Swelling Properties and Intrinsic Reactivities of Coal Chars Produced at Elevated Pressures and High Heating Rates

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Background

Why High-Pressure

- To increase conversion efficiency in combined cycle (from 34% to ~60%!!!)
- Less CO_2 per MW of electricity
- Has the potential to reduce pollutants
  - Sulfur removal easier
  - Concentrated CO_2 stream may help CO_2 sequestration efforts
- To reduce reactor size

Why not High-Pressure

- Unproven technology:
  - Demonstration projects with government support
  - 30-year guarantees required
- Not cost effective:
  - Currently must deliver electricity at a lower cost than conventional PC
  - No penalties currently in place for inefficiency and/or CO_2 production

High-Pressure Coal Combustion Conditions

- Integrated Gasification Combined Cycle (IGCC), 25-30atm
- Pressurized Fluidized Bed Combustor (PFBC), 15-25 atm
- Pulverized Coal Injection (PCI), <5 atm

Objectives

- Measure coal combustion characteristics at:
  - High pressure (1-30 atm)
  - High temperature (up to 1300°C)
  - High heating rate (10^5K/s)
- Find effect of pressure on resulting char properties, such as chemical nature, swelling ratio etc.
- Validate or improve coal/char high-temperature, high-pressure combustion mechanism

Rationale

- Few reliable data at high pressures and high temperatures (lots of TGA data, but not much at practical conditions)
- Form of char oxidation rate expression is still debated in literature (nth order vs. Langmuir-type expressions)

Previous High Pressure Work at BYU

- Monson and coworkers
  - High pressure drop tube
  - Chars generated at 1 atm
  - Char reaction rates at 1-15 atm in 5-21% O_2
  - Activation energy as a function of pressure

- Hecker and coworkers
  - Chars generated in FFB at 1 atm
  - High pressure TGA work (n = 0.7)

- Hong and coworkers
  - Simple Langmuir rate expression with Thiele modulus
  - Explained several sets of data, including Monson's burnout data (but not measured T_p's)

Approach

Previous Approach

1 atm FFB char → 1 atm TGA
1 atm FFB char → 4 atm TGA
1 atm FFB char → 8 atm TGA
1 atm FFB char → 16 atm TGA

New Approach

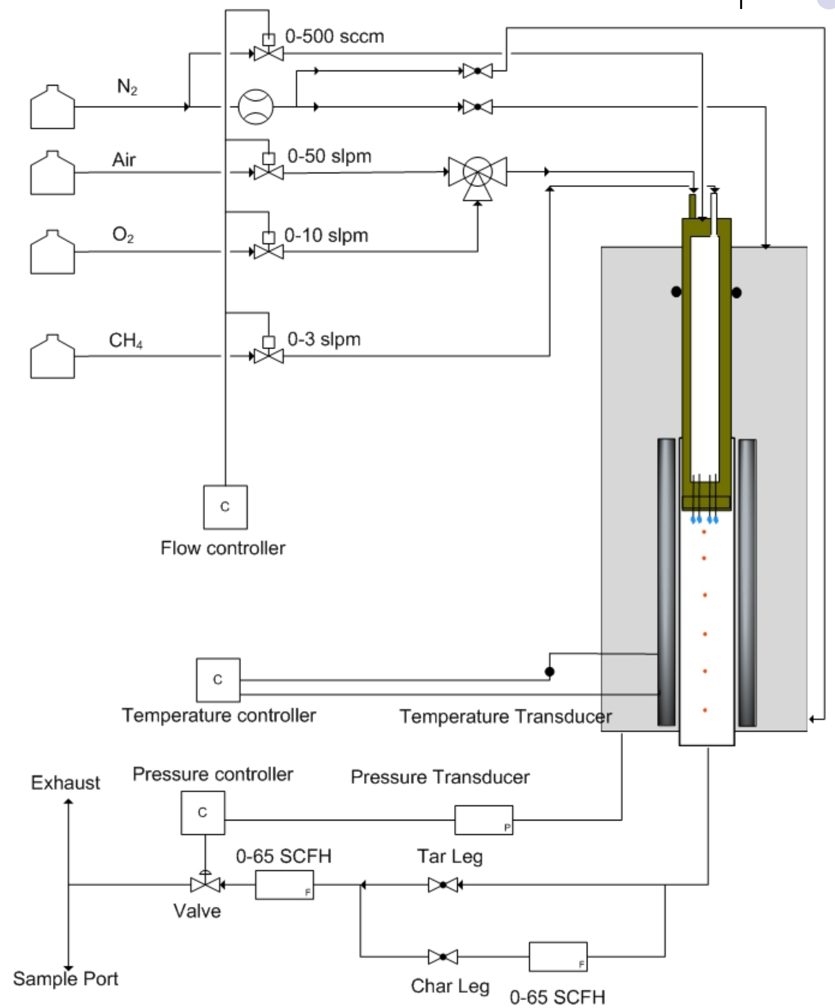
1 atm drop tube char → 1 atm TGA
6 atm drop tube char → 6 atm TGA
10 atm drop tube char → 10 atm TGA
15 atm drop tube char → 15 atm TGA

Why?

