Pressurized Coal Pyrolysis and Gasification at High Initial Heating Rates

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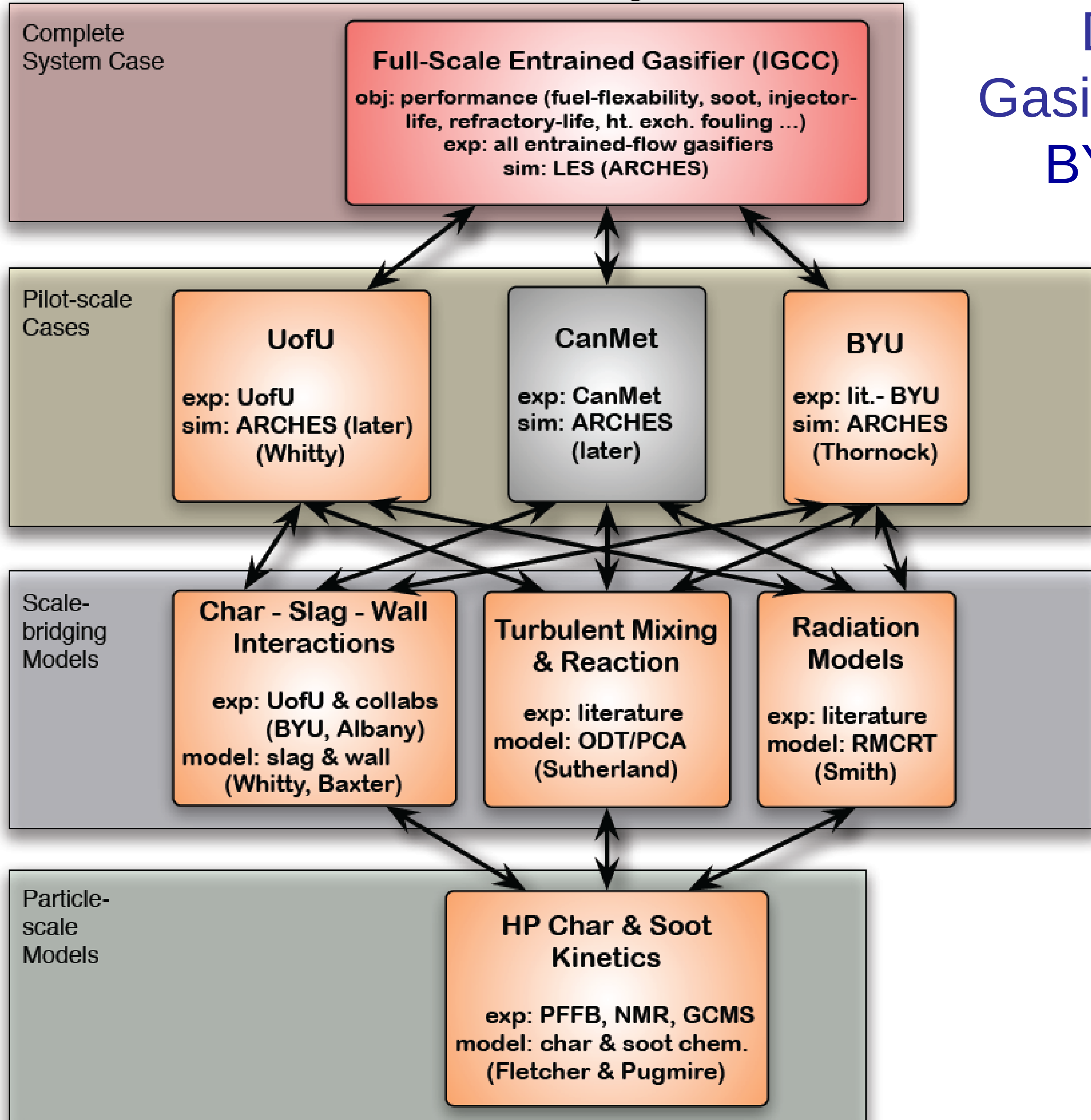
Utah Clean Coal Program



DOE-sponsored Gasification Research at BYU and U of Utah

BYU Flat-Flame Burner

Equipment to Study Particle Reactions

Equipment	Heating Rate (K/s)	Temperature (°C)	Advantages	Disadvantages
TGA	0.1-1	25-1000	Well-controlled T and gas concentration, Precise mass measurement	Not representative of industrial conditions, hard to collect tar, Small samples
Heated grid	1-1000	25-1000	Moderate heating rate, quick quench of tar, direct mass measurement	Small samples, char not available after test
Drop Tube	10,000	25-1700	Electric heaters easily controlled, high heating rate, char and tar in quantity	Hard to measure T_p, secondary tar reactions
Radiant heaters	10,000	25-1200	Avoids secondary reactions, char and tar in quantity	T_p not known
Flat-flame burners	100,000	1100-2000	Very high heating rate, char and tar/soot in quantity	Minimum temperature, secondary tar reactions, effect of post-flame gases (CO_2 & H_2O)

