# 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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**Abstract**

This project has the objective of providing the information needed to develop a coal-based electric power generation process that involves coal conversion in supercritical water (SCW) with $CO_2$ capture and storage. In efforts to date, we have constructed a system-level model of the proposed plant that can be used to evaluate the viability of the overall concept in terms of efficiency. In the thermodynamic analysis, the coal composition is based on that of a sub-bituminous coal. The combustion products stream is treated as an ideal solution of real fluids (water, oxygen, carbon dioxide, and nitrogen), with property data computed using a linear mixing rule. The Brayton cycle helium heat engine is modeled as an ideal gas. The work requirement for the air separation unit used to obtain process oxygen is taken from the literature. Aquifer conditions and well pressure losses used to calculate the work requirements of the aquifer water pumps are also taken from the literature. Representative state-of-the-art values are used for other component performance parameters.

The model was used to calculate the power balance for a 500 MW power plant. For a combustor outlet temperature of 1650 K and a Brayton compressor inlet pressure of 79.5 bar, overall efficiency, after energy penalties for oxygen separation, carbon sequestration, and non-ideal components, is just over 42% on a lower heating value basis. The model indicates that the overall efficiency of the system increases with combustor outlet temperature. For a selected outlet temperature, the overall efficiency usually increases with the Brayton inlet pressure, however at certain inlet pressures, the combination of conditions in the SCW system loop causes decreased efficiency.

Also to date, the reactor that will be used in tests to characterize coal extraction, devolatilization and gasification in SCW environments has been designed and built. It provides up to 125 s of reaction time under isothermal conditions. A base-case coal for study has been selected and the models that will be developed to predict coal extraction and devolatilization rates in the reformer have been identified. Development of a reaction mechanism that describes the rate-limiting reaction pathways during reaction between char and water vapor has also been initiated.

The major hardware for the supercritical water combustor experiments has been identified and an experimental facility that will permit various burner geometries to be tested has been planned. A high-pressure stack consisting of a reactant preheater, a supercritical combustor, an experimental heat exchanger, and a cooling section has been designed.

Work has started on development of a procedure to determine thermodynamic property data at supercritical water conditions where gas behavior is not ideal.  Multi-parameter fits for the Helmholtz energies of carbon dioxide and water have been developed.  Property data are derived from derivatives of the Helmholtz energy with respect to reduced density and inverse reduced temperature.  A software library has been written to create a comprehensive thermodynamic properties resource for $CO_2$ and $H_2O$.  In order to determine the thermodynamic properties of mixtures, a mixing model has also been developed that models the departure from an ideal Helmholtz solution using a modified corresponding-states approach.  In work focused on the calculation of transport properties, two models for viscosity and thermal conductivity have been examined for their applicability at supercritical water conditions.

An extensive materials search has been conducted to determine the best option for the heat exchanger wall.  Molybdenum was determined to be the most suitable base metal, due to its high melting point of 2890 K.  An alloy of molybdenum, titanium-zirconium-molybdenum, is an even better option, for it maintains its strength more so than molybdenum, allowing for a thinner wall (rendering better heat transfer).

**Introduction**

This project has the objective of providing the information needed to develop a coal-based electric power generation process that involves coal conversion in supercritical water with $CO_2$ capture and storage in an inherently stable form.  The only process effluents are supercritical water, containing dissolved coal conversion products, and solids, composed of fly ash and salts that precipitated from the water.  Having no gaseous emissions, such a system eliminates the need for costly gas cleanup equipment.  In addition, it provides a carbon dioxide sequestration option that may be more acceptable to the public.

Coal-fired power plants 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 have no gaseous emissions 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 conversion product.

Deep saline aquifers have been recognized as suitable locations for the storage of $CO_2$.  In the United States, the sites identified have the potential 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 a 30-m thick aquifer having 1-Darcy permeability and 20% porosity can store the effluent of a 500 $MW_e$ power plant over its nominal 40-year lifetime.  The proposed scheme for electric 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) 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, coal conversion takes place in supercritical water ($T_{c,H2O}$ = 647 K, $P_{c,H2O}$ = 221 bar), the water being obtained from a deep saline aquifer. Owing to the solvation properties of supercritical water (SCW), the small polar and nonpolar organic compounds released during coal extraction and devolatilization are dissolved in the water and the larger ones are hydrolyzed, yielding dissolved $H_2$, $CO$, $CO_2$, and low molecular weight hydrocarbons, without tar, soot or PAH formation. Sulfur, nitrogen and many of the trace elements in coals are oxidized to insoluble salts in SCW that precipitate from the fluid mixture. The insoluble salts are removed from the system with the coal ash. The water is returned to the same or nearby aquifer after use. In this coal conversion scheme, 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 not directed to the aquifer is the solid material, the ash and precipitated inorganic salts.

Since inorganic salts are insoluble in supercritical water, the saline water from the aquifer must be desalinated before use. If not, the ability of the water to absorb coal conversion products would be reduced and the salts would precipitate in the gasification reactor, mixing with the ash. The salts would have to be separated from the ash if the ash were to be used, for instance, as aggregate material.

Besides the fact that gases and organic compounds are miscible in supercritical water, SCW is a dense phase ($\rho_{c,H2O}$ = 322 kg/m³) in which both mass transport and chemical reaction rates are high. The short characteristic times for transport and chemical reaction permit reduced sizes for gasifiers and combustors compared to other coal conversion technologies.

**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 power plant with $CO_2$ capture and sequestration. The project is divided into four research areas - Area 1: Systems Analysis, Area 2: Supercritical Coal Reforming, Area 3: Synthesis Fluid Oxidation and Heat Extraction, and Area 4: Aquifer Interactions. In Area 1, thermodynamic analysis of the scheme 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.

Research efforts in Area 2 (Supercritical Coal Reforming) are aimed at determining the supercritical water 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. 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 obtaining the data needed to characterize coal extraction and pyrolysis rates and char gasification and oxidation rates in supercritical water environments as functions of temperature, pressure and properties of the coal and its char.

The research efforts associated with Area 3 (Synthesis Fluid Oxidation and Heat Extraction) are focused on the design of the oxidation reactor and transfer of the energy released to a heat engine in order to extract work. 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.

Research activities associated with Area 4 (Aquifer Interactions) 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.

Materials degradation represents one of the most critical issues in the development of 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. A research project that is focused on identifying materials for construction of the process units is needed before commercial acceptance of this technology.

**Project Status**

Area 1: Systems Analysis (Edwards)

*Development of Plant Concept*

The first task of the project was to construct a system-level model of the proposed plant. The purpose of this model is to evaluate the viability of the overall concept in terms of efficiency. In this section we present our current system concept. In a subsequent section we present the results of the corresponding efficiency analysis.

The block diagram for a coal-fired SCWO plant is shown in Fig. 1. The defining characteristic of this system is the use of aquifer water as a processing medium, so we follow the path of water through the plant. An amount of aquifer brine sufficient to dissolve all of the carbon dioxide produced by complete combustion of the coal enters the plant from production wells. If all of this water passed through the SCWO system, its outlet temperature would be low, leading to poor efficiency. Hence, the flow rate of water through the SCWO system is determined by its desired outlet temperature. Figure 2 shows the SCWO system outlet temperature as a function of the fraction of total dissolution water directed through it. The remainder of the aquifer water bypasses the SCWO system and heat engine and is mixed back into the effluent from the heat engine in the regenerator/desalinator.
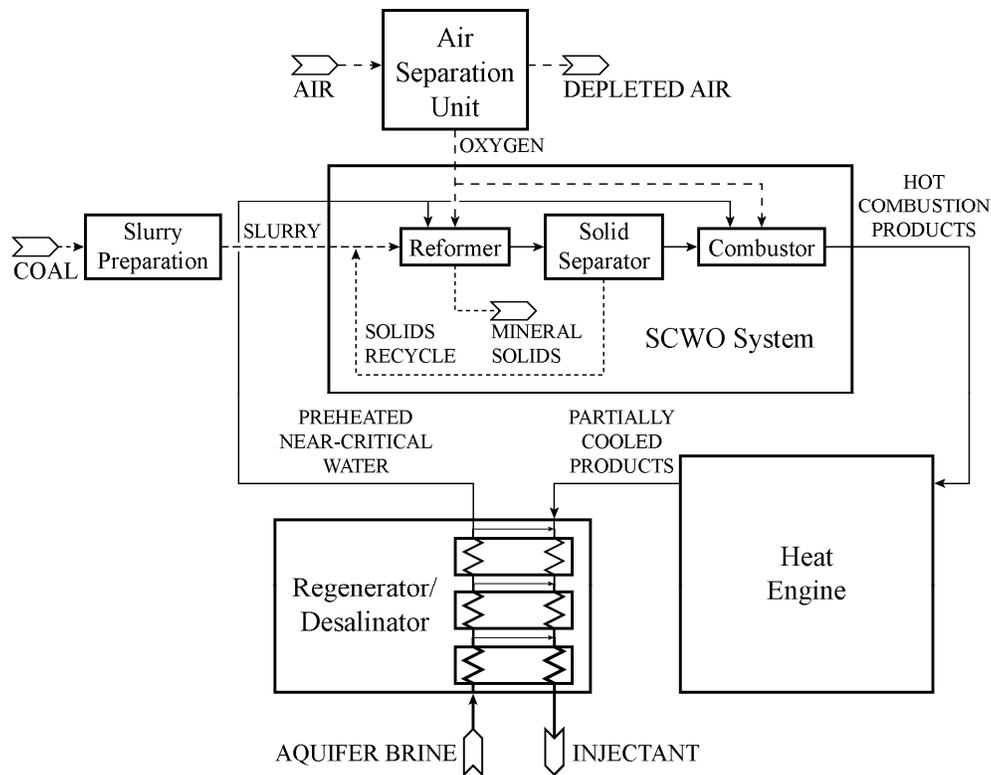


**Figure 1:** Diagram of a SCWO-based power plant. A regenerator is used for desalination and to improve thermal efficiency. Multiple stages prevent formation of a gas phase in the product stream. (Three stages are shown for illustration.) Oxygen from an ASU is used instead of air since nitrogen is much less water soluble than carbon dioxide. Coal processing is divided into reformer and combustor sections to facilitate mineral matter removal and protection of vessel walls. The choice of heat engine is left open at this stage.