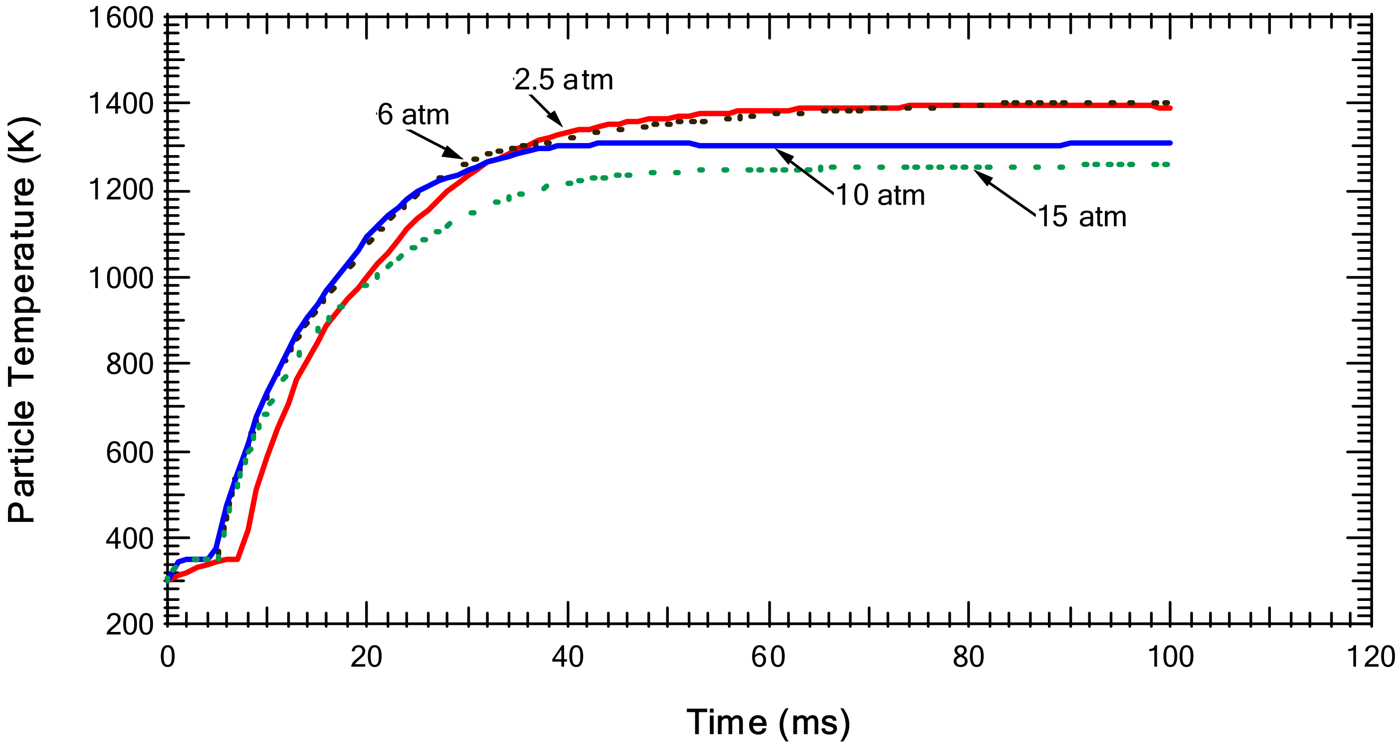
char density and diameter = f(P_{tot}, heating rate)
intrinsic char reactivity = f($T_{final,}$ heating rate)??

High-Pressure Flat-Flame Burner

- Advantages:
  - Char formation at high temperature and heating rate (~1500 K, 10^5 K/s)
  - Adjust stoichiometry for %O_2 in post-flame zone
  - Fast heat-up and shut-down times for ease of use
  - Automatic control
- Disadvantages:
  - Fuel-rich operation at pressure produces soot from CH_4
  - Axial temperature profile not constant at elevated pressure



Temperature Profile of HP-FFB



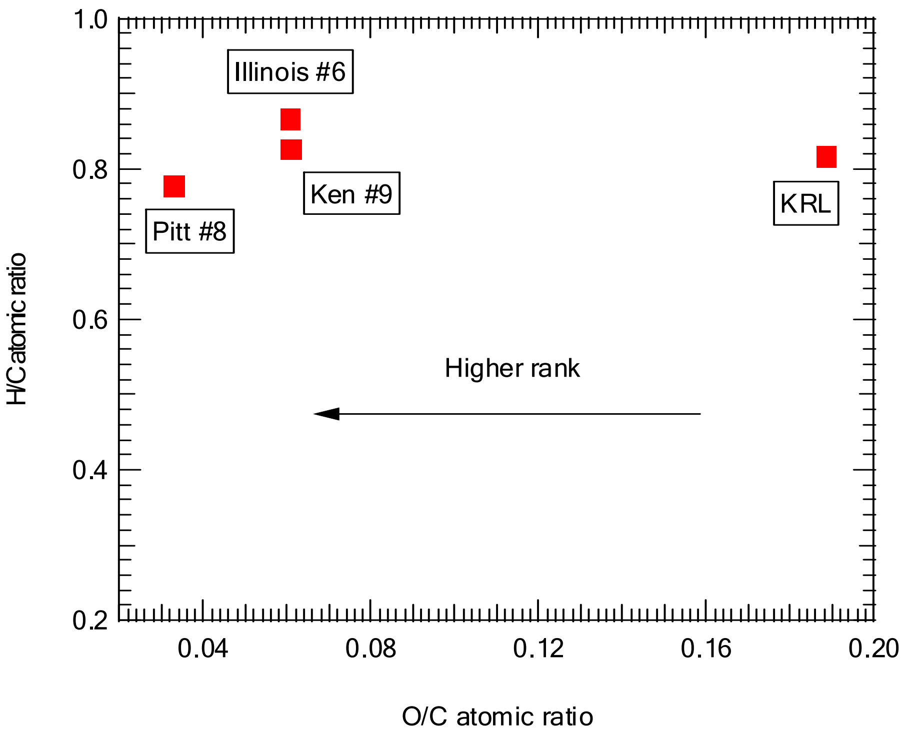
☞ **HP-FFB has much higher particle heating rate than drop tube (10^5 K/s vs 10^4 K/s)**