Effects of Pressure Studied

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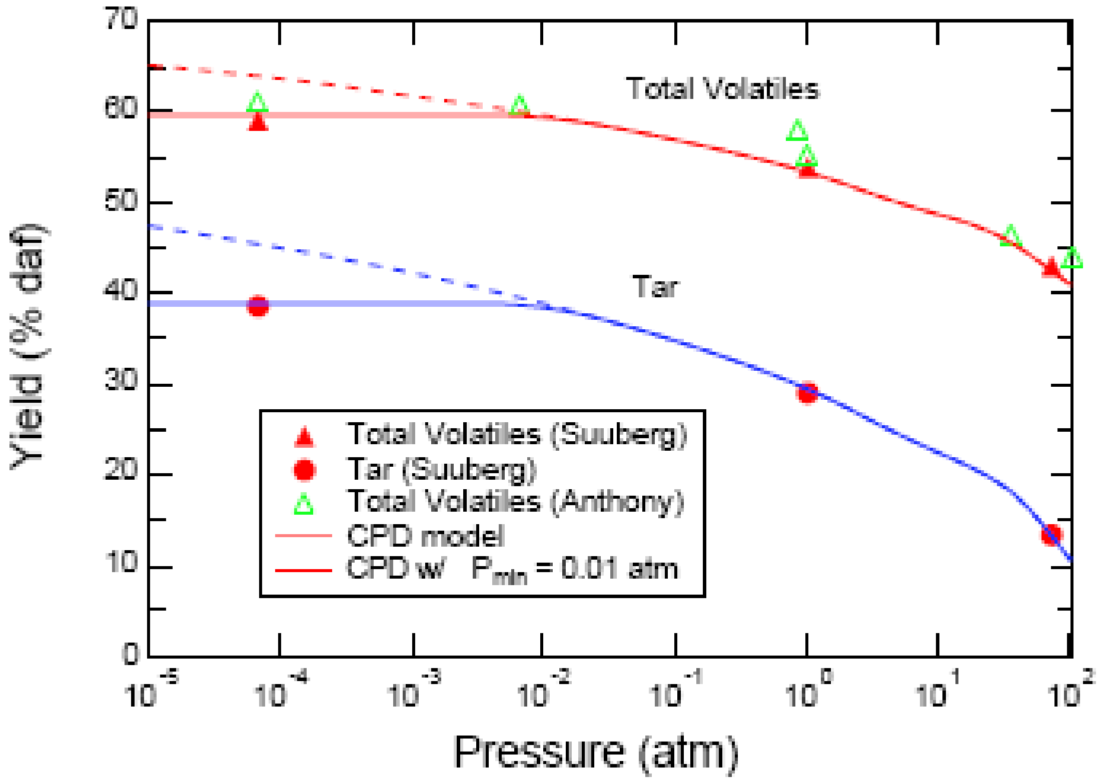
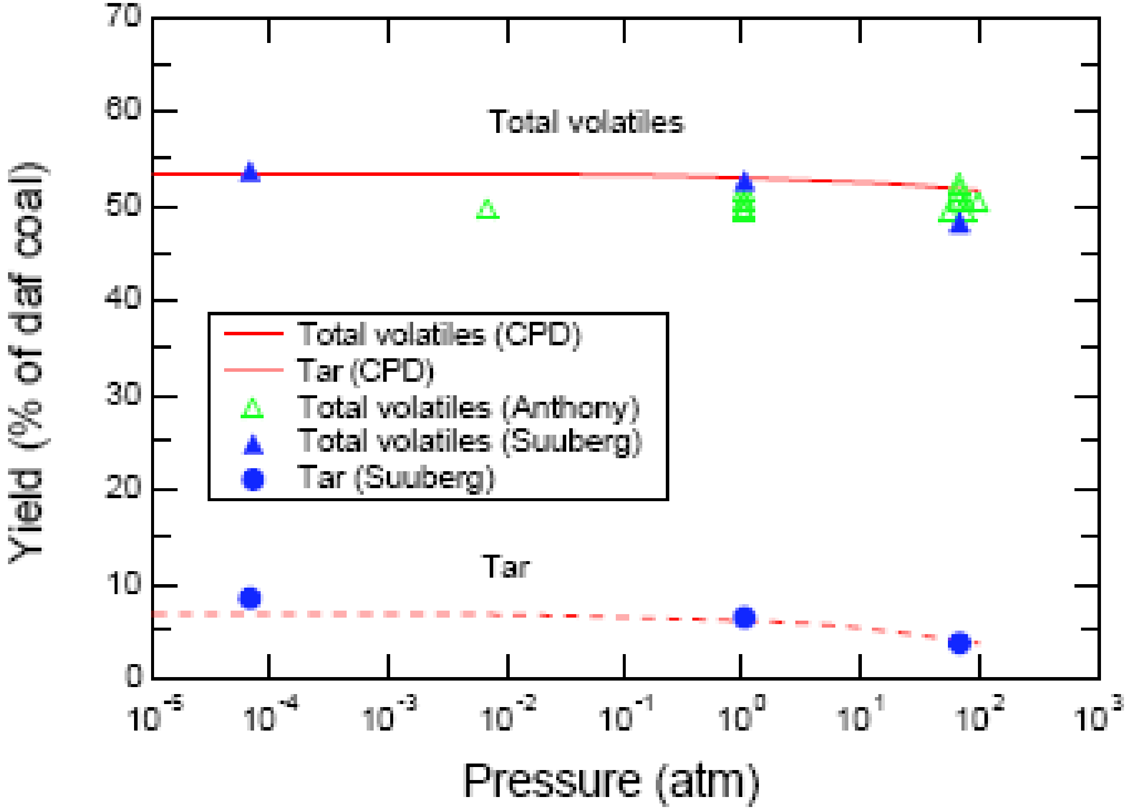
Heated grid	1-1000	25-1000	Moderate heating rate, quick quench of tar, direct mass measurement	Small samples, char not available after test, mass transfer affects char reactions
Drop Tube	10,000	25-1700	Electric heaters easily controlled, high heating rate, char and tar in quantity	Hard to measure T_p, secondary tar reactions
Radiant heaters	10,000?	25-1200	Avoids secondary reactions, char and tar in quantity	T_p hard to calculate
Flat-flame burners	100,000	1100-2000	Very high heating rate, char and tar/soot in quantity	Minimum temperature, secondary tar reactions, effect of post-flame gases (CO_2 & H_2O)

Total Volatile and Tar Yields Decrease with Increasing Pressure for hv Bituminous Coals