The water that is used for fuel processing must be preheated to near-critical conditions. Preheating in a regenerator with heat transfer from the warm effluent stream improves the efficiency of the system, since it raises the average temperature of heat addition to the heat engine. Note that this regenerator is not part of the power cycle, but its purpose is similar. A side effect of heating the inlet brine to near the critical temperature is the precipitation of salts; while organics and gases become highly soluble in water above the critical point, ionic materials have low solubilities in supercritical water. Salt removal at this stage is desirable since it precludes precipitation in the combustor and high-temperature heat exchangers where it would be more difficult to manage than in a moderate-temperature regenerator. Hence, we envision a combination regenerator and desalinator unit where desalination is accomplished by temperature driven precipitation, followed by mechanical separation. Low-salinity, near-critical water leaves the regenerator. The small amount of impurities remaining may be removed by adsorption or filtration. Desalinated water passes into the SCWO system to moderate the reaction process.
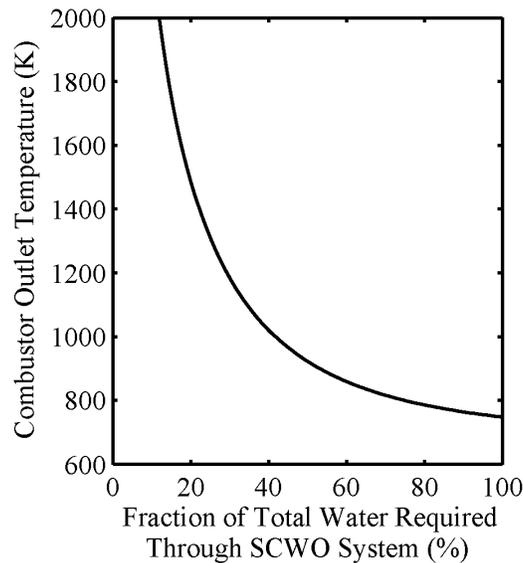


**Figure 2:** More water is required for dissolution of carbon dioxide in the aquifer than for moderation of combustion. The fraction of aquifer water required to achieve various adiabatic flame temperatures at the SCWO system outlet is shown.

The other inputs to the SCWO system are coal-water slurry and an oxidizer. Oxygen from an air separation unit (ASU) is shown in Fig. 1. Since nitrogen is much less soluble in water than carbon dioxide, nitrogen from air would separate into a gas phase in the cooled effluent leaving the plant. We use oxygen to ensure that the products will be a single-phase solution that can be securely stored in an aquifer. An alternative is to use air and circulate enough aquifer water to dissolve all of the nitrogen, but this would require a prohibitive amount of water. Although the proposed system still has an energy cost of separation that one might hope to avoid, the trade-off of carbon separation for air separation is advantageous since we now have the ability to sequester all fluid coal combustion products, including sulfur and metals, not just carbon dioxide.

Since coal is a complex, solid fuel, processing in the SCWO system is divided into reformer and combustor sections so that mineral matter (ash) can be removed. Mineral matter should be removed early to prevent deposition in downstream components where it would be more difficult to manage. In the reformer, near-critical water heats the coal particles, causing them to devolatilize. Oxygen from the ASU is used to assist with char burnout. These decomposition processes separate the carbonaceous fuel from the mineral matter so that it can be removed. The temperature rise through the reformer should be relatively low so that the process stream remains easy to handle in the solid separator. From here, any solids are recycled to the reformer so that they have sufficient residence time to achieve the required degree of carbon extraction.

The fluid output from the solid separator is a single-phase synthesis fuel solution of water, hydrocarbons evolved from coal, and products of reaction. This aqueous synfuel and most of the oxygen from the ASU meet in the combustor, where oxidation is completed. Since the fuel is a dense fluid and no heat exchange is desired within this component, the combustor can be similar to modern gas turbine combustors. These combustors feature intense, localized flames that are stabilized by fluid recirculation. Perforated liners allow cooling flows to protect surfaces from the destructive heat and oxidation of the flame zone. In gas turbine engines, stabilization and cooling flows use compressed air. In the proposed combustor, desalinated, preheated aquifer water is used.

After exiting the combustor, the process stream is a single-phase, supercritical solution of hot combustion products suitable for driving a heat engine. The choice of heat engine does not affect the plant concept at this point; an appropriate type will be introduced for the thermodynamic model below. The products pass through a heat exchanger, transferring their energy to the heat engine working fluid. A chief difficulty with design of heat engines is heat exchangers that can withstand very high temperatures, since this limitation affects the upper bound of cycle efficiency. To make construction of this heat exchanger feasible, the pressure of the working fluid should equal the pressure of the combustion products. The heat exchange surfaces must operate at very high temperatures, but by pressure matching the streams in the heat exchanger these surfaces do not have to withstand significant mechanical stress. With this design choice, stability and corrosion are the key material limitations instead of high-temperature creep strength.

After cooling to near the critical temperature in the heat engine, the product stream flows through the hot side of the regenerator/desalinator unit where it heats the incoming aquifer brine. To prevent the formation of a gas phase in the regenerator, the cooling is done in stages, with partially heated aquifer water (drawn from the inlet side) added between each stage. If the product stream were cooled completely without the addition of more water, it would become two-phase in the regenerator, since carbon dioxide is miscible in supercritical water but has a limited solubility below the critical temperature. Staged cooling ensures that the product stream at any location contains sufficient water to dissolve all of the carbon dioxide. Finally, the salts removed by the desalinator are reintroduced. This mixing could be done in stages with the aquifer water, or all at once after the product stream is completely cooled. Salts are re-added (rather than sold), in order to maintain solution density, since the objective of surface dissolution is to inject a stream that is denser than the original brine. The result after mixing is a pre-equilibrated,

single-phase solution of carbon dioxide and other fluid coal combustion products ready for injection into the aquifer.

Feasibility of this idea depends on, among other criteria, the amount of aquifer water that must be circulated for total dissolution. Figure 3 is a contour plot of the water required by a plant for varying aquifer conditions. Flow rates are given in thousands of kilograms per second ($10^3$ kg/s) for a 500 MW coal plant like the one introduced in the following section. An aquifer salinity of 20,000 ppm as sodium chloride is assumed. For reference, the amount of cooling water required by a traditional plant is around 12,000 to 13,000 kg/s.[1] (About the same amount is required for the plant design we are investigating.) Figure 3 shows that less water is required for dissolution than is needed for cooling. The amount needed is nearly an order of magnitude less with some aquifers. Although cooling and dissolution are completely separate processes in this scheme, and the water for them comes from different sources, this comparison shows that the amount of water that must be handled is not unusual.
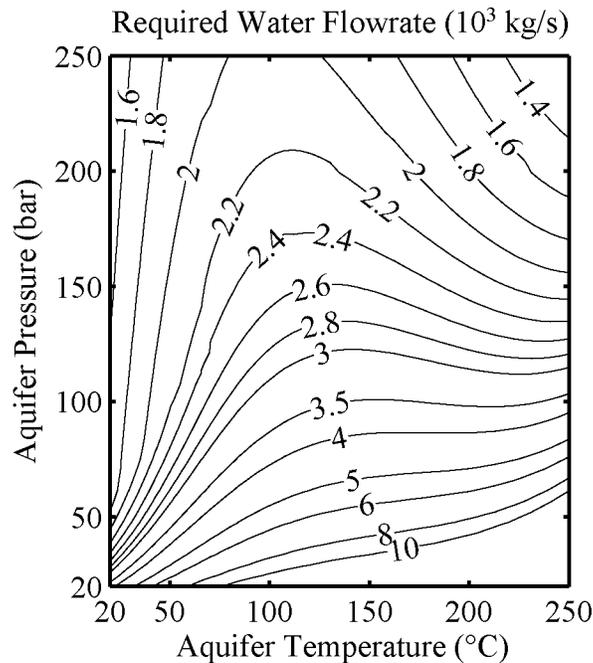


Figure 3: Carbon dioxide dissolution water requirement as a function of aquifer temperature and pressure. Salinity is 20,000 ppm as NaCl. Water flow rates are shown for a 500 MW plant in thousands of kilograms per second.

*Thermodynamic Model Description*
We now turn to thermodynamic analysis to see if this type of plant is efficient enough to merit further study. The modeled system is shown in Fig. 4. There are three major differences from the block diagram of Fig. 1. First, the multi-stage regenerator/desalinator is replaced by a single-stage regenerator that preheats both the water and the oxygen. Precipitation of salts by reduction of solubility is a consequence of

this heating. Physical removal of salts is not energetically significant and is therefore not modeled. Second, the process details and kinetics of the SCWO system are not included. From a thermodynamic point of view, only its inlet and outlet states are important. Finally, the details of the heat engine must be provided. We choose a combined cycle with a closed helium Brayton topping cycle and a Rankine bottoming cycle. This arrangement is similar to combined cycle systems presently in use, except that the Brayton cycle is closed. (Closed Brayton cycles have been considered in the past as candidates for some nuclear applications.[2]) A combined cycle where energy is input to the topping cycle through a heat exchanger instead of from combustion within the cycle is known as an indirectly fired combined cycle, or IFCC. Thus, the complete system presented here may be called a supercritical water oxidation, indirectly fired combined cycle, or SCWO/IFCC.
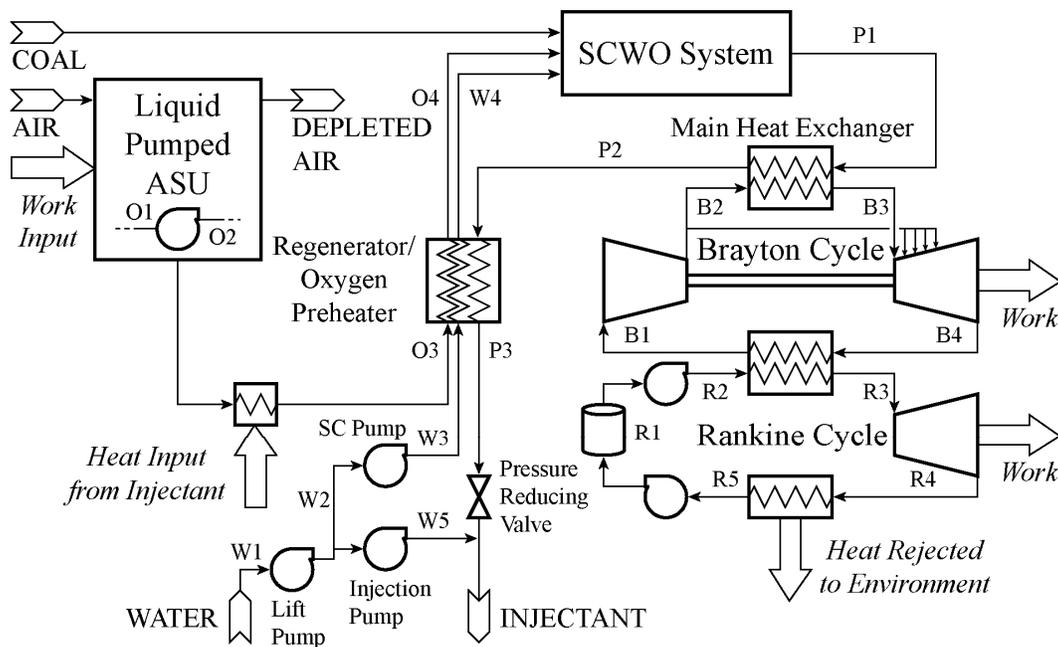


**Figure 4:** The SCWO/IFCC system as implemented in the thermodynamic model. Details of the SCWO system are not important in this efficiency analysis, but the specifics of the heat engine are required. A closed combined cycle is used for this assessment.

Since the main heat exchanger should be pressure matched to ease materials limitations, the pressure at the Brayton compressor outlet (station B2 in Fig. 4) is set at the pressure of the SCWO system outlet (P1). Cooling of the first four turbine blade rows is included in the analysis using the methods and parameters of Horlock.[3] The Rankine cycle is conventional, with an operating pressure that satisfies other requirements of the system (it is not constrained to be either sub- or supercritical). For simplicity, further refinements to increase combined cycle efficiency, such as intercooling, are not considered in this analysis.

