposed by heavy metal discharge into the physically isolated deep brines but in the research efforts, a combination of equilibrium based predictions and spectroscopic/microscopic characterization of the energy system products will be performed to verify reaction end-points.

Project Status

The Principle Investigators were notified in late December 2006 that the proposal submitted to GCEP to perform the proposed work was granted and that work could begin in January 2007. Besides the research participants from Stanford University, the project participants included researchers from Brigham Young University (BYU) and the University of Utah. After review of the contractual obligations by administrators at these universities, it was decided that the contract violated the intellectual property policies of the universities, and in March 2007, the PI at Stanford and GCEP administrators were notified that researchers at BYU and the University of Utah would not be able to participate in the project. Researchers at these universities had primary responsibility for tasks associated with the life cycle analysis and the materials research with shared responsibilities in the tasks associated with characterizing and modeling coal conversion phenomena in the reformer, including development of models for the prediction of thermodynamic properties for supercritical water media. The BYU group also had the responsibility of investigating hydrogen production during the coal conversion process in the supercritical water environment.

The Stanford participants are currently having discussions to determine the best way to proceed. The researchers at Stanford have expertise in all areas of the work to be undertaken except for the task associated with materials research. In our initial proposal to GCEP, a complete thermodynamic analysis and tasks to characterize the rates of coal conversion to synthesis fluid in SCW media were proposed. We had also proposed to design the synthesis fluid combustor and to define the thermodynamic states of the Brayton and Rankine cycles for the combined-cycle heat engine. We had not proposed tasks to characterize hydrogen production in this SCW scheme or tasks concerned with materials research.

We are surveying faculty members at Stanford (and considering surveying researchers at SRI International) who have backgrounds in materials science, hoping to find someone with the expertise needed to perform the work described in the proposal associated with identifying materials that can withstand the high-temperature, high-pressure, corrosive environments that will exist in the process units. Assuming that someone will be found, we plan to rewrite the project work statement, identify the new participants, modify the budget to reflect a redistribution of the funds awarded for the project, and present the revised plan to the GCEP administration for approval, by the first part of June 2007.

Significant Results

The project is in its fifth month. Although no significant experimental results have yet been obtained, progress has been made as described below.

Thermodynamic analysis (Edwards)

Efforts during the first four months of this project focused on refining the thermodynamic model of the proposed plant. The purpose of this model is both to evaluate the viability of the system in terms of overall efficiency and to allow for complete definition of the heat exchange and combustor components.

A schematic of the system was shown above, in Fig. 1. Not all of the components indicated are necessary for evaluating the efficiency of the plant, for example, the salt separator and the slurry plant have little impact on efficiency. The components that are critical for efficiency (the oxygen preheater, brine preheater, and main heat exchanger and the reformer and combustor) are modeled in detail in Fig. 2. The thermal processing system of the reformer and combustor is represented as a single combustor since the end result of this subsystem is a fully reacted products stream. (The details of solid separation and oxygen split between reformer and combustor are unimportant when using the complete reaction/major-products assumption.)

Figure 2: Schematic of the plant as presently modeled. Hot combustion products (stream P1) leave the combustor and drive an indirectly fired combined cycle (IFCC) through the main heat exchanger. The moderately cooled products (P2) then heat the incoming oxygen (O2) and aquifer water (W1) before leaving the plant to be pumped back

The most significant aspect of the refined model is the heat engine, which is an indirect combined cycle. Unlike NGCCs, which burn fuel in an open Brayton cycle, this concept uses a closed Brayton cycle bottomed with a conventional Rankine cycle. Since there is no chemistry occurring (and thus no oxidizer needed in the top cycle) we are free to choose the working fluid. Helium is selected due to its large ratio of specific heats and high thermal conductivity. The model incorporates cooling of the first four turbine blade rows of the gas turbine using bleed helium from the compressor outlet. Without this

detail, the efficiency of the Brayton cycle would be overstated since the inlet temperatures would exceed state-of-the-art limits on turbine materials.