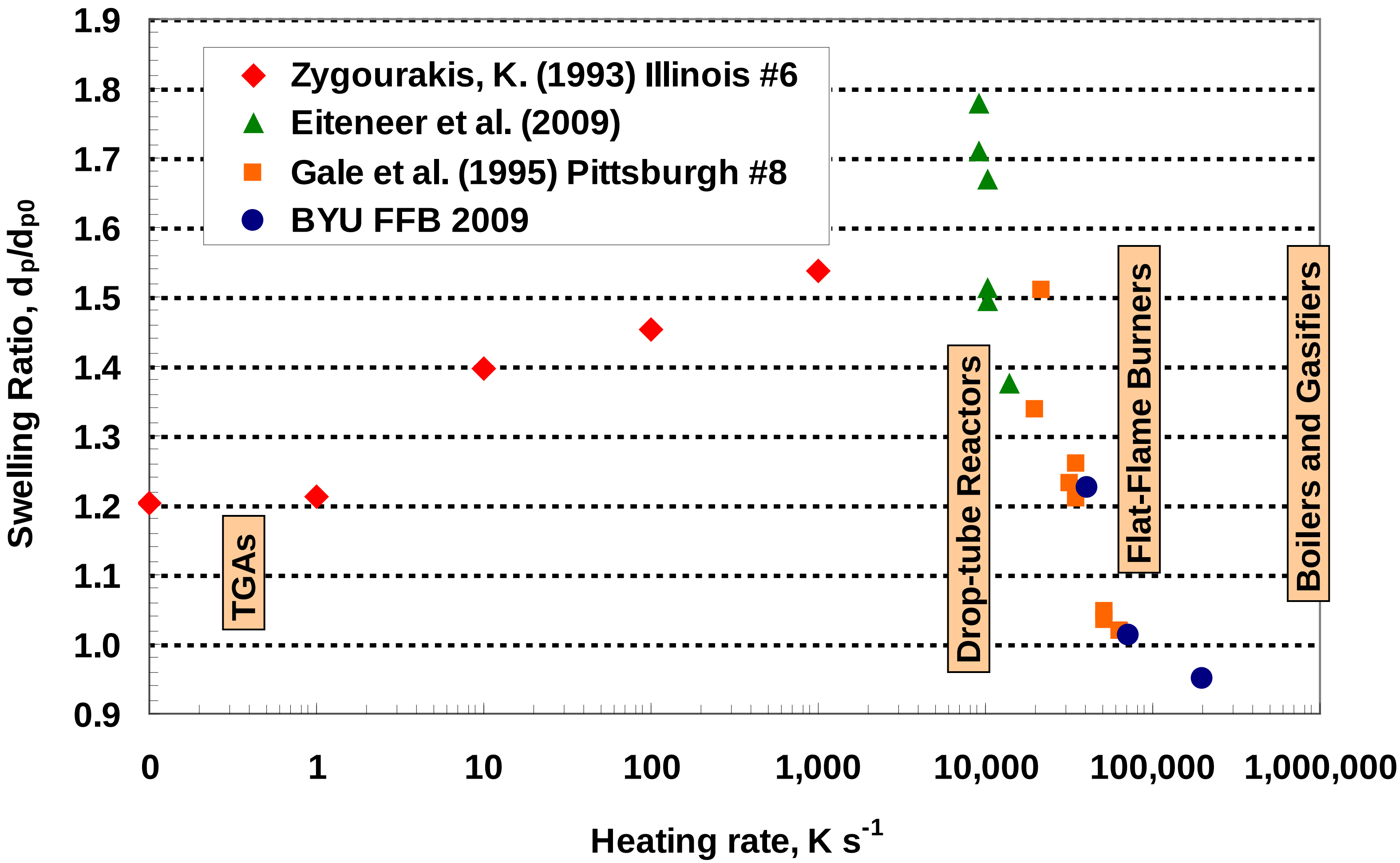
Pittsburgh hv bituminous coal data from heated grid experiments, Anthony (1974) and Suuberg (1977), 1000 K/s to 1000 ^{o}C. CPD model predictions from Fletcher, et al. (1992)

Effect of Pressure on Low Rank Coal Devolatilization is Small



Zap lignite data from heated grid experiments, Anthony (1974) and Suuberg (1977), 1000 K/s to 1000 ºC. CPD model predictions from Fletcher, et al. (1992)

Effect of Heating Rate on Swelling



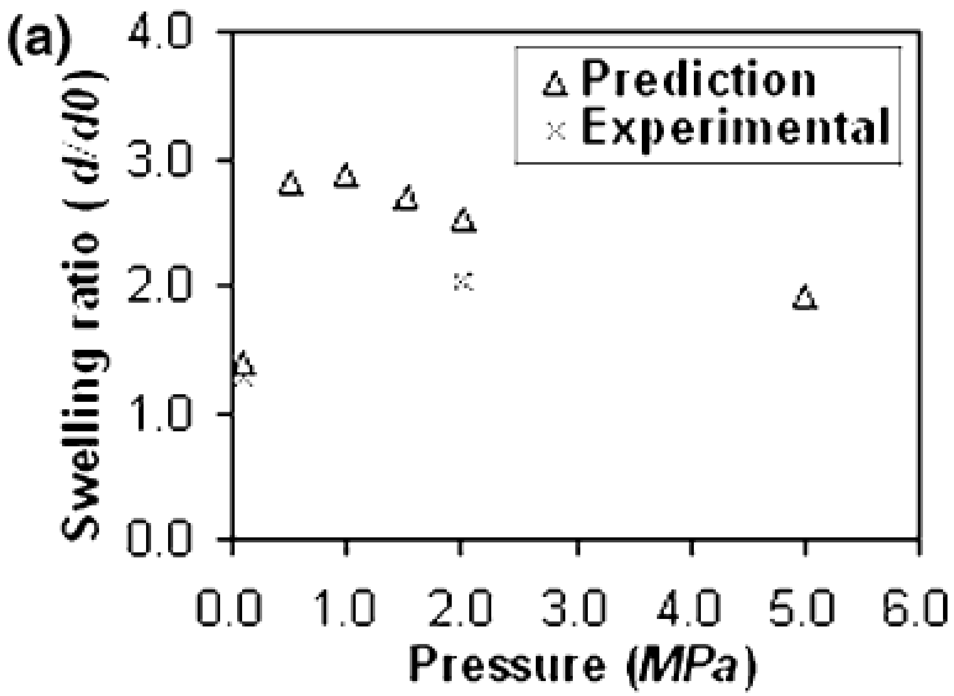
Zygourakis, K., *Energy & Fuels* **7**, 33-41 (1993).

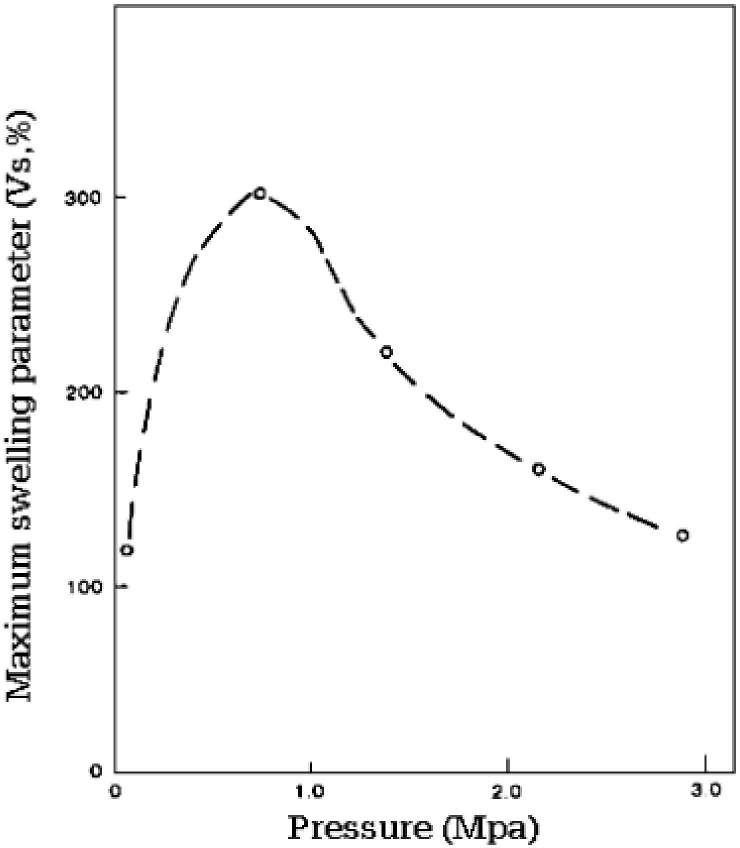
Gale, T. K., C. H. Bartholomew and T. H. Fletcher, *Combustion and Flame,* **100**(1-2), 94-100 (1995).