Instead of modeling a complete ASU, a work requirement (energy per mass of oxygen produced) is taken from the literature.[4] This value assumes production of low-pressure oxygen, so our model explicitly includes a high-pressure liquid oxygen pump

within the ASU.  The model fuel is moisture-and-ash-free (MAF) coal, with composition based on a Powder River Basin sub-bituminous coal.[5]  Only carbon, hydrogen, oxygen, and nitrogen atoms are included in the model since real fluid data were readily available for major products involving these elements.  The neglected trace elements are not energetically important since they are present in relatively small amounts.  Water, oxygen, carbon dioxide, and nitrogen are modeled as real fluids using the formulations of Reynolds.[6]  The combustion products stream (found at stations beginning with P) is treated as an ideal solution of these real fluids, with property data computed using a linear mixing rule.  The Brayton cycle helium is modeled as an ideal gas.  Aquifer conditions and well pressure losses used to calculate the work requirements of the three aquifer water pumps are taken from Burton & Bryant.[7]  Representative state-of-the-art values are used for other component performance parameters.

The model is solved as follows: for a fixed flow rate of MAF coal, the flow rate of aquifer water at W1 for $CO_2$ dissolution is calculated for specified aquifer conditions. Carbon dioxide solubility is obtained from relations reported by Hangx.[8]  The oxygen flow rate for stoichiometric combustion is computed from the coal composition.  Next, the temperature at the SCWO system outlet (P1) is chosen.  An adiabatic flame temperature calculation at this station gives the flow rate at W2 of aquifer water required in the SCWO system loop.  (The major products combustion model is used in this calculation.)  The enthalpy balance of the main heat exchanger determines the Brayton cycle helium mass flow rate.  The Rankine cycle pressure ratio is set to achieve a specified steam quality at the turbine outlet (R4).  The pinch point temperature difference in the HRSG fixes the Rankine cycle mass flow rate.  Temperatures in the Rankine cycle are calculated starting at the condenser outlet (R5) saturation temperature and moving around the loop.  The temperatures in the Brayton cycle and the SCWO system loop are not prescribed at any station.  Starting with temperature guesses at B1 and O4/W4, these loops are iterated until the temperatures converge to a physical solution.  Using this procedure, the only remaining free parameter of the model is the Brayton cycle compressor inlet pressure at station B1.  For a chosen SCWO system outlet temperature, this parameter is varied to optimize the efficiency of the system.

*Thermodynamic Model Results*
Table I gives the power balance for a 500 MW plant with a SCWO system outlet temperature of 1600 K and Brayton compressor inlet pressure of 79.5 bar.  Overall efficiency is defined as the net work output divided by the lower heating value (LHV) of the MAF coal:

$$\eta_{ov} = \frac{W_{Brayton} + W_{Rankine} - W_{ASU} - W_{pumps}}{m_{MAF} \cdot LHV}$$

Figure 5 shows plots of overall efficiency versus Brayton compressor inlet pressure for five SCWO system outlet temperatures.  As expected, the overall efficiency increases with SCWO system outlet temperature since the product stream is the heat source for the combined cycle.  For each outlet temperature, the overall efficiency usually increases with Brayton inlet pressure.  At certain inlet pressures, the combination of conditions in the SCWO system loop causes decreased efficiency.  From Table I it is clear that the net output of the combined cycle dominates the overall efficiency.  This work output is the

product of combined cycle efficiency and the amount of energy input from the product stream that passes through the main heat exchanger into the heat engine. Combined cycle efficiency increases with Brayton inlet pressure, but not enough to account for the trend in overall efficiency. The increasing cycle efficiency also fails to explain the marked decrease in overall efficiency seen over a small range of pressures. But Brayton inlet pressure also affects the amount of energy input. This effect strengthens the increasing trend and accounts for the decrease in overall efficiency.

**Table I:** Model Plant Power Balance

| Component | Power (MW) |
|---|---|
| Brayton Cycle | |
| Compressor | -388.4 |
| Turbine | 659.9 |
| Net | 271.5 |
| Rankine Cycle | |
| Condensate Pump | -0.026 |
| Feed Pump | -2.27 |
| Turbine | 331.6 |
| Net | 329.3 |
| ASU | -73.2 |
| Water Pumps | -27.5 |
| Overall Plant | 500.0 |
| Fuel Heat Rate (LHV) | 1188.4 |
| Efficiency (% LHV) | 42.1 |

Energy input to the combined cycle generally increases with Brayton inlet pressure for the following reasons. The Rankine cycle condenser operates at a specified pressure, so the states at the condenser outlet (R5) and storage tank (R1) are fixed. The feed pump between stations R1 and R2 operates at different pressure ratios for different plant conditions, but since it pumps a liquid (water), the temperature at station R2 is essentially constant. Cooling of the Brayton cycle working fluid in the HRSG is limited by the pinch point. Still, since the temperature at R2 is roughly constant, the temperature at B1 is approximately independent of Rankine pressure ratio and Brayton inlet pressure. As Brayton inlet pressure increases, the pressure ratio across the Brayton cycle compressor decreases, and the temperature at the compressor outlet (B2) decreases. Since the main heat exchanger cools the product stream at P2 to near the temperature at B2 (limited by its effectiveness), the temperature at P2 also decreases. Similarly, the temperatures of the SCWO system inlet oxygen (O4) and water (W4) decrease. Since the flow rate of SCWO system water is chosen to regulate the SCWO system outlet temperature, the water requirement decreases as this inlet water gets cooler. With less inlet water, the flow rate of the product stream drops. At any operating condition, the mass flow rate of products is

greater than the mass flow rate of incoming water and oxygen (since coal is added in the SCWO system). Due to this mismatch, the products at P3 are not fully cooled, and there is available energy leaving the plant. Since increasing Brayton inlet pressure causes the product flow rate to drop, the enthalpy flux leaving with the products also drops. More energy is transferred to the heat engine instead, and the overall plant efficiency increases.
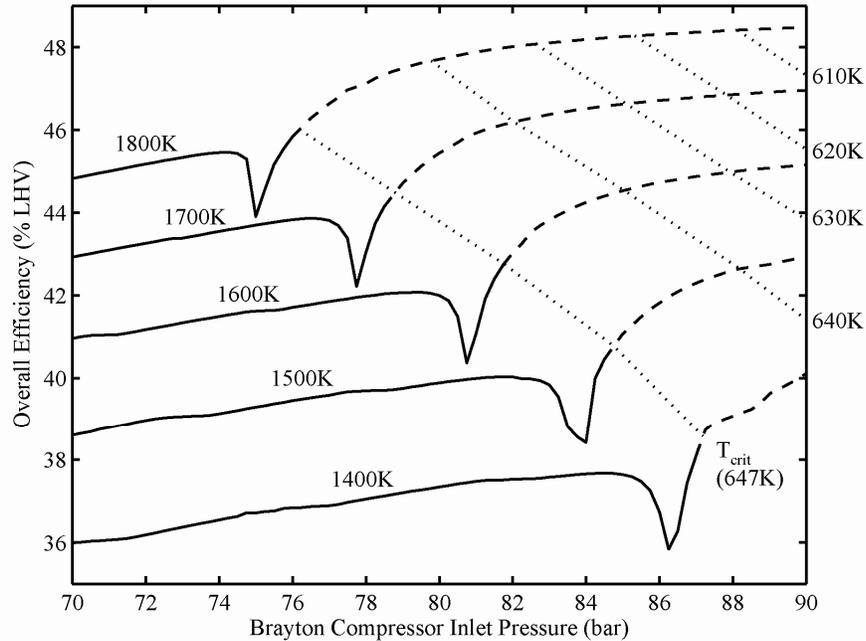


**Figure 5:** Overall efficiency versus Brayton compressor inlet pressure for five SCWO system outlet temperatures from 1400K to 1800K. Solid portions are operating conditions with supercritical SCWO system inlet temperatures; dashed portions are those with subcritical inlet temperatures. Dotted lines are contours of equal inlet temperature.

With ideal heat exchangers, the trend in overall efficiency would be strictly increasing over the Brayton inlet pressure range shown for the reasons cited above. With more realistic heat exchangers, a sharp decrease in efficiency occurs just before the steepest gain. This decrease is mainly a result of the peak in heat capacity of the reactants and products occurring at different temperatures. Fig. 6 shows enthalpy flux ($\dot{m}h$) isobars for the reactants and products in the regenerator at two operating conditions. Here, "reactants" means water and oxygen only, since coal does not go through the regenerator. These show how much enthalpy flux each stream of fixed composition and pressure would have at different temperatures. The enthalpy reference state for the reactants is the regenerator inlet state at stations O3 and W3, which have the same temperature and pressure. The reference state for the products stream has the same composition and pressure as the regenerator outlet (P3), but is at the environment temperature (taken as 300K). With these references, the enthalpy flux shown for the reactants is the amount of heat transfer in the regenerator required to raise the reactants to the corresponding temperature, while the product enthalpy flux is the amount of waste heat leaving the plant with a product stream at a given temperature. We assume no heat

loss from the regenerator, so the heat transfer from the products equals the heat transfer to the reactants.
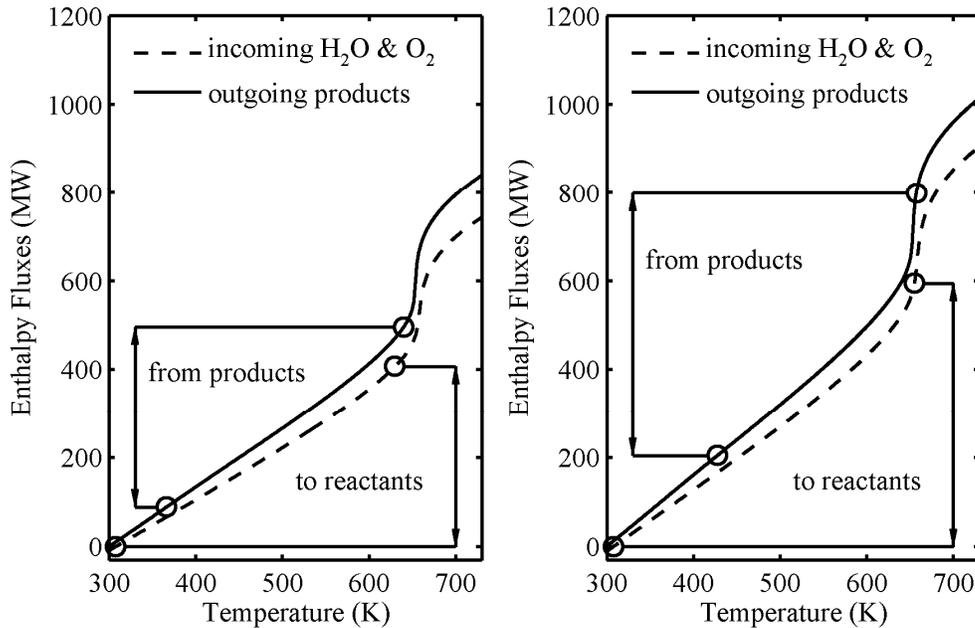


**Figure 6:** Enthalpy fluxes through the regenerator. Pressure losses and heat exchanger ineffectiveness result in a rise in product outlet temperature and drop in overall efficiency at specific operating conditions.