Previous Work in this Study

- **Only slight increases observed in swelling behavior as pressure increased**
  - The swelling behavior observed for the four coals at each pressure was lower than reported in high pressure drop tube experiments.
  - High heating rates (>10^5 K/s) limit swelling behavior, even at elevated pressure
- **SEM photos revealed that bituminous coal has large physical structure transformations, with popped bubbles due to the high heating rate**
- **TGA char oxidation reactivity tests were performed at the same total pressure as the char formation pressure**
  - Char oxidation reactivities decreased with increasing char formation pressure
  - Formation pressure has <u>no</u> distinct effect on intrinsic char oxidation activation energy (E) and order (n)
  - Formation pressure therefore seems to affect the pre-exponential factor (A) in the reactivity expression

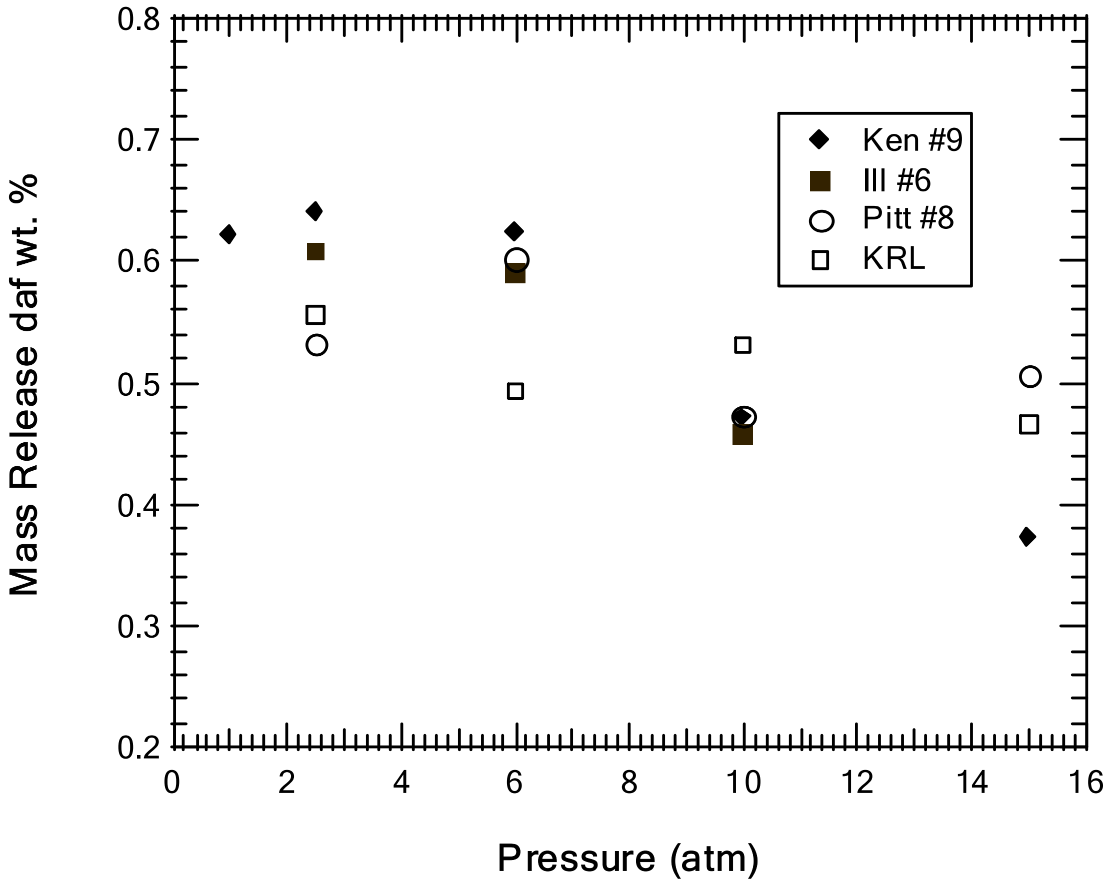
Coals Tested

- Four sets of chars produced and analyzed
  - Pittsburgh #8 hva bituminous coal (63-75 μm)
  - Kentucky hvb bituminous #9 (44-74 μm)
  - Illinois #6 hvc bituminous coal (75-90 μm)
  - Knife River lignite (<45 μm)