Eiteneer, B., et al., *26th Annual International Pittsburgh Coal Conference*, Pittsburgh, PA (2009).

Shurtz, R. C., et al., *26th Annual International Pittsburgh Coal Conference*, Pittsburgh, PA (2009).

Effect of Pressure on Swelling





- Effect of pressure on swelling at ~10^4 K/s
- Swelling ratios as high as 3 reported

Yu, J., D. Harris, J. Lucas, D. Roberts, H. Wu and T. Wall, *Energy & Fuels,* **18**(5), 1346-1353 (2004).

Yu, J., J. A. Lucas and T. F. Wall, Progress in Energy and Combustion Science, 33(2), 135-170 (2007).

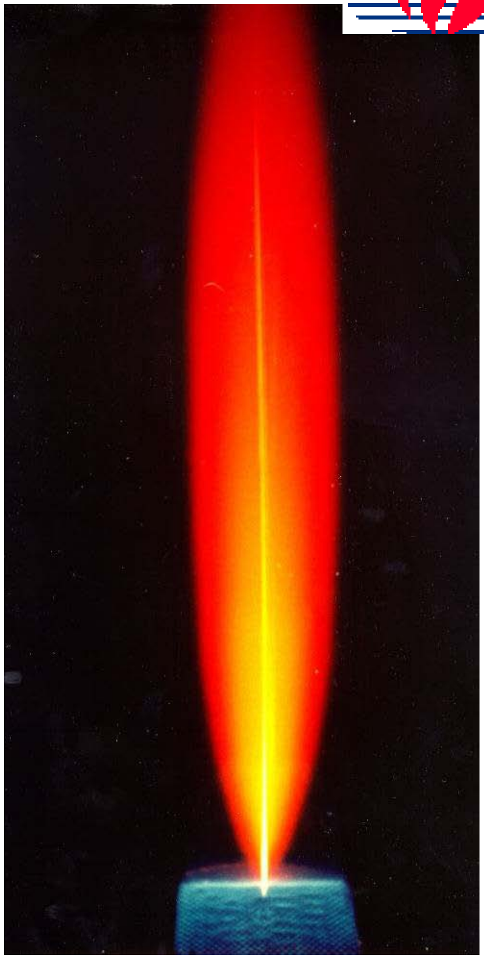
Lee, C. W., R. G. Jenkins and H. H. Schobert, Energy & Fuels, 6(1), 40-47 (1992).

Why Is Particle Swelling Important?

- Influences particle heatup rate (external surface area)
- Affects net heterogeneous reaction rate (drive towards film diffusion limit)
- Affects ash particle size distribution
  - Highly swollen particles fragment, yielding smaller ash particles

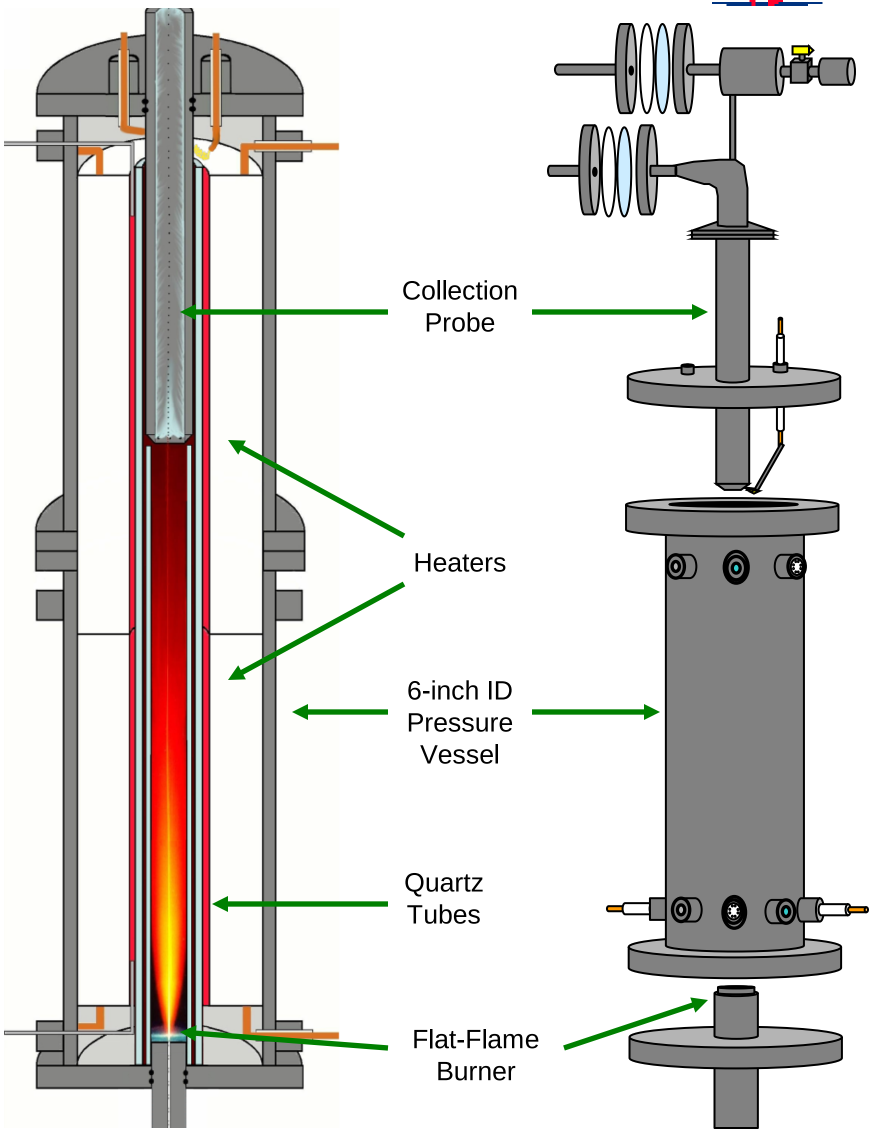
Atmospheric Flat-Flame Burner (FFB)

- Advantages:
  - Char and soot formation at high heating rate (~10^5 K/s)
  - Fueled by CH_4 or CO
    - Allows temperature flexibility (1100 K to 2000 K)
  - Adjust stoichiometry for % O_2 in post-flame zone
  - Very fast heat-up and shut-down times for ease of use
  - Residence time adjusted easily
- Disadvantages:
  - Limited to experiments at ambient pressure

