Coal and Biomass Gasification under Supercritical Water Conditions

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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 cooled solution, a fully equilibrated, single-phase brine solution carbonated to just below CO2 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 H2, CO, CO2, 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.

- Peng-Robinson Equation

  \[ P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \]

  where

  - \( a = 0.45724 T_c \left[ \frac{P_c}{T} \right]^2 \]
  - \( b = 0.87906 \left[ \frac{P_c}{T} \right] \]
  - \( T_c = 647.3 \text{ K} \)

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

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Water Pressure and Heating Value

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

- Reactants with a lower solids loading (=Mass fraction of solids fuel in slurry) contain more heated water; therefore, the heating value ratio is higher.

- 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.

Critical Points of Multi-Component Mixtures

- Critical temperature of the mixture is in between the critical temperatures of pure components.
- In mixtures, Water/CO2 system is in a single phase above the critical temperature of pure water.

Synthesis Fuel Composition

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

- 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.

Continuing Work

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

Proposed C + H2O Mechanism

1. C + H2O → CO + H2
2. CO2 + H2O → CO + H2
3. (CO) + (OH) → (CO) + (OH)
4. C + (OH) → (CO) + (OH)
5. (CO) + (OH) → (CO) + (OH)
6. (CO) + (OH) → (CO) + (OH)
7. (CO) + (OH) → (CO) + (OH)

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.