As shown in Fig. 6a, for most temperatures on the hot side of the regenerator the outlet temperature of the products is only slightly above the inlet temperature of the reactants. However, at certain plant conditions (Fig. 6b) the temperature of the products is just above the temperature of maximum specific heat of the products, while the temperature of the reactants is just below the temperature of maximum specific heat of the reactants. As a result, the temperature and enthalpy flux of the products leaving the regenerator increases significantly. Since waste heat is increased, less enthalpy must be available for the heat engine, and overall efficiency drops. Figure 6b corresponds to the worst-case Brayton inlet pressure of 80.75 bar at 1600 K SCWO system outlet temperature, as seen in Fig. 5. At slightly higher or lower hot-side temperatures (Fig. 6a), the reactant and product states are either both above or both below their respective jumps in enthalpy flux, and overall efficiency follows the normal increasing trend. The dip in efficiency occurs over a small range of Brayton inlet pressure because the maximum specific heats of the reactants and products occur at temperatures close to each other (near the critical temperature of water, the primary component of both streams). Smaller pressure drops and higher effectiveness in the regenerator and main heat exchanger reduce the size of the efficiency dip until it disappears completely in a system with ideal devices.

We have seen that as Brayton inlet pressure increases, the regenerator outlet temperature of the reactants decreases (W4, O4). In the present model, this temperature is also the SCWO system inlet temperature, as the SCWO system is directly downstream

of the regenerator.  The operation of the supercritical water oxidation system depends on its contents being supercritical, so its inlet temperature should be near, if not above, the critical temperature.  In Fig. 5, the solid parts of each efficiency curve are for plant conditions with supercritical SCWO system inlet temperature, and the dashed parts correspond to operation with subcritical inlet temperature.  For any SCWO system outlet temperature in the range shown, the requirement of supercritical inlet temperature is a significant handicap.  Overall efficiency could be more than two percentage points higher if the fuel oxidation system could accommodate slightly subcritical inlet temperatures. The dotted contours connect operating points accessible when subcritical inlet temperatures are acceptable.  Another way to make the system function with subcritical reformer outlet temperatures is to raise the temperature of the reactants after leaving the reformer.  Conditions similar to these may be reachable in the model by including a second stage of reactant preheating by heat transfer from the SCWO system.  The corresponding change to the plant of Fig. 4 is preheating by heat transfer from the regenerator.  This change would allow the regenerator outlet temperature to be lower than the SCWO system inlet temperature.  In this case, the higher overall efficiencies shown to the right on Fig. 5 could be achieved without a subcritical reformer section.  As an added benefit, this heat transfer would help limit the temperatures in the reformer.

With the design as shown in Fig. 4, a good choice of Brayton inlet pressure is the pressure that gives maximum efficiency but is to the left of the efficiency dip.  Slightly higher efficiencies with supercritical inlet temperatures can be found to the right, but the local maximum on the left is a conservative choice that relies less on assumptions of process controllability, and avoids operating regions near the critical temperature where fluid properties vary rapidly with temperature.  For a SCWO system outlet temperature of 1600 K, the optimum value is about 79.5 bar.  Table I gives the power balance for a 500 MW plant operating at these conditions.  Overall efficiency, after energy penalties for oxygen separation, carbon sequestration, and non-ideal components, is just over 42% on a lower heating value basis.

An important design choice in the SCWO/IFCC system presented is pressure matching in the main heat exchanger.  As a result, the Brayton cycle runs at much higher pressure than similar cycles currently in use.  The requirement of very high pressure operation does not, by itself, make construction of the Brayton turbomachinery impractical.  A better picture of the design challenge is given by the pressure ratio, which is an output of the model.  In fact, the pressure ratio turns out to be quite reasonable at 3.4 or lower for the operating regime of interest according to Fig. 5.   Also due to the high pressures in the Brayton cycle, the pressure difference across the heat recovery steam generator (HRSG) linking the two power cycles is higher than in usual practice. However, the temperatures in this component are significantly lower than in the main heat exchanger, so strength of materials at high temperatures is less problematic in the HRSG than in the main heat exchanger.

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Area 2: Supercritical coal reforming (Mitchell)

*Experimental facility*

A coiled, tubular flow reactor has been built for use in studies designed to characterize coal extraction, devolatilization and gasification processes at SCW conditions.  The reactor was constructed from a 9/16-in (14.29 mm) O.D. x 5/16-in (7.94 mm) I.D x 50-ft (15.2 m) coiled length of Inconel 625 tubing, yielding a reactor having a total volume of 754.1 cm$^3$.  At the design flow rates, residence times up to about 125 s can be realized.  The coil diameter is 10 in (25.4 cm).  The reactor will be immersed in a fluidized bed sand bath to maintain isothermal conditions over the entire length of the reactor.  Thermocouples will be located at the reactor inlet and exit so that isothermal conditions can be verified.  This particular reactor design was based on the design of the reactor used in the successful supercritical water oxidation studies of Ploeger [1] and Boukis *et al*. [2].  A schematic of the facility designed to deliver water, coal and oxygen to the reactor and to permit the stream leaving the reactor to be monitored is shown in Fig. 7.

De-ionized water from a feed tank will be pressurized and delivered to the reactor using a high-pressure liquid chromatography (HPLC) pump.  The de-ionized water will be obtained from an in-house distilled water supply and a water purification system to remove ionic and organic impurities.  The de-ionized water will be degassed with helium to remove all residual oxygen and pressurized to a helium head pressure of about 2 bar in the feed tank.  The water feed tank will be connected to the HPLC pump via 340 stainless steel tubing.  The pump has the capacity to deliver supercritical water to the reactor at the

rate of 0.15 kg/min.  The water will be heated to the desired reaction temperature in the sand bath before it is admitted into the reactor.

A feed tank containing a concentrated coal-water mixture will be prepared using coal and helium-degassed, de-ionized water.  The feed tank will be maintained at a pressure of about 2 bar using helium.  Stainless steel tubing will be used to connect this feed tank to a slurry pump that is capable of delivering the coal-water mixture to the reactor at pressures in the range 200 – 300 bar at a rate sufficient to supply about 0.03 kg/min of coal.  The actual flow rate will depend upon the desired solids loading to the flow reactor (from 10% - 20% solids, by mass), and the coal-to-water ratio in the feed tank (from 50% - 60% solids, by mass).  The coal-water mixture will be injected into the de-ionized supercritical water at the reactor inlet-mixing junction.  To prevent any coal conversion before injection of the coal into the SCW reactor, the coal-water mixture is not preheated.  At the design flow rates, if the supercritical water is heated to a reaction temperature of 650 K and the coal-slurry is at room temperature (300 K), the mixed-mean temperature of the mixture leaving the inlet mixing junction is about 590 K, 60 K below the desired reaction temperature.  Roughly 10 s of flow time is needed before the mixture reaches the reaction temperature.  Coal conversion over this time period is relatively minor.
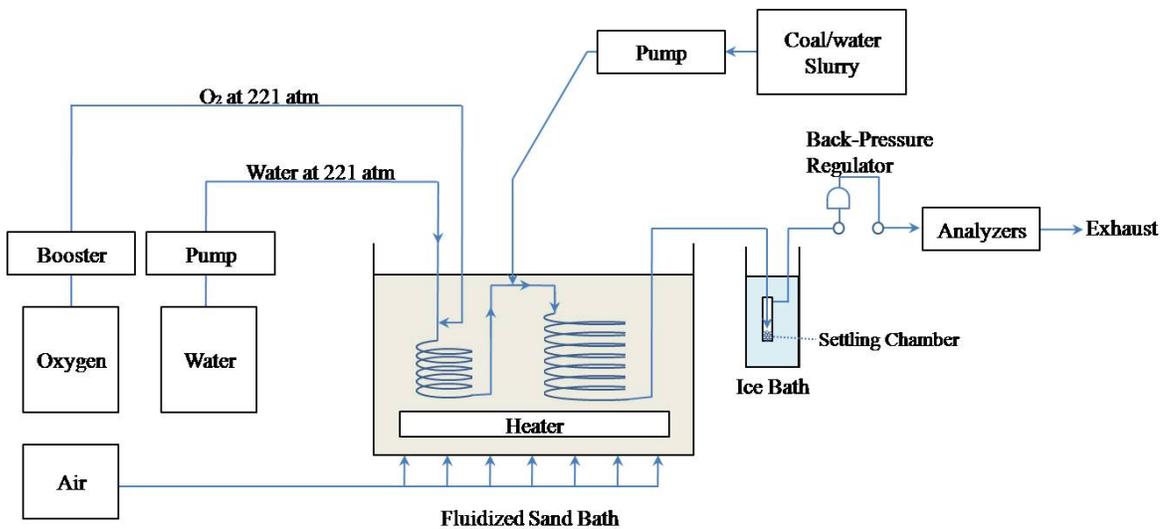


**Figure 7:** Schematic of the experimental system used in the coal reforming studies

Oxygen will be supplied to the reactor from a large, high-pressure storage tank containing reagent grade oxygen.  An air-driven gas booster pump capable of delivering oxygen to the reactor at pressures in the range 200 – 300 bar at a nominal rate of 20 slpm is utilized.  The oxygen is mixed with the high-pressure water and heated in the sand bath before it is injected into the reactor.  The pressurized, 65-liter oxygen storage tank is sufficient to supply high-pressure oxygen to the reactor for about 5 hours of testing at SCW conditions.

The stream leaving the reactor will be quenched by injecting the flow into a water-cooled solids-settling chamber, which also removes solids, and then passed through a back-pressure regulator that controls and reduces the pressure, and then through a gas-

liquid separator.  Streams leaving the separator will be directed through analytical equipment to determine the composition of the coal conversion products, and then vented.  Of primary interest are the CO, $CO_2$, $H_2$, $CH_4$, $C_2H_4$, and $C_2H_6$ mole fractions. The solids collected in the settling chamber will be analyzed to determine the extent of conversion and other solids properties (*e.g.,* specific surface area, apparent density and particle size distribution).

Linear mass flow meters will be used to control all flow rates to the reactor.  Due to the corrosive nature of SCW containing oxygen, Inconel 625 tubing and fittings will be used throughout the flow configuration downstream of the reactor's inlet-mixing junction.  The facility will be enclosed within a bullet-resistant polycarbonate shield as a safety measure, in the unlikely event of tube failure due to corrosion.

*Materials for study*

One of the goals of this project is to characterize the conversion rate of a base-case coal to synthesis-fluid in the supercritical water reactor.  This requires determining the rates of coal extraction and devolatilization and the reactivity of the resulting char to water, and developing models for each of these processes.  To facilitate data analysis as well as to aid in model development, an activated carbon will be tested inconcert with the base-case coal.  The activated carbon selected was produced via high-temperature pyrolysis of a de-ashed, coconut char.  Being low-ash, nearly all carbon and somewhat uniform in pore structure, the activated carbon will yield data having less scatter than that obtained with real coal-chars, thereby providing data that are more amenable to interpretation.  The proximate and ultimate analyses of the activated carbon are shown in Table II.  Also shown are the proximate and ultimate analyses for Wyodak coal, the base-case coal selected for study.