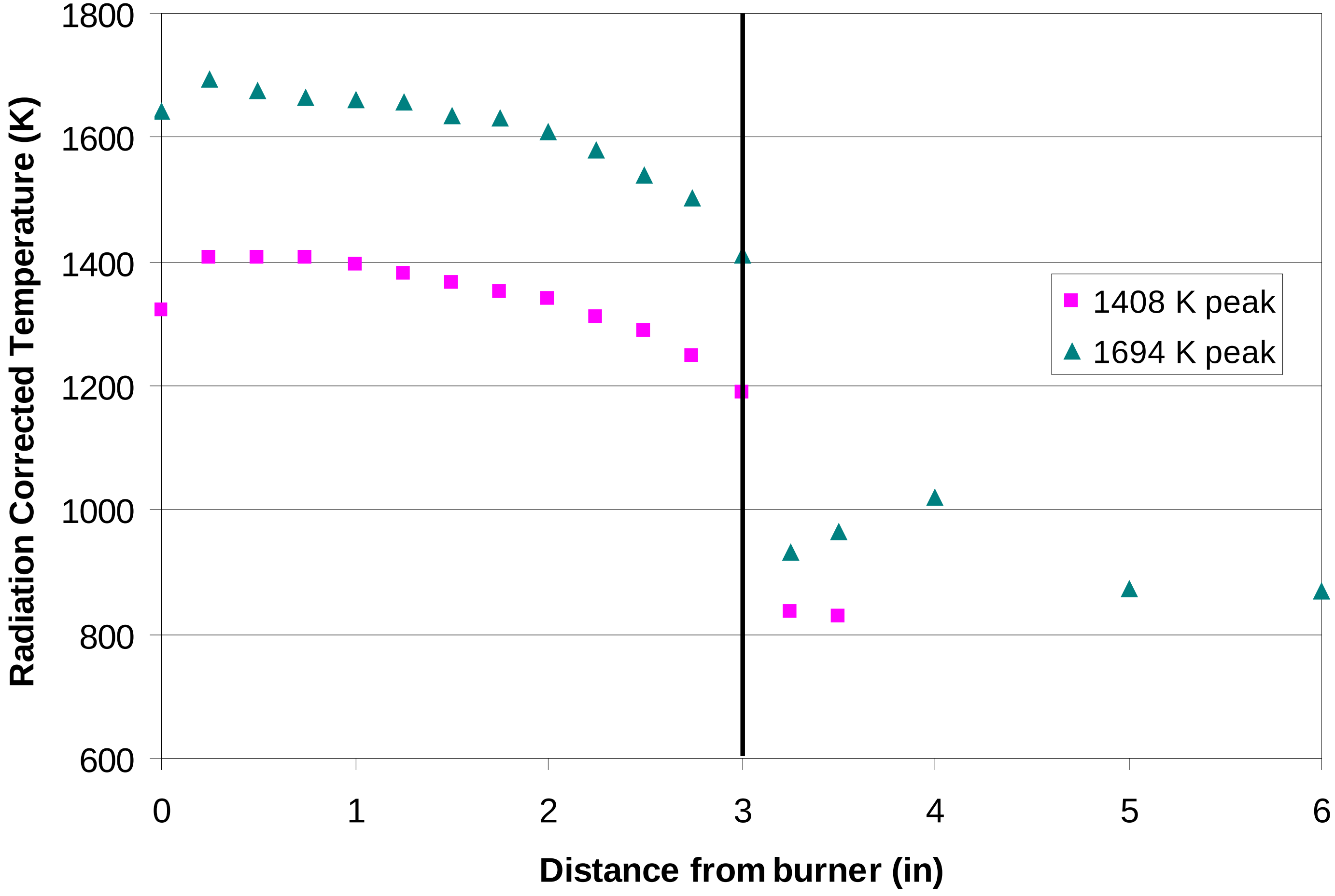


Upgraded HPFFB

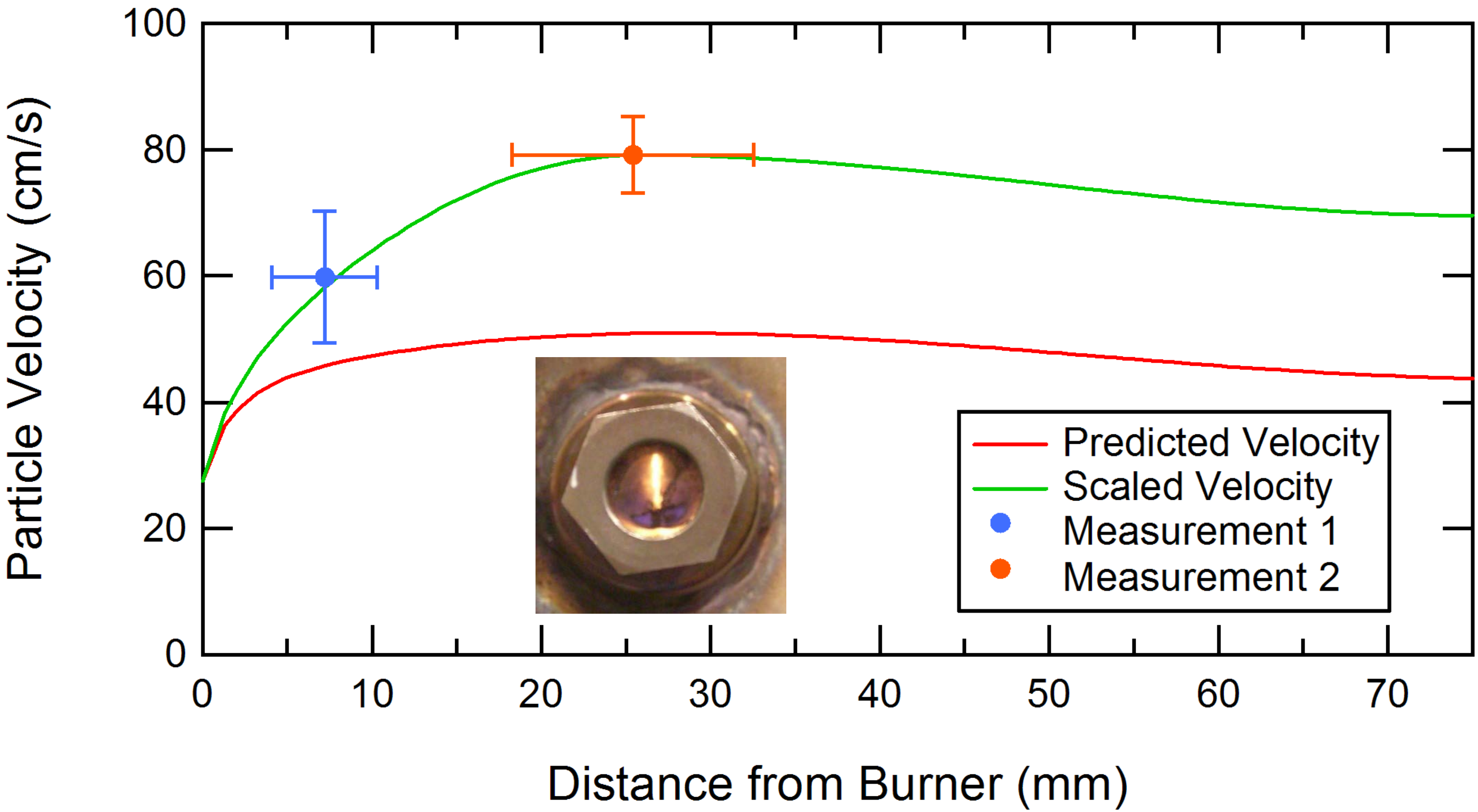
- Changed to up-flow
  - Reduces wear on the burner
  - Recently reduced burner diameter to 1”
- Probe moves to change residence time
  - Up to 800 ms for 1 section
  - Up to 1600 ms for 2 sections
  - Very short residence times available
- Operational pressures of 2.5-15 atm
  - Upgradeable to 30 atm
- Uses either CH_4 or CO with some H_2
  - Greater flexibility in gas composition
  - CO will not form soot
- Optical access available near burner
  - Check particle feeding
  - Limited optical particle velocities
- Faster startup
- Easier to disassemble