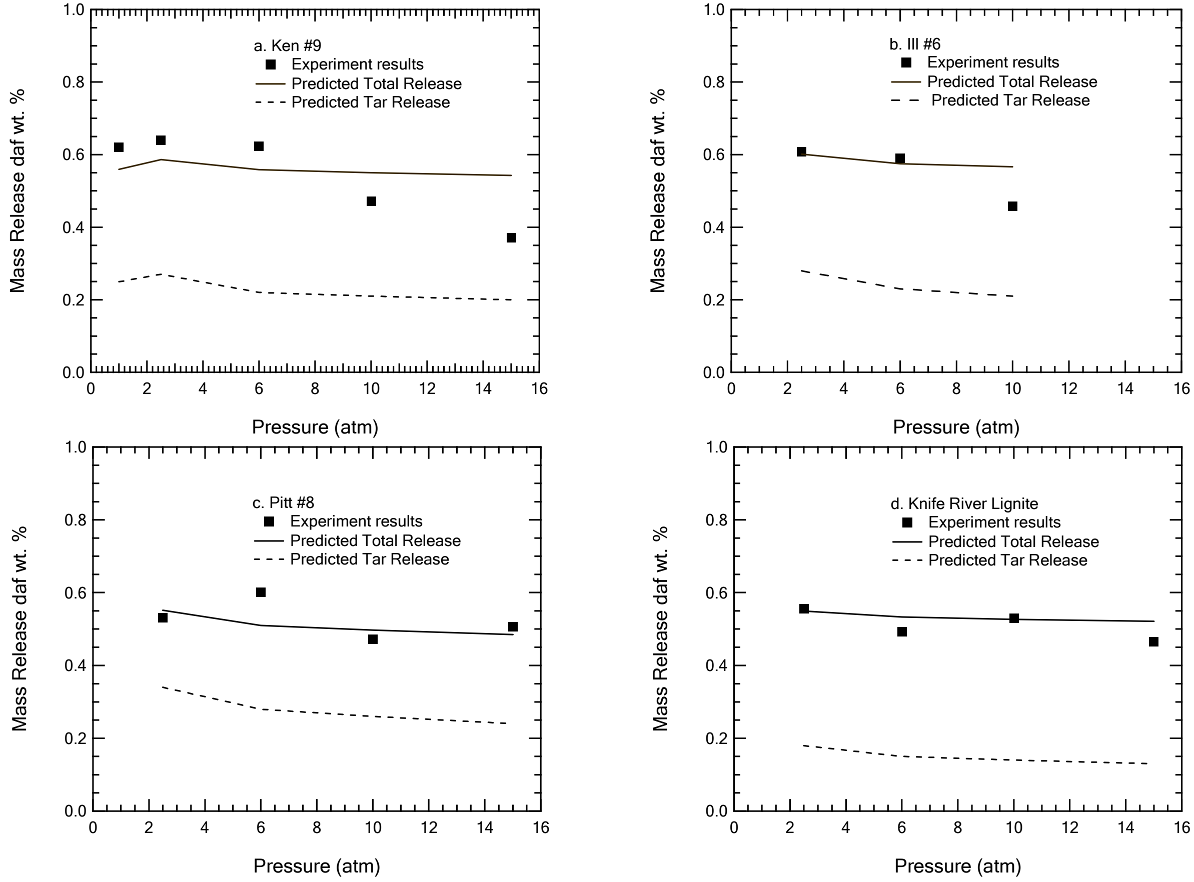
1. Coal Pyrolysis

Coal Mass Release



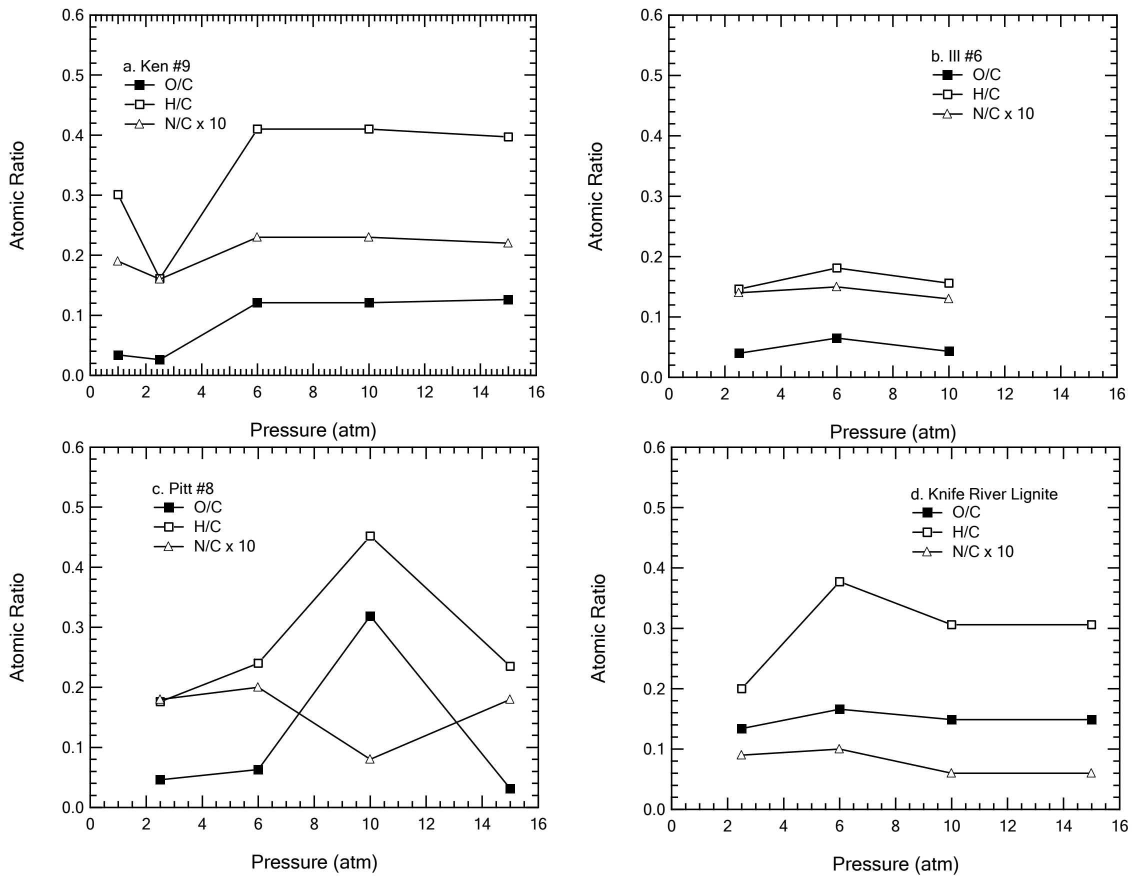
•The measured volatiles yields exceeded the ASTM total volatiles yields for all coals at low to moderate pressures (< 7 atm);
•The effect of coal rank on coal mass release is not very clear.