Due to the high temperature required for efficient heat engine operation, our strategy is to match the pressure of the Brayton cycle working fluid to that of the post-combustor fluid stream in order to minimize material stress at the heat-exchange surface. This pressure must be greater than the critical pressure of water, and is set to 225 bar. Because the working fluid is a thermally prefect, nearly ideal gas, the Brayton cycle temperature ratio depends on the cycle pressure ratio but only weakly on the actual values of pressure used. The temperature ratio here is standard, thus the pressure ratio is as well. Hence the low pressure in the Brayton cycle is correspondingly very high, higher in fact than the high pressure in most Brayton cycles. As a consequence, the physical construction of the heat exchanger linking the topping and bottoming cycles will not be as simple as that of the standard HRSG as seen in NGCC systems. However for the purposes of this model, it is still thought of as consisting of economizer, boiler and superheater sections. (A pinch-point temperature difference of 20 K is assumed in the analysis.)

The Rankine bottoming cycle is standard except for the high fire-side pressure in the HRSG. Water is the working fluid, operating between 312 K at 6.7 kPa and a high temperature in the 900 - 1100 K range, dictated by the Brayton turbine outlet temperature and the prescribed HRSG heat exchange effectiveness.

The remaining components of the model are associated with the most basic elements of heat integration. One is an aquifer water (brine) preheater operating with heat from the product stream exiting the main heat exchanger. The other is an oxygen preheater. The low temperature of the Brayton cycle could be reduced, thus lowering the temperature of the products leaving the main heat exchanger, but it is kept high intentionally so that these preheaters may be used to bring the aquifer water and oxygen up to the supercritical temperature required for proper operation at the combustor inlet (and desalination of the brine stream).

A detailed air separation unit (ASU) model is being developed and will be integrated with the remainder of the plant. At present we are assuming use of a non-integrated ASU that delivers oxygen at 300 K and 227.3 bar. The oxygen is pumped to the combustor pressure in the liquid state, regeneratively heated back to ambient temperature in the ASU, and heated to the desired combustor inlet temperature in the preheater depicted in the Fig. 2. Liquid pumping is used to avoid the large compressor work required to achieve supercritical combustor pressures. For the ASU, we assume a work requirement of 220 kWh/tO_2 based on state-of-the-art data reported in the literature [1]. This requirement is similar to that for oxygen delivery at low pressures since the liquid pumping work is small. The required heating to combustor inlet temperature comes from heat exchange with about 10% of the partially cooled product stream leaving the main heat exchanger.

The model is solved to match key parameters as follows: The minimum Rankine turbine exit quality specification (90%) determines the Rankine pressure ratio. The pinch-point temperature difference (20K) in the HRSG then fixes the Rankine mass flow rate relative to the Brayton cycle. Fuel oxygen demand gives the oxygen mass flow rate. The aquifer combustor water requirement is set by the desired combustor adiabatic exit

temperature (1600 K in the tables below). While the water acts as a medium for combustion and CO_2 dissolution, to the combustion reaction enthalpy balance it is merely a diluent as is nitrogen in air-fired combustion.

Conditions at various stations in the plant are shown in Table I, and the resulting power balance is presented in Table II (as scaled for a 500 MW plant). For the chosen plant parameters the overall efficiency is 43.5% on an LHV basis.

Table I: Model Plant Conditions

Stream	O1	O2		W1	W2
Temperature (K)	300	700		344.3	700
Pressure (bar)	227.3	225		227.3	225

Stream	P1	P2	P3		
Temperature (K)	1600	728.4	369.0		
Pressure (bar)	225	222.8	220.5		

Stream	B1	B2	B3	B4	
Temperature (K)	347.1	556.7	1548	1070	
Pressure (bar)	81	225	202.5	90	

Stream	R1	R2	R3	R4	R5
Temperature (K)	311.6	313.0	993.3	311.8	311.6
Pressure (bar)	1.0	191.0	163.8	0.068	0.067

Table II: Model Plant Power Balance

Component	Power (MW)
Brayton Cycle	
Compressor	-259.9
Turbine	453.9
Net	194.0
Rankine Cycle	
Condensate Pump	-0.0027
Feed Pump	-5.43
Turbine	375.9
Net	370.4
ASU	-64.4
Overall Plant	500.0
Fuel Heat Rate (LHV)	1149.5
Efficiency (% LHV)	43.5