**Table II.**  Proximate and ultimate analyses of materials selected for study

|  | Activated carbon | | Wyodak coal | |
|---|---|---|---|---|
| Proximate analysis | As-rec'd | Dry | As-rec'd | Dry |
| Moisture | 14.65 | - | 26.3 | - |
| Ash | 2.59 | 3.03 | 5.58 | 7.57 |
| Volatile matter | 6.87 | 8.05 | 33.06 | 44.86 |
| Fixed Carbon | 75.89 | 88.92 | 35.06 | 47.57 |
| Ultimate analysis | As-rec'd | Dry | As-rec'd | Dry |
| Moisture (wt-%) | 14.65 | - | 26.30 | - |
| Carbon (wt-%) | 80.56 | 94.39 | 51.42 | 69.77 |
| Hydrogen (wt-%) | 0.46 | 0.54 | 4.16 | 5.65 |
| Nitrogen (wt-%) | 0.30 | 0.35 | 0.69 | 0.94 |
| Sulfur (wt-%) | 0.11 | 0.13 | 0.32 | 0.43 |
| Oxygen[a] (wt-%) | 1.33 | 1.56 | 11.53 | 15.64 |
| Ash (wt-%) | 2.59 | 3.03 | 5.58 | 7.57 |
| HHV (MJ/kg) | 32.4 | | 30.8 | |

[a] by difference

Wyodak coal, a resource that is widely used for power generation, is a sub-bituminous-B coal from the Powder River Basin area of Wyoming. The ultimate analysis (see Table II) indicates a somewhat high oxygen content, the reason for the coal's relatively low rank. Its heating value, however, is in the range for a high-volatile-C bituminous coal. Wyodak coal is considered to be a low-ash, low-sulfur coal. About 81% of the sulfur is organic-sulfur; 16% is pyritic and the remainder is sulfatic.

The activated carbon and Wyodak coal will be ground and size classified before testing. Particles in the 75 - 126 μm size-range will be selected for study. The particle size distributions, apparent densities and specific surface areas of samples of the feed materials used in selected tests will be measured. These properties will be measured for the chars produced from the Wyodak coal, as well. We will also select a bituminous coal for study once tests with the base-case coal and activated carbon are completed.

*Coal extraction and devolatilization*

One of our project goals is to characterize coal extraction and devolatilization in supercritical water environments. Although we had proposed to develop a sophisticated chemical percolation model to describe the rate of mass loss from coal when exposed to supercritical water, we have decided to first test simpler models. It is not our goal to develop a coal extraction and devolatilization model that is applicable over a wide range of temperatures, heating rates and pressures. Our model need only predict the overall mass loss rate at SCW conditions. The extractables and volatiles are rapidly converted to $CO$, $H_2$ and low molecular weight hydrocarbons in the supercritical water.

The simplest description of kinetics of the extraction and devolatilization reactions is to use a first order reaction for the total weight loss of the extractables and volatiles:

$$\frac{dV}{dt} = k\left(V^* - V\right)$$

Here, $V$ represents the total of extractable and volatiles evolved up to time $t$ and $V^*$ represents the ultimate yield of extractables volatiles at an infinitely long time. The values of $V^*$ and $k$ will be determined experimentally, from analysis of data obtained in tests performed in the supercritical water reactor. Previous work has indicated that the value of $V^*$ is temperature dependent, increasing with temperature. Consequently, the extraction and devolatilization model will be applicable only near supercritical water conditions.

We will use this simple model initially to determine its applicability to coal extraction and devolatilization under supercritical water conditions. If this model is too simple and is found not to sufficiently correlate the data, we will develop a more complex model, one that assumes that the coal consists of several extractable and volatile species each of which decomposes via an independent first order reaction:

$$\frac{dV_i}{dt} = k_i\left(V_i^* - V_i\right)$$

The reaction rate coefficient is expressed in Arrhenius form, as follows:

$$k_i = A\exp(-E_i/RT)$$

Whereas the pre-exponential factor is treated as a constant, the activation energy is expressed as a Gaussian distribution function f($E$) such that f($E$)d$E$ represents the fraction of potential extractables and volatiles having an activation energy between $E$ and $E + dE$. For all the extractable and volatiles,

$$dV^* = V^* \mathrm{f}(E)dE$$

Combining the above three equations and integrating yields the following expression for the total amount of extractable and volatiles evolved up to time $t$:

$$\frac{V^* - V}{V^*} = \int_0^\infty \exp\left[-At\exp\left(E/RT\right)\right] \mathrm{f}(E)dE$$

This type model has been found to correlate the devolatilization data obtained with many coals and biomass materials quite accurately over narrow temperature ranges. Low activation energies are associated with the release of $CO_2$ and $H_2O$ from the coal while the high activation energies are associated with the formation of light hydrocarbons, CO and $H_2$. The peak in the distribution is associated with tar formation reactions. The model contains four parameters: the ultimate yield of extractables and volatiles at SCW conditions ($V^*$), the pre-exponential factor ($A$), and the mean value ($\bar{E}$) and standard deviation ($\sigma$) of the distribution function. It is quite likely that this model will correlate the extractable and devolatilization data obtained in the SCW environments accurately.

*Char Reactivity to Water*

Work has started on development of a reaction mechanism that explains the overall course of reaction between carbon and water vapor. At the high temperatures (> 1200 K) and relatively low pressures (< 20 bar) of typical steam gasification processes in proposed IGCC schemes, the primary coal conversion products are CO and $H_2$. As the temperature is lowered and the pressure is raised, $CH_4$ formation becomes important. Under supercritical water conditions ($T \sim 650$ K, $P \sim 221$ bar), $CH_4$ is the dominant carbon-containing product. Any realistic carbon-$H_2O$ mechanism must characterize this shift in key reaction pathways as pressure is increased and temperature is decreased. Thus, the rate-limiting reaction pathways need to be determined that explain the global reactions $C + H_2O \rightarrow CO + H_2$ and $3C + 2H_2O \rightarrow CH_4 + 2\,CO$ and their relative rates as functions of temperature and total pressure.
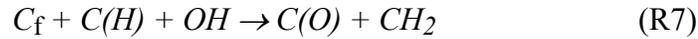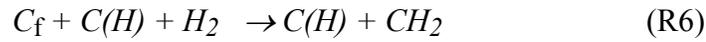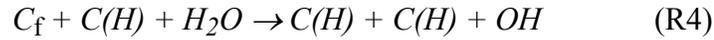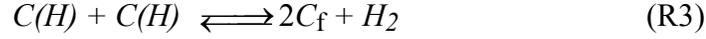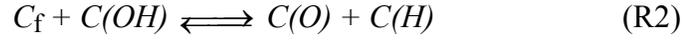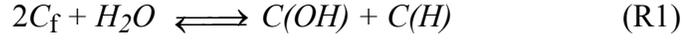
A mechanism that we are considering to explain carbon reactivity to water vapor is presented in Table III. In the mechanism, $C(X)$ denotes an adsorbed species (*i.e.*, a carbon site filled with either a H or O atom or OH radical), $C_f$ denotes a free carbon site (*i.e.*, a carbon site available for adsorption), and $C_b$ denotes a bulk carbon site (an underlying site that will be exposed upon desorption of a carbon atom from the carbonaceous matrix). Dual-site dissociative chemisorption of water is assumed to be the initial, rate-limiting step.

Water vapor chemisorption leads to adsorbed-H and adsorbed-OH species on the carbonaceous surface (reaction R1). The adsorbed-OH can dissociate yielding adsorbed-O and adsorbed-H atoms (reaction R2). Recombination of adsorbed-H atoms yields $H_2$ (reaction R3) and desorption of adsorbed-O atoms yields CO (reaction R8), removing a carbon atom from the bulk. Note that desorption of adsorbed-H atoms also removes a carbon atom from the bulk, yielding a fluid-phase CH radical (reaction R9). Carbon
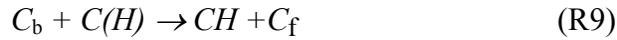
atoms are also removed from the carbonaceous surface via complex enhanced chemisorption reactions, yielding fluid-phase $CH_2$ radicals (reactions R5, R6, and R7).

**Table III.** Reaction mechanism for carbon reactivity to water vapor
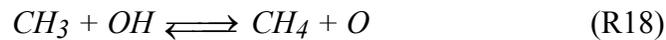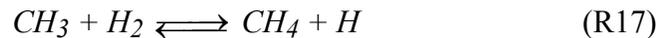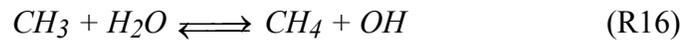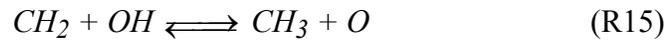
*Chemisorption reactions*

$$2C_f + H_2O \rightleftharpoons C(OH) + C(H) \qquad \text{(R1)}$$

$$C_f + C(OH) \rightleftharpoons C(O) + C(H) \qquad \text{(R2)}$$

$$C(H) + C(H) \rightleftharpoons 2C_f + H_2 \qquad \text{(R3)}$$

$$C_f + C(H) + H_2O \rightarrow C(H) + C(H) + OH \qquad \text{(R4)}$$

$$C_f + C(H) + H_2O \rightarrow C(OH) + CH_2 \qquad \text{(R5)}$$

$$C_f + C(H) + H_2 \rightarrow C(H) + CH_2 \qquad \text{(R6)}$$

$$C_f + C(H) + OH \rightarrow C(O) + CH_2 \qquad \text{(R7)}$$

*Desorption reactions*

$$C_b + C(O) \rightarrow CO + C_f \qquad \text{(R8)}$$

$$C_b + C(H) \rightarrow CH + C_f \qquad \text{(R9)}$$

*Homogeneous-phase reactions*

$$CH + H_2O \rightleftharpoons CH_2 + OH \qquad \text{(R10)}$$

$$CH + H_2 \rightleftharpoons CH_2 + H \qquad \text{(R11)}$$

$$CH + OH \rightleftharpoons CH_2 + O \qquad \text{(R12)}$$

$$CH_2 + H_2O \rightleftharpoons CH_3 + OH \qquad \text{(R13)}$$

$$CH_2 + H_2 \rightleftharpoons CH_3 + H \qquad \text{(R14)}$$

$$CH_2 + OH \rightleftharpoons CH_3 + O \qquad \text{(R15)}$$

$$CH_3 + H_2O \rightleftharpoons CH_4 + OH \qquad \text{(R16)}$$

$$CH_3 + H_2 \rightleftharpoons CH_4 + H \qquad \text{(R17)}$$

$$CH_3 + OH \rightleftharpoons CH_4 + O \qquad \text{(R18)}$$
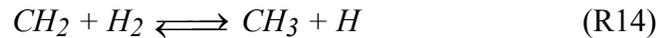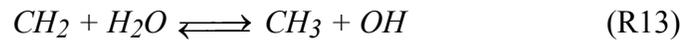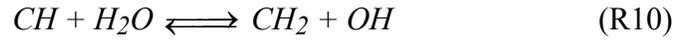
Methane is formed via fluid-phase, homogeneous reactions from the CH and $CH_2$ radicals, which are quite reactive. Although included in the mechanism for completeness, reactions R12, R15, and R18 are not expected to be important since SCW environments are reducing environments. The OH produced in reactions R4 and R10 is more likely to be consumed in the chemisorption reaction R7 due to the low fluid-phase concentrations of CH, $CH_2$ and $CH_3$.