Predicted and Measured Mass Release as a Function of Pressure



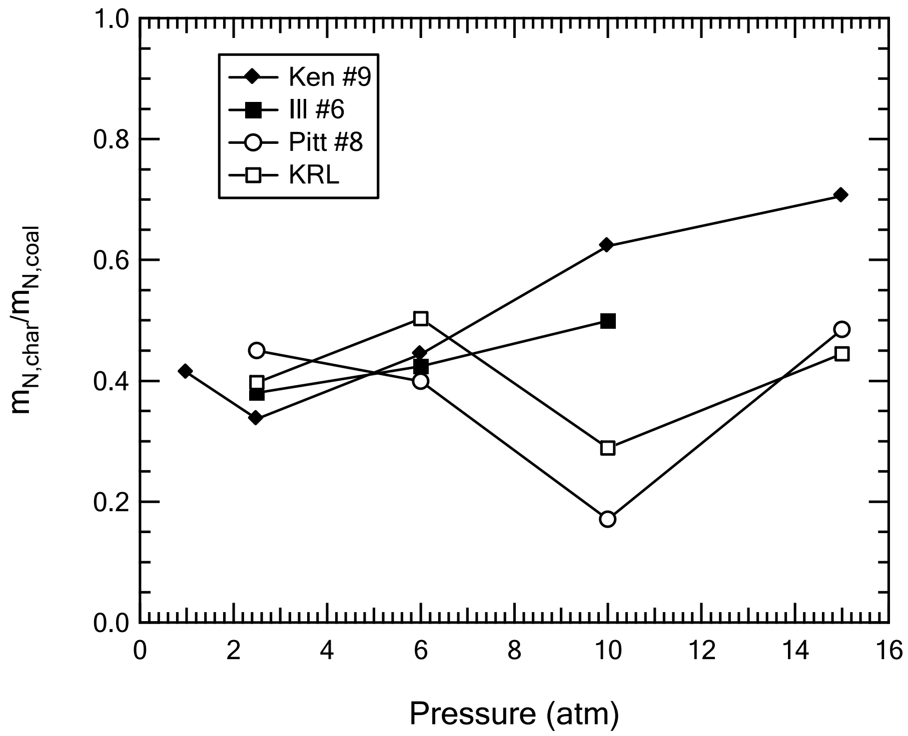
- CPD Modeling results are generally comparable to the experiments

Elemental Compositions of Chars as a Function of Pressure



- H/C and O/C ratios remained relatively stable when pressure was higher than 6 atm

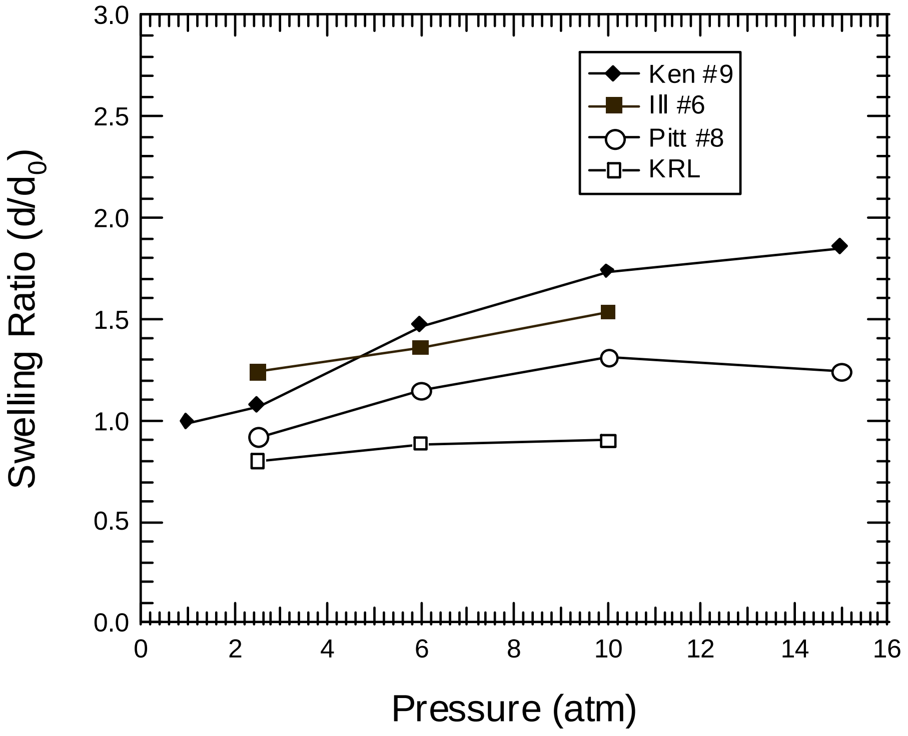
Fraction of Initial Nitrogen Remaining in the Char



- The N/C ratios in the chars do not change significantly as a function of pressure