15 atm Centerline Temperature with Quench at 3”



Optical Particle Velocities



Problems Encountered

- Fuel-rich CH_4 flame found to form soot at slightly elevated pressures (2.5 atm)
- Sooting eliminated by using 84% H_2 and 16% CH_4
  - High H_2 increased flame speed
  - Preheated burner surface
  - Caused clogging for bituminous coals due to early pyrolysis
  - Sub-bituminous coals did not clog

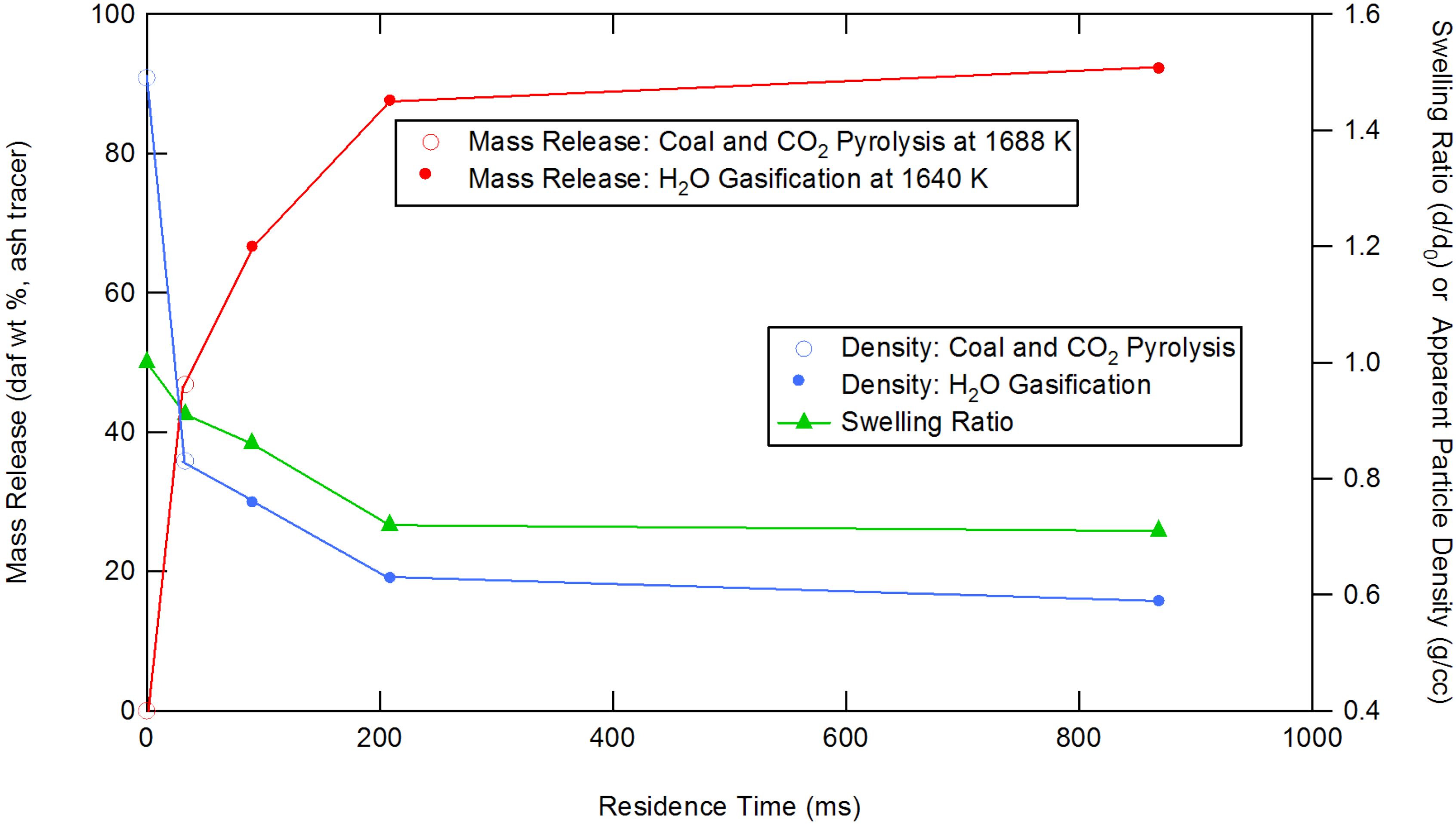
Particle Analysis

- ICP for tracer analysis (Ti, Si, Al)
  - Mass release determined from tracers
- Tap density
  - Bulk density ratio (ρ/ρ_0) = Apparent density ratio
- Average diameter
  - $m/m_0 = (\rho/\rho_0)\,(d/d_0)^3$

Experimental Conditions

Condition	H_2O-rich	CO_2-rich
Pressures (atm)	2.5	2.5, 5, 10, 15
Peak Temperature (K)	1640	~1700, 1900
Inlet Fuel Mixture	84% H_2, 16% CH_4	97.5% CO, 2.5% H_2
Post-flame composition		
CO_2 mol %	3.0	15.7 – 21.0
H_2O mol %	27.4	0.6 - 2.1
CO mol %	1.1	7.5 - 11.9
H_2 mol %	1.8	0.1 - 0.4
N_2 mol %	66.7	69.0 - 70.8