Arrhenius parameters that describe the rate coefficients for the homogeneous-phase reactions are available in the literature. Although the rate parameters were determined in experiments at pressures much less than 221 bar, pressure-scaling of these reactions is well characterized, assuming ideal gas behavior. However, there are many reactions that

may be important in aqueous mixtures containing organic species that have not been considered in gas-phase reaction mechanisms, reactions involving hydrates, for example. Since the rates of the heterogeneous reactions are slow compared to the rates of the homogeneous reactions, it is quite likely that the fluid-phase reactions become equilibrated, in which case equilibrium constants can be used to relate the fluid-phase $CH_4$, $CH$ and $CH_2$ concentrations. The Peng-Robinson equation of state will be used to determine fugacity coefficients of species so that account can be made for non-ideal gas effects in the equilibrium calculations.

The heterogeneous reactions are the rate-limiting reactions. As a consequence of these reactions, the intrinsic reactivity of carbon to water vapor (in kg/m$^2$·s) is given by

$$R_{iC,H_2O} = \hat{M}_C\left(\hat{R}\hat{R}_5 + \hat{R}\hat{R}_6 + \hat{R}\hat{R}_7 + \hat{R}\hat{R}_8 + \hat{R}\hat{R}_9\right)$$

where $\hat{M}_C$ is the molecular weight of carbon and $\hat{R}\hat{R}_k$ denotes the net molar rate of reaction $k$. The molar production rates of CO, $H_2$ and $CH_4$ (in mol/m$^2$·s) are given by the following relations:

$$\hat{R}_{CO} = \hat{R}\hat{R}_8$$

$$\hat{R}_{H_2} = \hat{R}\hat{R}_3 - \hat{R}\hat{R}6 - \hat{R}\hat{R}_{11} - \hat{R}\hat{R}_{14} - \hat{R}\hat{R}_{17}$$

and
$$\hat{R}_{CH_4} = \hat{R}\hat{R}_{16} + \hat{R}\hat{R}_{17} + \hat{R}\hat{R}_{18}$$

The rates of reactions $R_{10}$ through $R_{18}$ depend upon the CH, $CH_2$ and $CH_3$ fluid-phase concentrations, which depend upon the rates that adsorbed-CH and adsorbed-$CH_2$ are released from the bulk carbonaceous matrix.

For each material studied, reaction rate coefficients for reactions R1 to R9 will be determined using data obtained in reactivity tests performed in our pressurized thermogravimetric analyzer (PTGA). Tests will be performed over a range of temperatures centered about 650 K and at pressures from 1 to about 50 bar, the maximum operating pressure that we have used in PTGA tests. Various mixtures of water vapor and helium and hydrogen and helium will be employed in tests designed to yield the data needed to determine reaction rate coefficients for each of the heterogeneous reactions. We have already purchased and calibrated a HPLC pump that will be used to deliver water to the PTGA in the char-water vapor reactivity tests.

In order to obtain coal chars for testing, the parent coal will be devolatilized under high-temperature/high-heating rate conditions in our atmospheric entrained flow reactor. Devolatilization at high temperatures and high heating rates is important if char reactivity data are not to be influenced by residual volatiles release. This method of obtaining coal chars for reactivity tests is a standard procedure in our laboratory. Quite reproducible data are obtained when chars are produced at temperatures higher than the temperatures used in the reactivity tests.

The above rate expressions will be used in a plug flow model that we will develop to simulate the coiled supercritical reactor. The model will predict the carbon mass loss and the fluid-phase mole fractions of CO, $CO_2$, $H_2$, $CH_4$, and $H_2O$ as a function of reactor residence time. Agreement between calculated and measured weight loss and mole

fraction profiles will gauge the validity of the reaction mechanism. Parameters will be adjusted, as needed, to get better agreement between calculations and measurements. The model will be used to determine operating conditions that enhance carbon conversion to fluid-phase species.

**Future Plans** (Supercritical water reforming)

The design, construction, assembly, and testing of the SCW reactor and flow control panel are scheduled to be completed by the beginning of the summer. Coal conversion tests in SCW environments should begin by the end of the summer. Carbon-water vapor reactivity tests in the PTGA are in the initial stages.

**Contact** (Supercritical water reforming)

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**References** (Supercritical water reforming)

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Area 3: Synthesis Fluid Oxidation and Heat Extraction (Edwards)
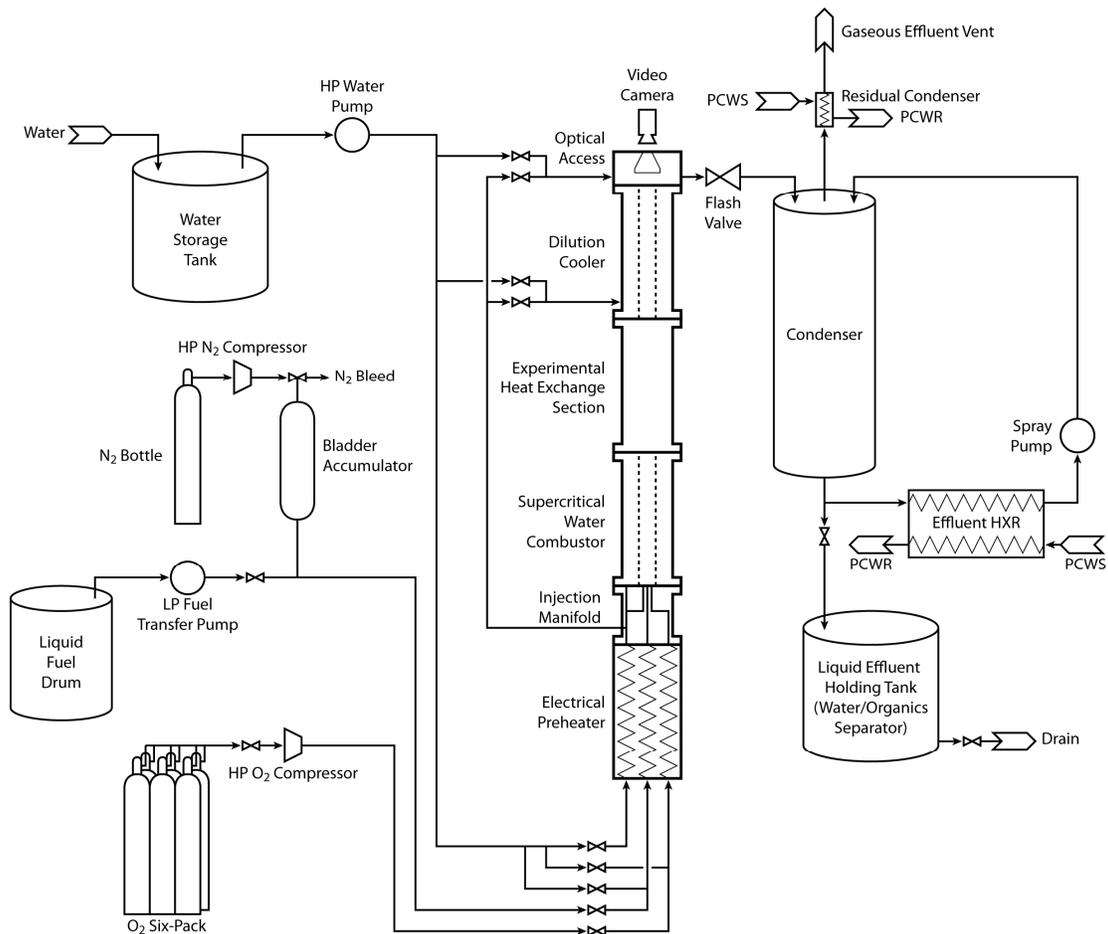*Supercritical Combustor Development*

Our goal in this task is to demonstrate stable combustion of an aqueous hydrocarbon fuel in supercritical water at near-stoichiometric conditions with high volumetric firing rate.

In previous research into highly exothermic SCWO, Wellig identified six tasks must be performed by a SCWO apparatus: reactant storage, pressurization, preheating, reaction, pressure let down, and effluent discharge.[1] Due to the firing rates we intend to use, and the amount of fluid we will preheat, cooling of effluent is also a concern, lest the ambient temperature in the laboratory rise to an unmanageable level.

Shown in Fig. 8 is a schematic of the major hardware for the supercritical combustor experiments. On the left are components to bring in and pressurize the reactants. Water is fed to the system via a high-pressure positive-displacement pump. Liquid hydrocarbon fuel (as a surrogate for coal-derived synfuel) is delivered via a high-pressure, nitrogen-driven accumulator. Gaseous oxygen is fed via a boost compressor. Oxygen is supplied from a six-pack of bottles since one six-pack contains, approximately, a stoichiometric amount of oxygen for a conventional fuel accumulator. Both the fuel and oxygen streams are mixed with prescribed amounts of water just before heating.

Illustrated in the center of Fig. 8 is the high-pressure stack, consisting of the reactant preheater, supercritical combustor, an experimental heat exchanger, and a cooling section. The electrical preheater heats the incoming water, fuel/water solution, and oxygen to temperatures above the critical temperature of water prior to injection into the combustor. While subcritical injection has been demonstrated, the combustor inlet will normally be supercritical when coupled with an upstream reformer.[1] We may investigate subcritical injection in connection with combustion stability, however. The combustor is the focus of this task of the project, and it is where all fuel oxidation takes place. Various

burner geometries will be tested, with emphasis on core oxygen injection with the fuel solution in a coaxial annulus. Water without fuel will be used to control the flame zone and prevent hot, reactive fluid from reaching the vessel wall. The amount of water added here will be varied to control the mixed mean temperature at the combustor outlet, where the fluid is a hot, homogeneous solution of combustion products. This stream passes into the experimental heat exchange section. This section of the apparatus will not be in place for initial supercritical combustion investigations. When in use, it will mate directly to the combustor, and be used to test geometries and materials for heat exchange from the hot products. Possible materials and geometries are discussed later in the section on heat exchanger development.



**Figure 8:** Diagram of supercritical combustor experiment. Reactant storage and pressurization components are shown to the left of the vertically oriented high pressure stack. At right are components to remove waste heat from the lab and separate the effluent components for disposal.

The upper portion of the high pressure stack is a dilution cooler. In the absence of a well-characterized heat exchanger, we need a reliable way to decrease the temperature of the product stream from temperatures as high as 1800 K. The first stage of cooling will

be done by simply diluting the stream with cooler water. This dilution water will itself be preheated to near-critical conditions since dilution of products with subcritical water could result in zones of near-critical water along the optical path. Critical opalescence in these areas could block the otherwise clear path from the end window to the flame zone in the combustor. Optical access is provided at the top of the stack. The end window is a large sapphire window that will allow us to observe the radial position and size of the combustor flame. Direct observation is a straightforward way to verify that the flame is not reaching the combustor walls. The window will be replaceable with a port to accept a movable probe in order to make in-situ measurements of scalar profiles.