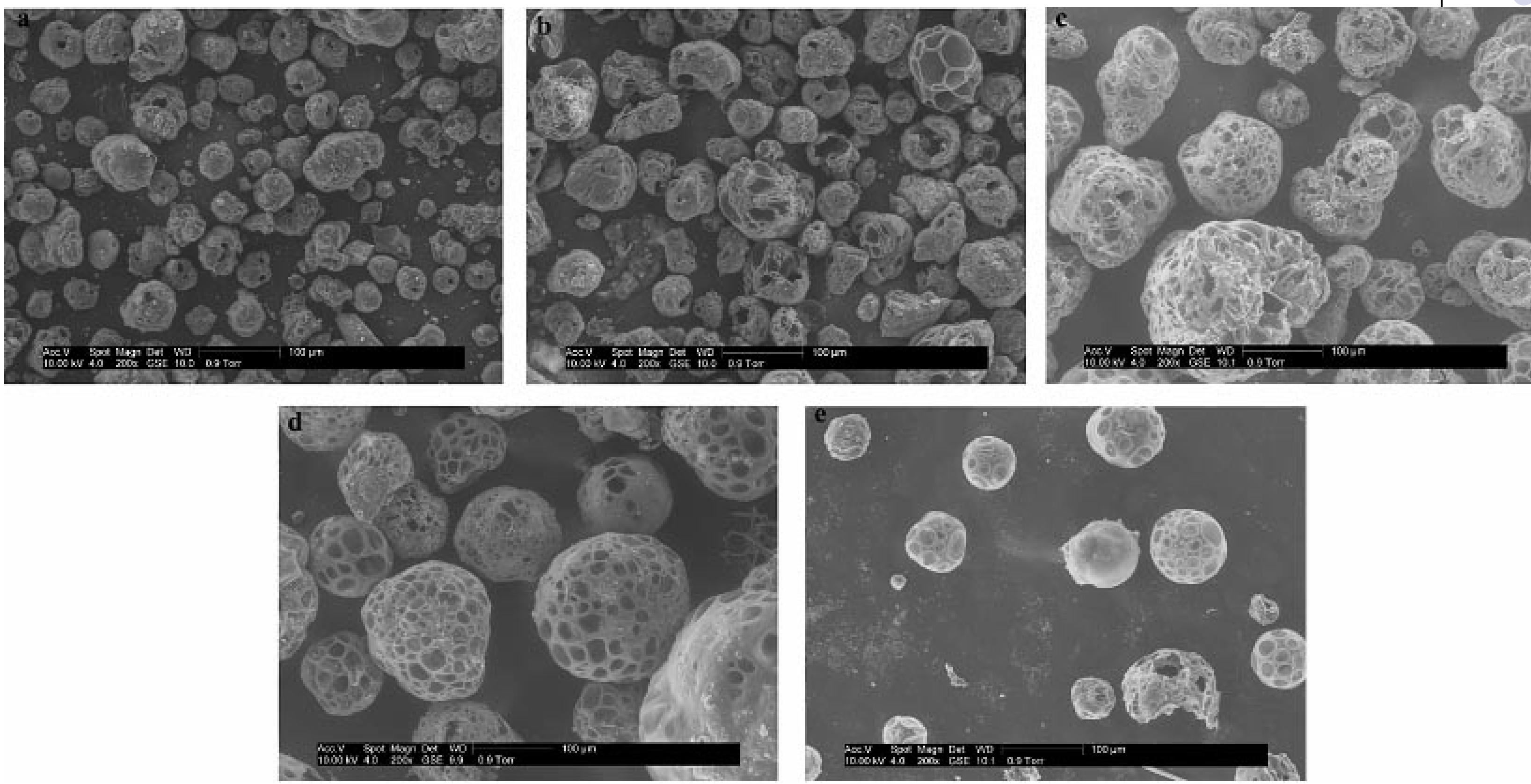
2. Char Physical Characteristics.

Swelling Ratios of Chars Obtained at Different Pressures



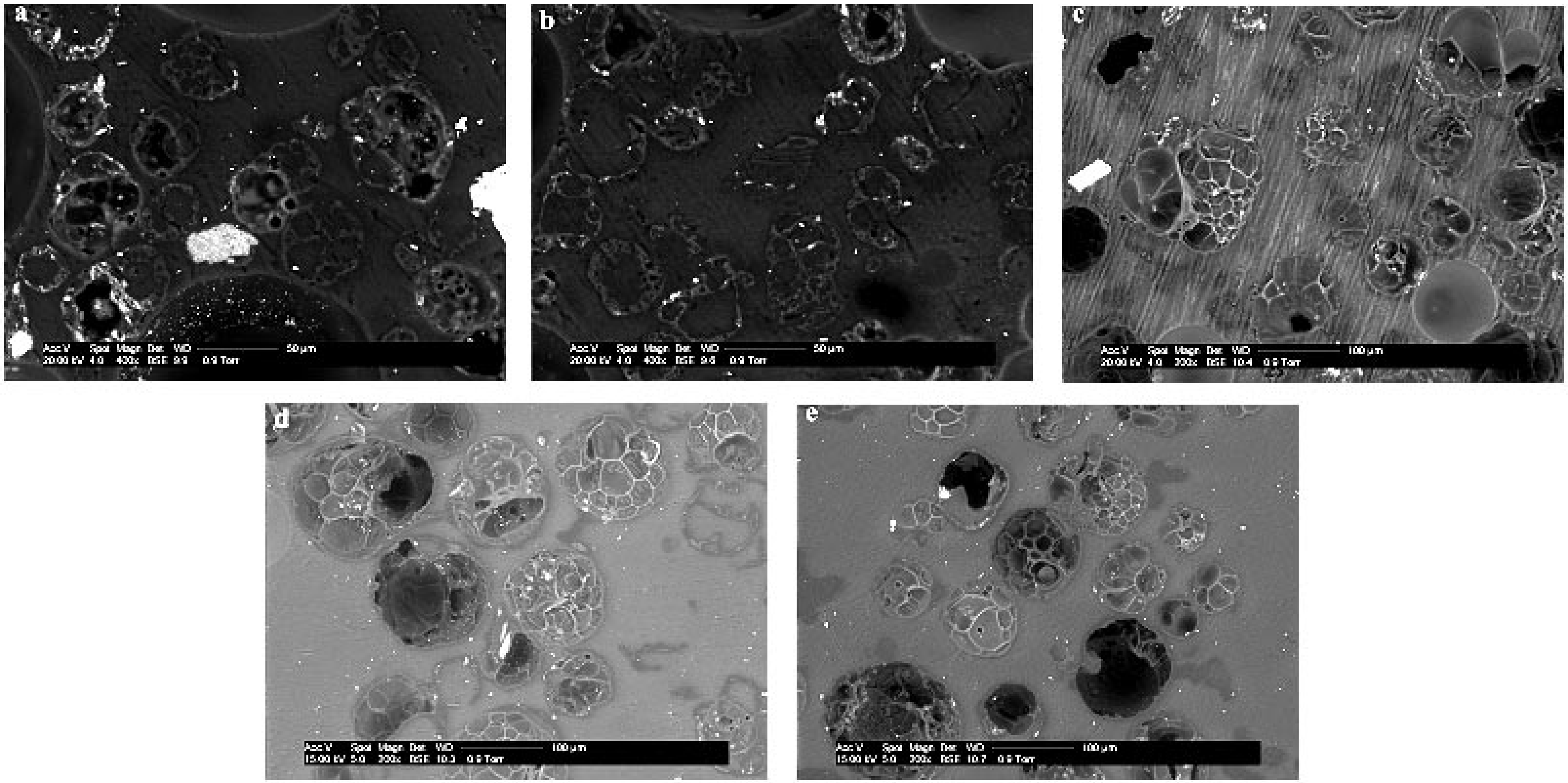
- **Tap densities measured, ratio eliminates packing factor using equation $m/m_0=(\rho/\rho_0)(d/d_0)^3$**

