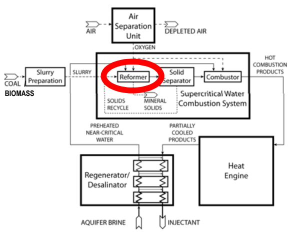
# Coal and Biomass Gasification under Supercritical Water Conditions

BumJick Kim and Reginald E. Mitchell, Mechanical Engineering Department, Stanford University

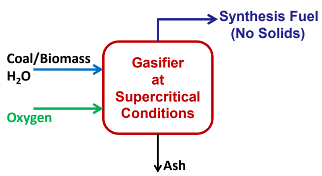
GCEP
Global Climate & Energy Project
STANFORD UNIVERSITY

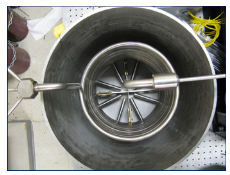
## Conceptual Plant Schematic – Aquifer-Based Conversion System




- Preheated and desalinated water from the aquifer is combined with pulverized coal/biomass to form a dilute slurry
- The slurry is partially oxidized in a reformer maintained at supercritical water conditions, producing compounds that are miscible in supercritical water
- The synthesis gas is combined with the remaining oxidizer, completing the chemical-to-sensible energy conversion
- The hot combustor products are used to drive a heat engine that produces work, cooling the hot product stream in the process
- The cooled solution, a fully equilibrated, single-phase brine solution carbonated to just below $CO_2$ saturation conditions, is injected back into the aquifer

## Supercritical Coal/Biomass Gasifier

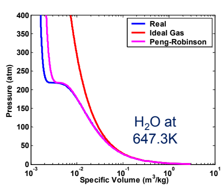


- Nonpolar organic compounds and oxygen are miscible in all proportions in water above its **critical point** (647.3 K, 220.9 bar) and many salts are insoluble. Consequently,
  - ✓ Small polar and nonpolar organic compounds released during coal extraction and devolatilization are completely miscible in SCW.
  - ✓ Large organic compounds released during coal devolatilization hydrolyze in SCW yielding $H_2$, CO, $CO_2$, and low molecular weight hydrocarbons, without tar, soot or PAH formation.
  - ✓ Sulfur, nitrogen and many trace elements in coals are oxidized to form insoluble salts in SCW.
- Coal gasification products will be dissolved in **supercritical water**, and any salts can be precipitated from the fluid mixture and removed from the system with the coal ash. There are no gaseous emissions.

## Real Fluid Effect

- The Peng-Robinson equation of state is used to describe the variations in pressure with specific volume and temperature.




< P-v plot of water at $T=T_{crit}$=647.3 K >

- Peng-Robinson Equation

$$P=\frac{RT}{v-b}-\frac{a\alpha}{v(v+b)+b(v-b)}$$
$$a=0.45724R^2T_c^2/P_c$$
$$b=0.07780RT_c/P_c$$
$$\alpha=\left[1+S\left(1-T_r^{1/2}\right)\right]^2$$
$$S=0.37464+1.5422\omega-0.26992\omega^2$$

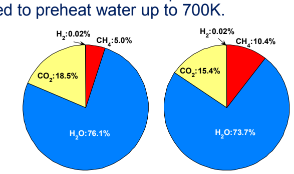
- Fugacity

$$RTd\ln f=vdP \qquad \lim_{P\to 0}\left(\frac{f}{P}\right)=1$$

- Cantera (a chemical kinetics software) is also used for the nonideality of water above the supercritical pressure.

## Synthesis Fuel Composition

- The residual heat from the supercritical combustor can be used to preheat water up to 700K.




< No Preheating > < With Preheating >

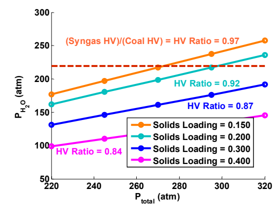
❖ Gas evolution at 290 atm and 647.3K
❖ Coal composition: 79.7% C, 4.2% H, 3.0% O, 1.5% N, 1.5% S (By weight)

- With preheated water and oxygen up to 700K, less oxygen is used to partially oxidize the coal/biomass slurry and more methane is produced.

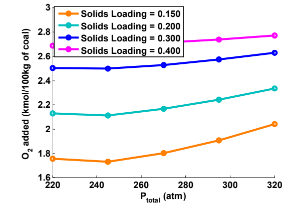
## Water Pressure and Heating Value

## Autothermal Gasifier Operation

With **PREHEATED** water and oxygen up to **700K**, required amount of oxygen is smaller and the HV ratio is greater.



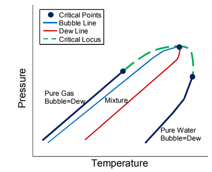

Coal Composition (By weight)
79.7% C
4.2% H
3.0% O
1.5% N
1.5% S



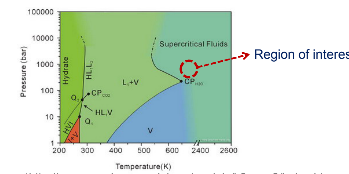

- Reactants with a lower solids loading (=Mass fraction of solids fuel in slurry) contain more heated water; therefore, the heating value ratio is higher.
- With preheating of water, required oxygen for autothermal operation increases as slurry solids loading increases.

## Critical Points of Multi-Component Mixtures

- Phase Diagram of Water/Gas Binary Mixture



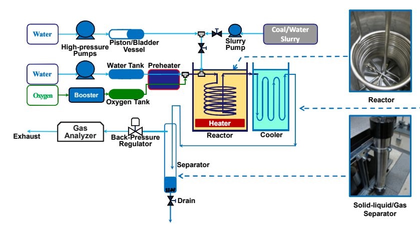

- Example: Water/$CO_2$ Binary Mixture

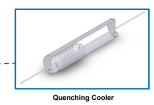


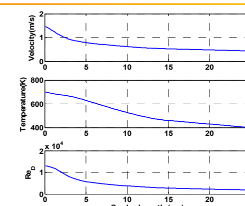

*http://www.geochem-model.org/models/h2o_co2/index.htm

- Critical temperature of the mixture is in between the critical temperatures of pure components.
- In mixtures, Water/$CO_2$ system is in a single phase above the critical temperature of pure water.

## Supercritical Gasification Facility




- The temperature, velocity and Reynolds number profiles established in the cool-down section (OD=0.25 in, ID=0.06 in, Total mass flow rate = 30 grams/min)

## Continuing Work

- Synthesis fuel composition data acquisition and data analysis from gasification experiments
- Development of a carbon conversion mechanism

**Proposed C + $H_2O$ Mechanism**

(1) $C_{af} + H_2O \leftrightarrow C(O) + H_2$
(2) $2C_{af} + H_2O \rightarrow C(H) + C(OH)$
(3) $C(H) + C(OH) \rightarrow C(O) + C(H_2)$
(4) $C(H_2) \rightarrow H_2 + C_{af}$
(5) $C(O) + C(H) \leftrightarrow C(OH) + C_{af}$
(6) $C_b + C(O) + C(OH) \rightarrow CO_2 + C(H) + C_{af}$
(7) $C_b + C(O) \rightarrow CO + C_{af}$

## Conclusions

- Above the critical temperature of water, the main gaseous products in the mixture are miscible in water in a single phase.
- Supercritical water's solvation properties will be studied at various pressures.
- With preheating, less oxygen is required and the heating value of synthesis fuel is higher.
- Experimental data analyses will yield kinetic parameters that describe the coal/biomass conversion process.