The stream exiting the high-pressure stack will have a moderate temperature (somewhat above critical), but since the first stage of cooling is done by dilution, there will be a significant amount of hot water leaving this apparatus. With up to 60 kW of electrical preheating and a 50 kW firing rate, thermal energy from this effluent must be actively removed from the lab so that the ambient temperature does not rise to an unacceptable level. The moderately supercritical solution at 250 bar will be flashed down to ambient pressure. The flashed mixture of steam and carbon dioxide will directly contact condensate of the same stream in a spray condenser. Hot condensate from the bottom of the condenser will reject heat to process cooling water in a stock heat exchanger. Most of the up to 110 kW of thermal energy from the experiment will exit the lab with this process cooling water. The gas vent line will be cooled with a small process cooling water flow to condense remaining water vapor. This final stage of cooling is intended to dehumidify the exhaust so that condensation will not occur in the vent line between the lab and the outside of the building.

Current efforts are focused on completing the experimental system definition, detailed design of the high-pressure stack, and acquisition of the supporting equipment. It is anticipated that system assembly will begin in June, with supercritical flow expected sometime around the end of September.

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*Development of Thermodynamic Property Data*
In performing thermodynamic systems analysis, we have relied heavily on the ideal solution model for properties. In order to perform a more accurate analysis, a more accurate scheme for finding mixture properties is required. Further, in order to move from general plant analysis to specific design, sizing, and flow rate considerations, a more precise understanding of the thermodynamics of our working fluids is necessary.

The most complete and accurate pure fluid models are multi-parameter equations of state that fit available experimental data to create a fundamental relation surface for a given species. Once the fundamental relation surface is created, any thermodynamic property of the fluid can be determined from the gradients of the surface at a given point

using well-known thermodynamic relations. The most common fundamental relation surface is the Helmholtz energy of a fluid. We use state-of-the-art multi-parameter fits with up to fifty-eight terms each for the Helmholtz energy $A$ of a species as our fundamental relation for the major products of hydrocarbon combustion: carbon dioxide and water. In order to deduce property data from the fundamental relation surface, it is necessary to calculate the first four derivatives of the Helmholtz energy with respect to reduced density (density normalized to the critical density) and inverse reduced temperature (inverse temperature normalized to the critical temperature). We can then compute all desired thermodynamic properties from these derivatives.

We have written a software library with more than twenty such functions to create a comprehensive thermodynamic properties resource for pure substances. Carbon dioxide and water are modeled to within the accuracy of the best data available, giving a density error of at most 0.25% in the pressure ranges necessary for the supercritical combustion system (see Fig. 9).
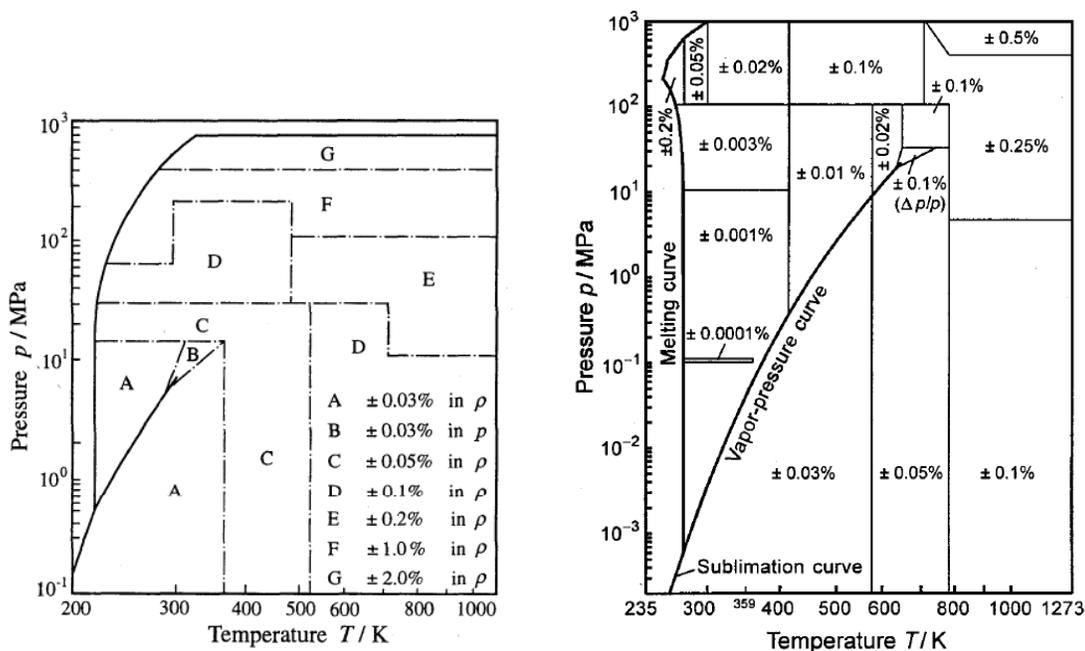


**Figure 9:** Error ranges for $CO_2$ (left) and $H_2O$ (right) Helmholtz fits.[1,2]

In order to accurately calculate thermodynamic properties for the post-combustion, multi-species product stream, a mixing model capable of accurately describing the interactions between the species under a wide-range of compositions and conditions is required. We use the state-of-the-art Lemmon-Jacobson mixture model, which models the departure from an ideal Helmholtz solution using a modified corresponding states approach, as implemented by Paulus and Penoncello.[3] This is accomplished using four shaping parameters to provide an accurate model for each pair of species. This model provides significant benefit over the ideal solution model previously employed.

Compared in Fig. 10 are the ideal gas, ideal solution, and Paulus-Penoncello mixture models for mass-specific enthalpy over a range of temperatures and pressures. As

expected all three models agree relatively well at high-temperature, low-pressure conditions. But as the temperature is lowered or the pressure raised significantly, the ideal gas model quickly fails while the ideal solution model is able to provide a reasonable representation of the enthalpy down to subcritical temperatures.
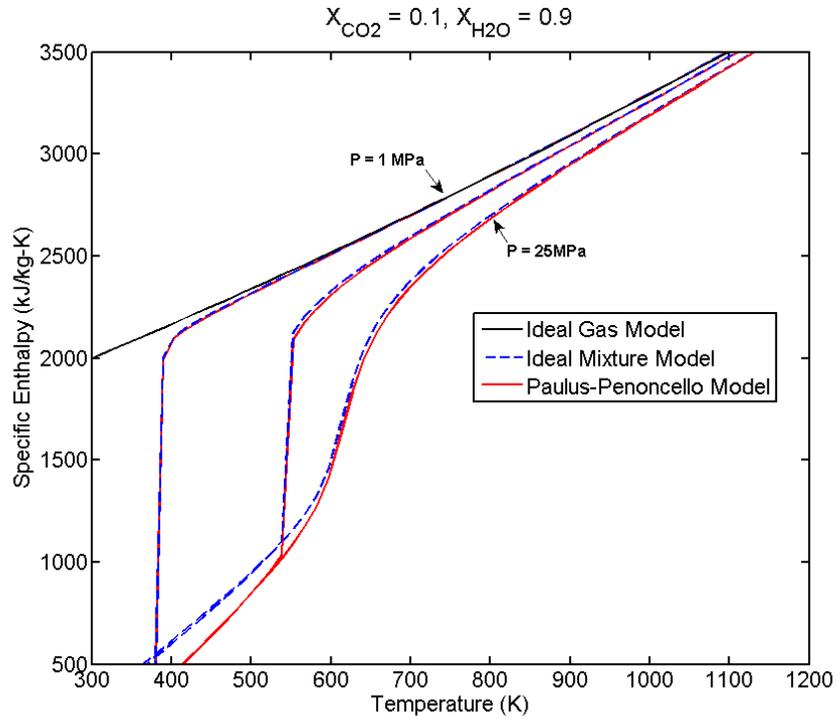


**Figure 10:** Specific enthalpy vs. temperature plot for three different property models at 1, 10, and 25 MPa.

The plots shown in Figs. 11 and 12 show the percentage difference between the ideal solution and the Paulus-Penoncello model for density and enthalpy for carbon dioxide + water binary mixtures with carbon dioxide mole fraction $X_{CO2} = 0.1$. These highlight the improved accuracy of the Paulus-Penoncello mixture model, especially in the high-pressure, low-temperature regions.

While significant errors appear in the ideal solution analysis at low temperatures and high pressures, Paulus and Penoncello's implementation of the Lemmon-Jacobson mixture model for the carbon $CO_2/H_2O$ system has only 0.1% error in the ranges we require. However, because of the large difference between the critical temperatures of carbon dioxide and water, as well as the lack of adequate liquid phase data for this binary system, the vapor and liquid chemical potentials for this system were not cross-constrained in the Lemmon-Jacobsen mixture model, causing pressure calculations in the vapor-liquid equilibrium (VLE) problem to have errors in excess of 10%.[3]
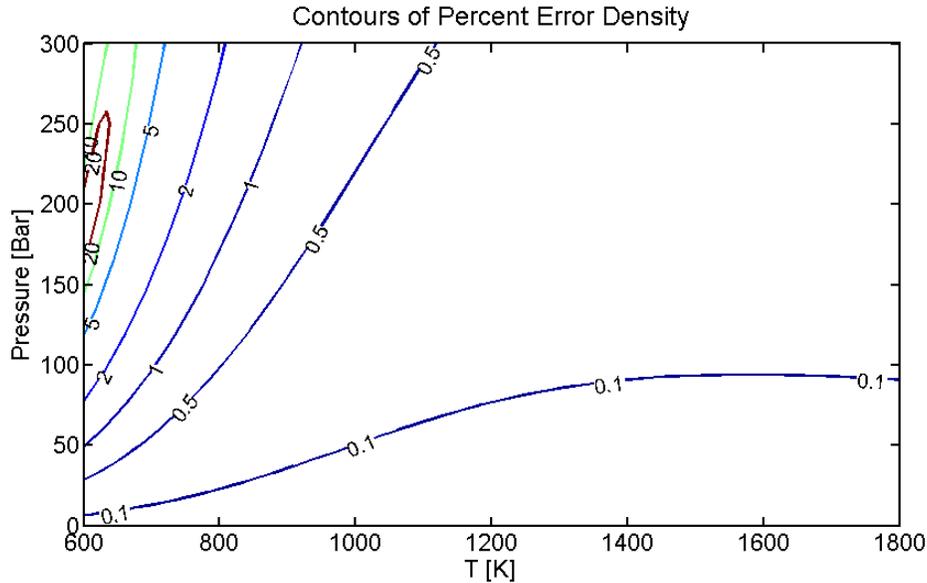
**Figure 11:** Contours of percent error in density between the ideal solution approximation and the Paulus-Penoncello mixture model for a mixture with mole fractions $x_{CO2} = 0.1$ and $x_{H2O} = 0.9$.
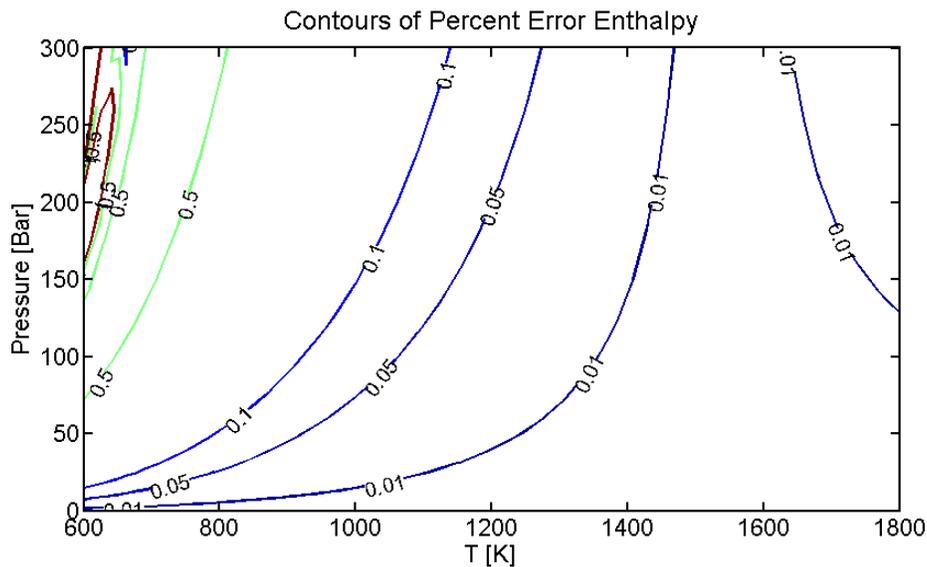