Exterior Morphology of Chars Produced from Pyrolysis of Ken #9 Coal



- The char particle surface became less coarse as pressure increased

Interior Morphology of Chars Produced from Pyrolysis of Ken #9 Coal



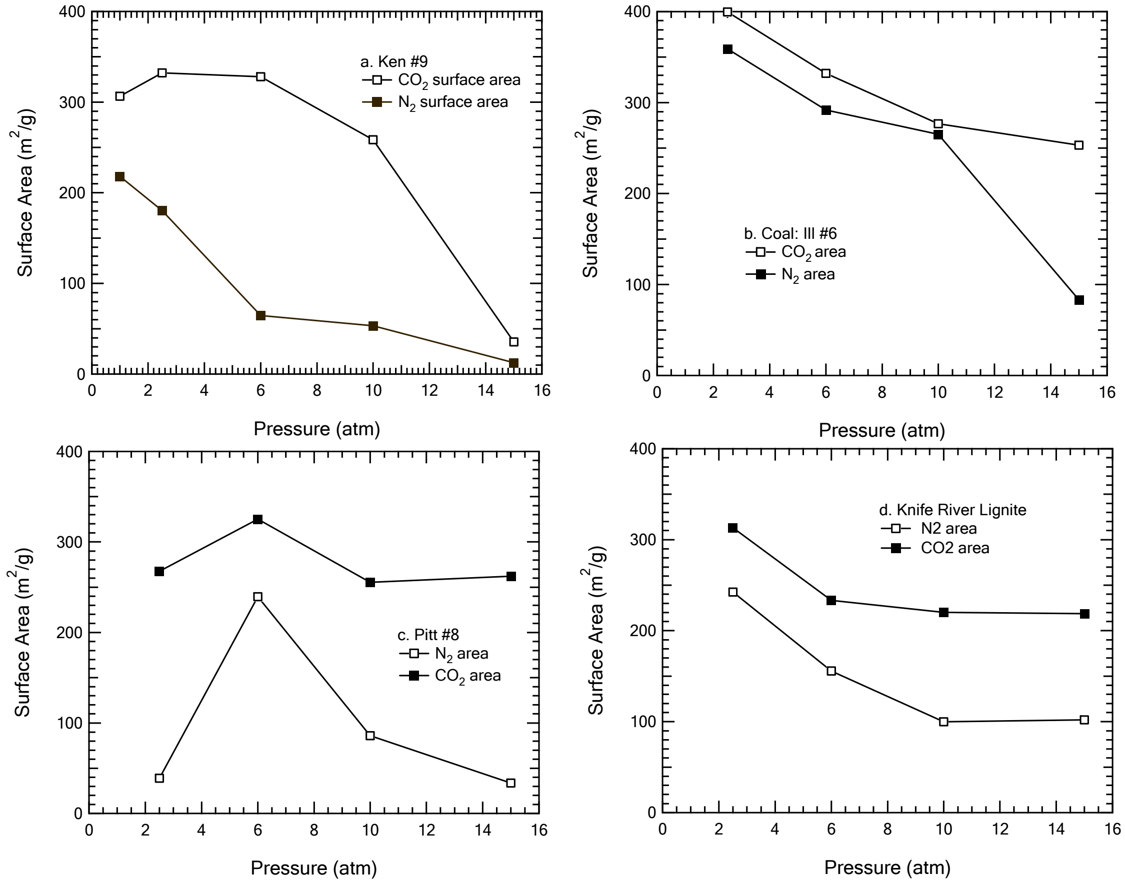
- Char bubble structure appears to be affected by the pressure
- Swelling ratio is related to bubble evolution mechanism