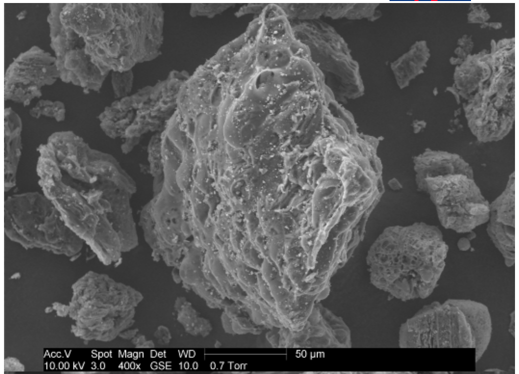
2.5 atm Wyodak Gasification



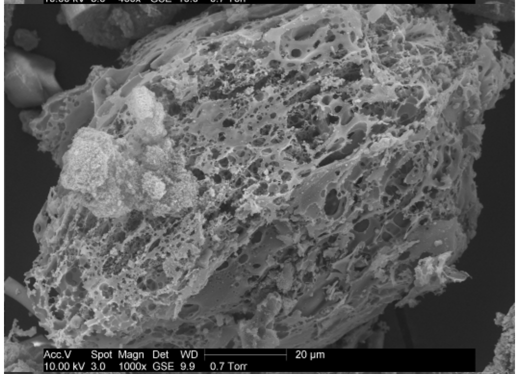
Steam Gasification of Wyodak Coal
(2.5 atm)

- 90 ms char fully pyrolyzed
  - CPD predicts ~62% MR_{daf}
- Little change in structure from 208-868 ms
  - Linear gas temperature decrease of ~300 K from peak over 14 inches
- Highly porous chars
  - N_2 surface area of 360 m^2/g at 208 ms
- Zone II behavior near burner
  - Both d_p and ρ_p changing in first 200 ms
  - Zone III calculations predict 100% conversion in ~60 ms