**Figure 12:** Contours of percent error in specific enthalpy between the ideal solution approximation and the Paulus-Penoncello mixture model for a mixture with mole fractions $x_{CO2} = 0.1$ and $x_{H2O} = 0.9$.

Again following the lead of Paulus and Penoncello, we calculate VLE data from the Peng-Robinson cubic equation of state. The Peng-Robinson mixture model is created using linear combining rules with a binary interaction parameter to find the "*a*" and "*b*" values in the cubic equation of state

$$P = \frac{RT}{V_m - b} - \frac{a\alpha(T)}{V_m^2 + 2bV_m - b^2}$$

This equation of state is then used with ideal gas specific heat fits to calculate the properties for each species within a mixture. VLE occurs when each species has the same chemical potential in each phase. In order to determine where this occurs for a given temperature and vapor concentration, it is necessary to iterate through different pressures to find the pressure at which the liquid and vapor chemical potentials are equal for some specific liquid mole fraction. Similarly, to determine the VLE for a given pressure and composition, temperature iteration is required. The importance of being able to solve the VLE problem for $CO_2/H_2O$ in our system is to ensure that we have single-phase flow through the heat exchangers. Figure 13 shows calculated dew lines up to 500 bar for four different mole fractions of carbon dioxide to ensure that we are in the single-phase region. Note that there is a retrograde region for each composition where the dew temperature decreases as pressure increases.
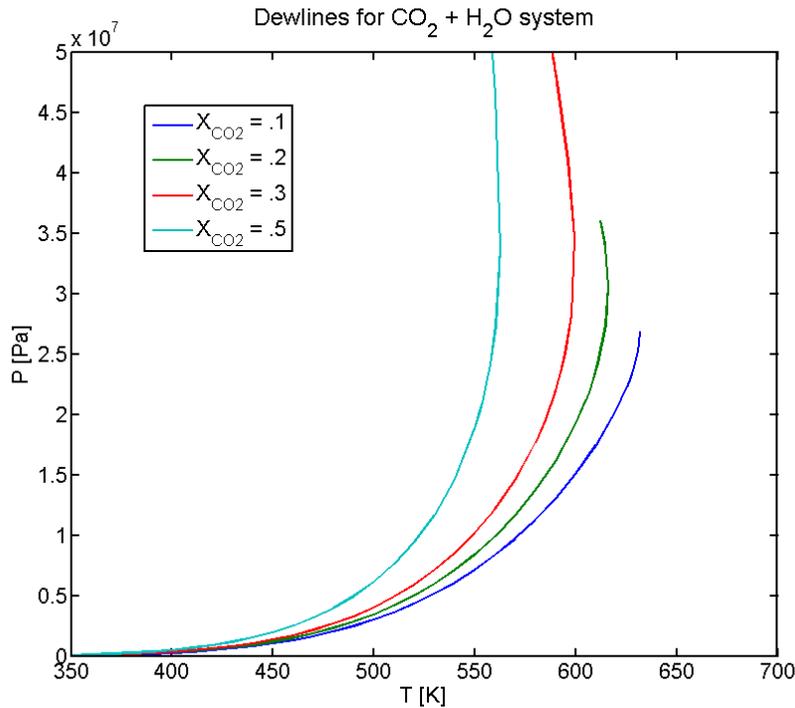


**Figure 13:** Temperature versus pressure plot for the $CO_2/H_2O$ system showing dew lines for four different compositions.

To complete our thermodynamic property analysis, we must also find the bubble lines for $CO_2/H_2O$ mixtures of interest, and solve the flash problem that describes the cooling and decompression of the product stream in the experimental setup. Once these properties have been calculated, all thermodynamic properties within the regions of interest will be known to within the accuracy of the best available data for this mixture. That will provide crucial sizing and design information for building the heating, cooling, and decompression systems.

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*Heat Exchanger Developments*

As mentioned in the previous sections, a heat engine is utilized after the combustor section.  The temperature that the main heat exchanger can operate at determines the overall efficiency of the system.  Unlike the combustor, where a cooling flow of 700 K supercritical water runs along the walls, the heat exchanger walls must contact the hot SCWO products.  Therefore, the exchange surface must be able to withstand very high temperatures as well as the corrosive environment of supercritical water and carbon dioxide.  A goal of 1800 K was set for the mixed-mean temperature at the inlet to the heat exchanger.  This far exceeds the operating temperatures of standard (and most advanced) equipment in use today.  As a result, there is very little validated information that may be drawn upon in the design of the heat exchanger, and an exploratory study into critical issues relevant to its design was undertaken.  The following section reports some of the insights obtained from this preliminary study.

An integral part of designing the heat exchanger is the calculation of transport properties for the system, including viscosity and thermal conductivity.  Two models for the properties of supercritical pure substances are being investigated at this time.  A generalized multi-parameter correlation given by Chung *et. al.*[1] has been used to determine the transport properties of neat water and neat carbon dioxide over the range of densities encountered in our system.  The correlation spans both dilute gases and dense fluids with two separate calculations.  For dilute gases, the Chapman-Enskog theory is used.  For dense fluids, an empirically correlated function of density and temperature is employed.  The two calculations are summed and weighted such that each calculation is the major contributor in the density region for which it was developed.

While the pure fluid properties calculated by this model show good agreement with available data, the model is designed to operate at lower temperatures than are of interest for our purposes.  An alternate model by Vesovic et al.[2] may be modified to work specifically with supercritical fluids and has been validated for use with carbon dioxide.  This model uses the zero-density viscosity of the pure fluids as a basis with excess viscosity determined for the pure supercritical fluids.  The excess viscosity is based on a corresponding states representation using reduced density, independent of temperature.

Determining the transport properties of supercritical *mixtures* is even more challenging given the limited reference data available.  Both Chung and Vesovic propose mixture models that are currently being examined.  Chung uses a conformal-solution model, which applies hard-sphere expansion theory.  This model is best used with substances that are very similar to each other.  However, binary interaction parameters are included in the model, and these could be used to account for mixtures that have polar or associated substances.  These interaction parameters must be determined from

experimental data and may be different for viscosity and thermal conductivity. Unfortunately there is little data in the operating range of our system for carbon dioxide and water mixtures, so this approach may be problematic. The model proposed by Vesovic uses a hard-sphere model with pseudo radial distribution functions. This model does not address its use with polar substances, which may prove to be a significant limitation.

An extensive material search was conducted to determine the best option for the heat exchanger wall. Refractory metals were the main focus due to their high melting points, and molybdenum was determined to be the most suitable base metal. With a melting point of 2890 K, its capabilities far exceed the highest temperatures envisaged for the combustor. But the main advantage of molybdenum is its good thermal transport properties: a thermal conductivity of 93 W/m-K at 1800 K. This is the highest of the refractory metals that are commonly used in industry. Molybdenum has good strength, but a recrystallization temperature between 1100 K and 1500 K. Once raised to these temperatures, the strength of the material drops to less than half of its original strength, with reduced hardness, and possible embrittlement. The reduction in strength may not pose a problem as the heat exchange surface is pressure matched on both sides, so little strength is required. An alloy of molybdenum, TZM (titanium-zirconium-molybdenum), is perhaps an even better option. Its recrystallization temperature is around 1750 K and even after recrystallization, it maintains strength double that of pure molybdenum. This may allow for a thinner wall and result in better heat transfer. It has very similar thermal properties to molybdenum. The ability to machine and weld molybdenum is another advantage over other refractory metals.

The main disadvantage of molybdenum and TZM is that they rapidly corrode in oxidizing environments above 1000 K, and in water above 350 K. This is compensated for by another advantage of molybdenum: It is a relatively common substrate for coatings. Suitable coatings to protect the molybdenum from chemical attack but still allow good heat transfer are currently being researched. A plasma sprayed coating of Yttria-Stabilized Zirconia (YSZ) can withstand temperatures up to 1920 K, however, porosity of the coating is an issue with this method of application. However, if a technique like chemical vapor deposition were used, an impermeable barrier might be obtained.

The thermal design of the main heat exchanger is also being examined. Since the heat capacity and thermal conductivity of helium is greater than any other inert gas, helium was chosen as the fluid to be heated by the SCWO products. Various designs are being considered, with the primary design consisting of concentric cylinders in counter-flow. A counter-flow annulus design is the most basic of heat exchangers and appears to be the main choice due to the extreme state of the fluids. Once the fluids have cooled to below 1400 K, more traditional materials, and possibly geometries, may be employed. Due to geometry constraints, there is a stagnation point in the combustion products, creating an optimal point for heat transfer with a high heat transfer coefficient. The design of the outer tube containing helium is being studied in order to take advantage of this effect.

Two experimental tests have been proposed to help with understanding and analysis of the heat exchanger. The goal of the first test is to investigate the use of protective

coatings on molybdenum.  There is very little existing thermal transport data on applicable coatings under these conditions and how they affect the heat transfer must be determined.  There is also limited information on the effectiveness of the coating protecting the molybdenum from SCWO products and this could also be investigated in the same geometry.  A two-foot section with the same diameter as the combustor will be inserted between the combustor and cool-down sections with a removable liner of coated molybdenum or TZM.  Multiple coatings could be analyzed to determine those best suited for this application and their effect on heat transfer.

The second experiment would test the design of the heat exchanger at its most critical point—the stagnation point just before the helium enters the turbine.  This would also be accomplished using a removable section downstream of the combustor.  Candidate heat exchange geometries would be investigated experimentally and requisite design data could be obtained.  This would allow for accurate analysis of the heat exchanger where predictive methods are limited due to complex geometry (as well as properties).

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