A key result of this model is the dependence of overall plant performance on the conditions at the heat-exchange interface between the combustor and the Brayton cycle. The relation between overall efficiency and combustor outlet (peak interface) temperature is shown in Fig. 3, indicating that efficiencies in the mid-40s (based on LHV) are achievable in the system as currently envisioned.
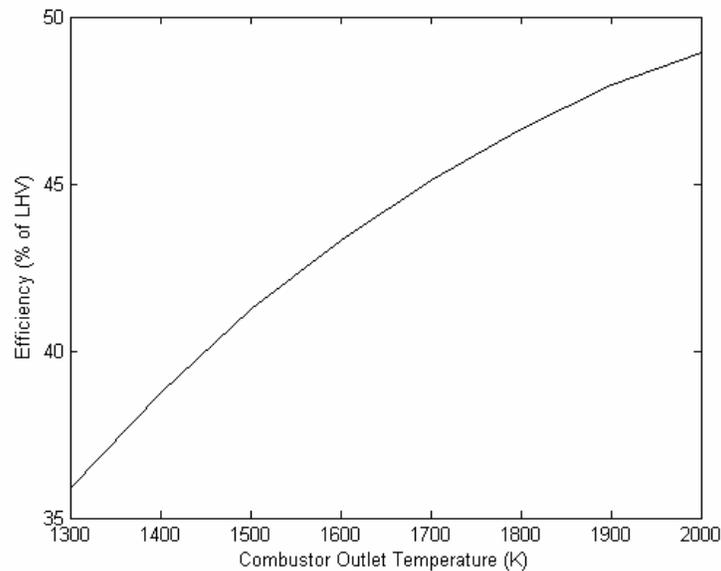
Figure 3: Plot of overall plant efficiency versus combustor outlet temperature. The maximum temperature and pressure of the combustor outlet stream that may be tolerated by the main heat exchanger is the critical driver of overall plant efficiency.

Future Plans (Thermodynamic analysis)

Although systems modeling will continue throughout the project (including complete heat integration and integration with the ASU) our focus will soon shift to detailed design and fabrication of the prototype combustor. This will form the major thrust of this task for the upcoming year and allow us to better define the requirements at the heat exchange interface that has been identified as critical for overall system performance.

References (Thermodynamic analysis)

1. IPCC, 2005: IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change [Metz, B., O. Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 442 pp.

Contacts (Thermodynamic analysis)

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Supercritical coal reforming (Mitchell)

A place to site the experimental facility in which experiments on coal conversion in supercritical water environments will be performed has been located. The experimental equipment already in place at the site had to be disassembled and properly disposed, which required finding faculty members who could use useful equipment and instrumentation, reporting all SU-tagged equipment that was to be discarded to the proper Stanford authorities, and dispensing all chemicals and solvents stored in cabinets in University-approved manners. Once completed, assembly of the experimental facility for the study of coal conversion to synthesis fluid in SCW media will begin.

The experimental facilities of other researchers who have performed experiments in supercritical water environments have been surveyed and it has been concluded that Inconel 625 is an adequate material for a laboratory facility. Our goal is to have an experimental arrangement that will permit the determination of coal weight loss and product composition as a function of the time the coal sample is exposed to supercritical water environments containing controlled amounts of oxygen. We would like to use our gas chromatograph (GC) and Fourier transform infrared spectrometer (FTIR) to determine the composition of the product stream leaving the SCR reformer, however our GC and FTIR are not capable of monitoring streams at pressures as high as 221 bar. Consequently we are reviewing options that would permit us to use these instruments at the highest permissible pressures, with modeling of changes in composition with pressure to relate the measured composition to that existing at the SCW condition.

Also, the graduate researcher working on the project is learning some of the procedures used in our laboratory to characterize the reactivities and specific surface areas of coal and biomass chars. Temperature programmed desorption measurements to determine the distributions of the strengths of adsorption sites on carbonaceous surfaces and CO_2 gas adsorption measurements to determine the area available for gas adsorption per unit mass of carbonaceous material are two procedures currently being mastered.

Future Plans (Supercritical water reforming)
Immediate plans are to continue to prepare the site at which the experimental facility for the study of coal conversion in SCW media will be located. The design, construction, assembly, and testing of the laboratory reformer and flow control panel are scheduled to be completed by the end of the summer. Coal conversion tests in SCW environments should begin by September 2007.

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