3. Char Reactivity

Change in Char Reactivity with Pressure

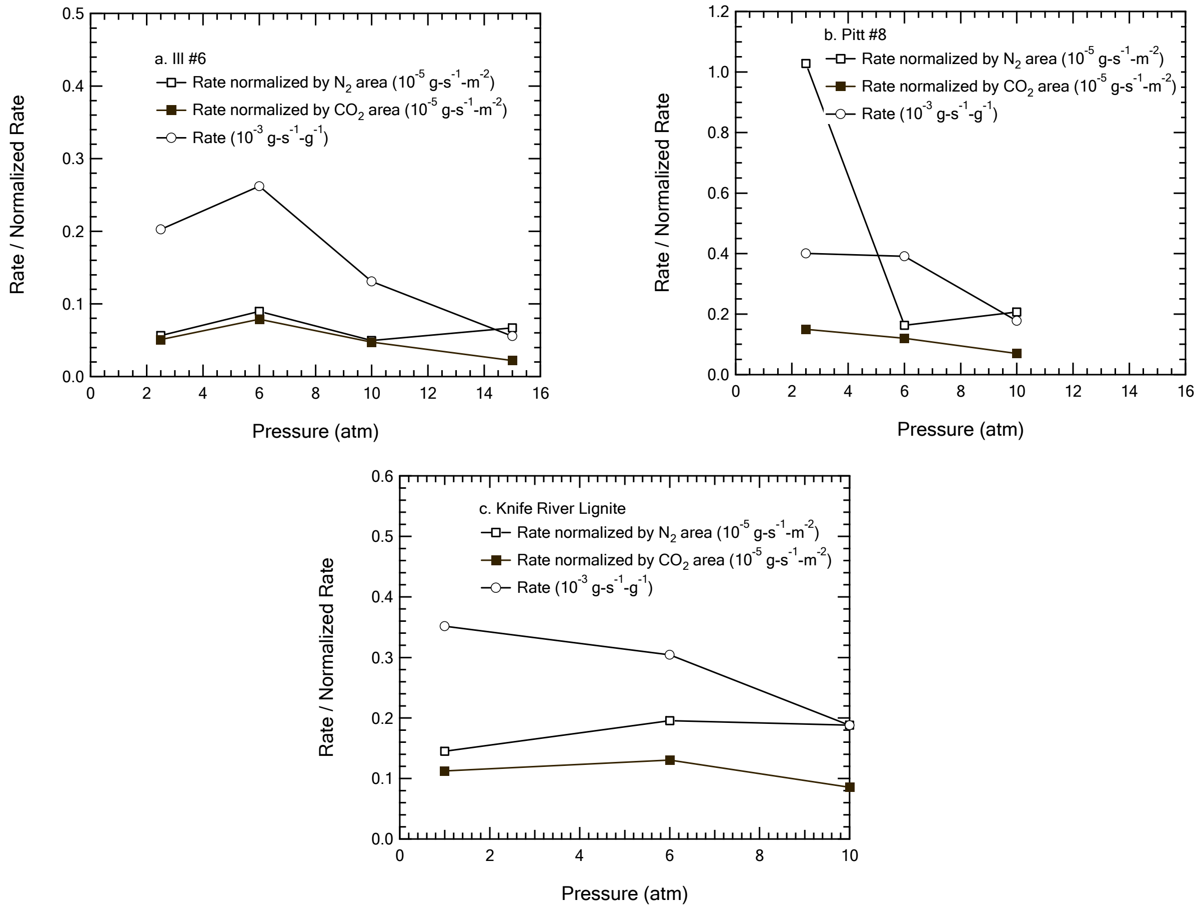
- In the previous results from this study
  - Char oxidation reactivities decreased with increasing char formation pressure
  - Formation pressure has <u>no</u> distinct effect on intrinsic char oxidation activation energy (E) and order (n)
  - Formation pressure therefore seems to affect the pre-exponential factor (A) in the reactivity expression
- The effect of formation pressure on char reactivity is not fully understood

Internal Surface Areas of Chars Prepared at Different Pressures



- CO_2 surface areas were larger than the N_2 surface areas at all pressures
- Chars produced at high pressure have fewer amounts of micropores than low pressure char

Intrinsic Char Reactivity and Reactivity Normalized by Internal Surface Area Versus Pressure



- **Intrinsic char intrinsic reactivity is mainly due to changes in the internal surface area**
- **The relative importance of CO_2 versus N_2 surface area is unknown**

Conclusions

- Four coals were pyrolyzed at pressures from 0.85 to 15 atm in the HPFFB
- The measured decreases in total volatiles yields with increasing pressure were predicted using the CPD model
  - Parameters based only on the elemental composition and ASTM volatiles yields
- The H/C and O/C ratios in the resulting chars initially increase with increasing pressure, but remain relatively constant at pressures from 6 to 15 atm
- Low pressure chars were in the advanced stages of foam structure evolution, high pressure chars were in the early stages of foam structure evolution
  - Increases in swelling ratio as pressure increases were consistent with bubble evolution
  - Chars formed at high pressures were more porous than low pressure chars, but exhibited a denser framework (i.e, the bubble walls were thinner but more dense)
- Both N_2 and CO_2 internal surface areas of chars generally decreased with increasing pressure
  - CO_2 surface area was always higher than the N_2 surface area.
- Normalized reactivity was found to be relatively constant with increasing pressure for both the N_2 and CO_2 normalizations
  - Strongly implies that the majority of the change in char reactivity with pressure can be attributed to changes in internal surface area

Acknowledgments

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