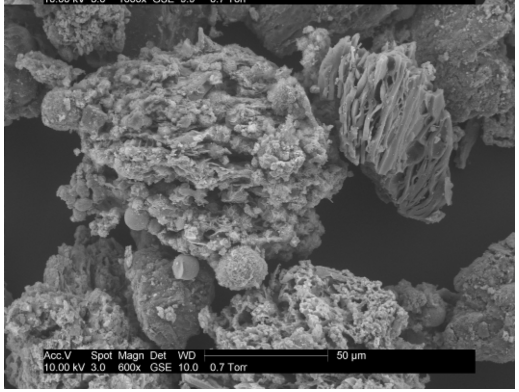
90 ms



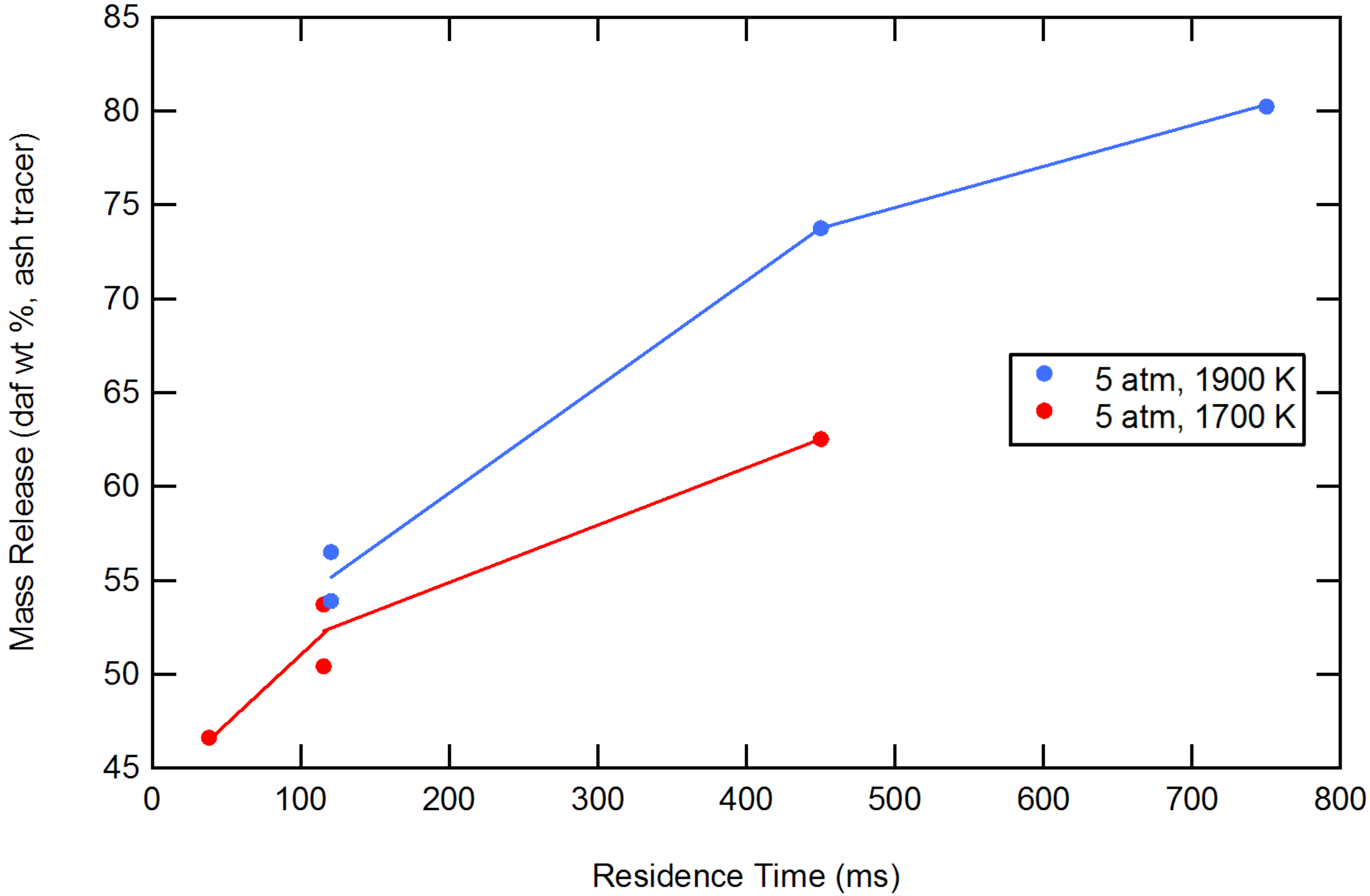
208 ms



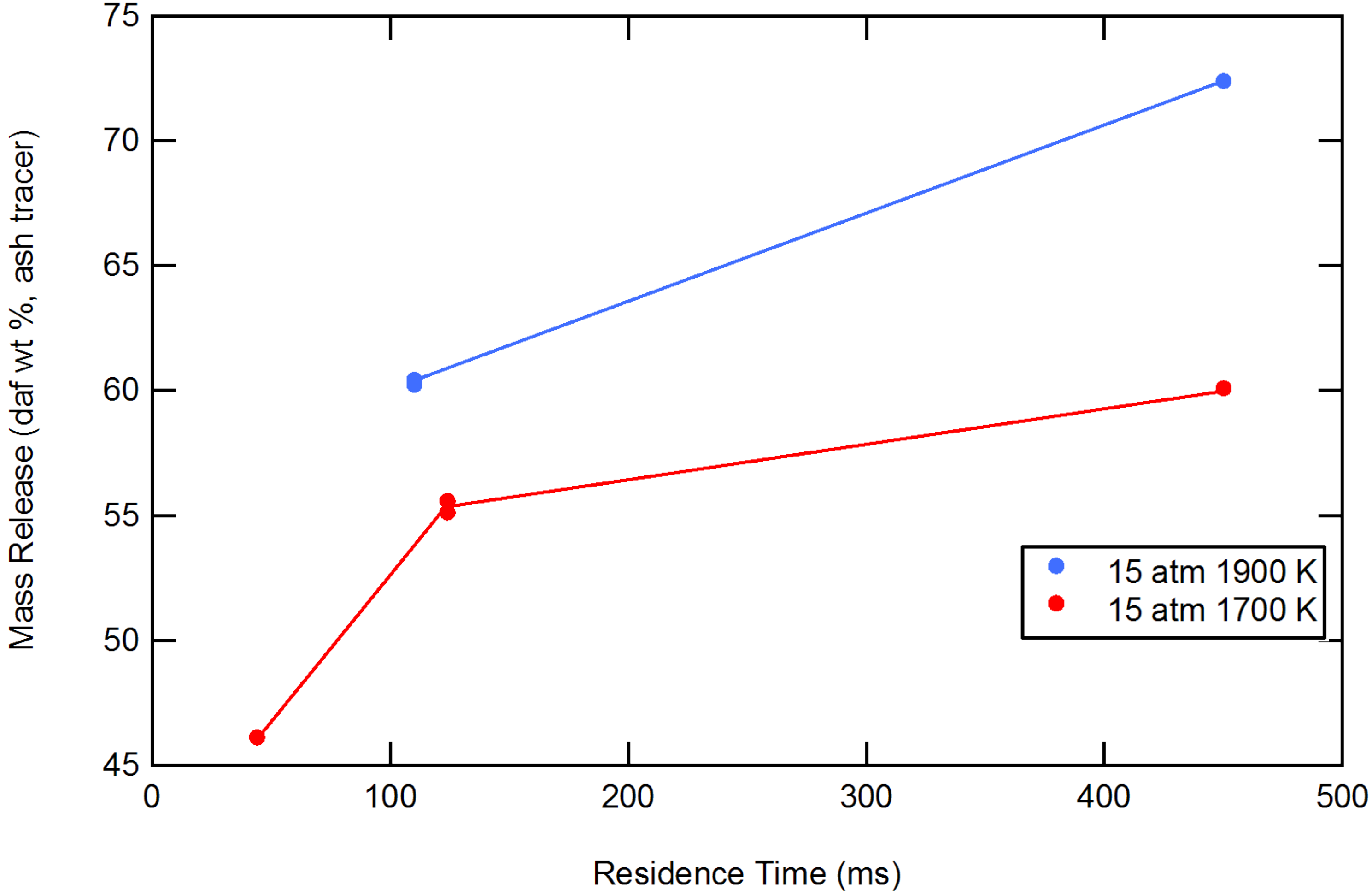
868 ms



Wyodak CO_2 Gasification, 5 atm



Wyodak CO_2 Gasification, 15 atm

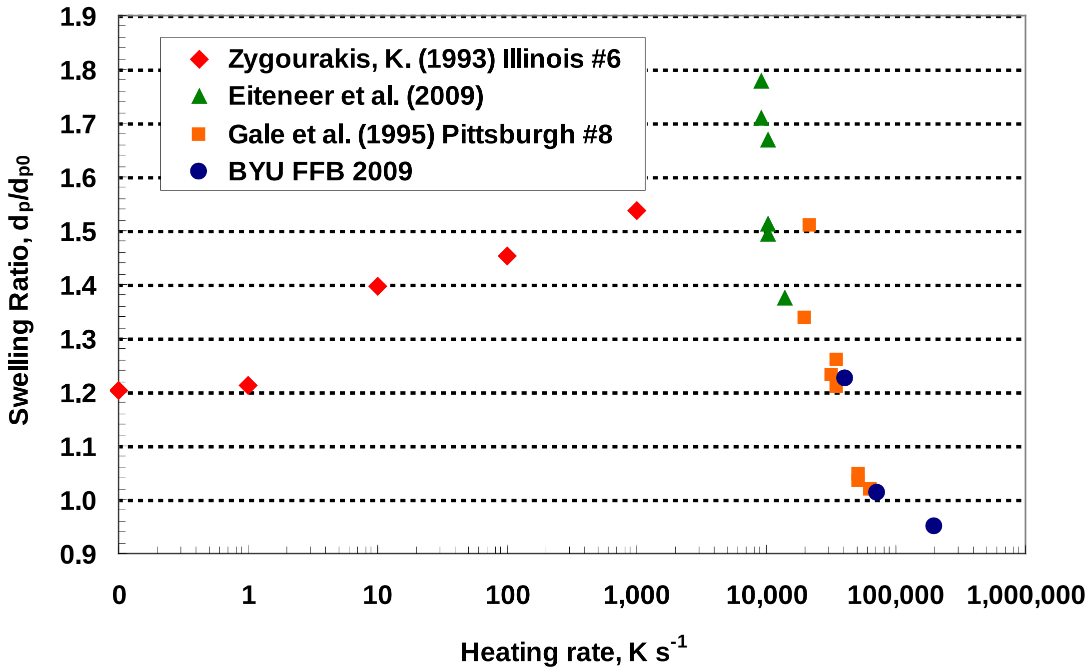


Bituminous Coal Data

(atmospheric pressure so far)

Atmospheric Swelling during Pyrolysis of a Bituminous Coal

- U.S. bituminous coal
- Atmospheric FFB
  - Varied particle size to change heating rate
- Swelling trends consistent with previous work
  - Sharp decrease between 10^4 -10^5 K/s
  - Apparent asymptote of ~0.9 above 10^5 K/s
  - Eiteneer data indicate maximum swelling occurs slightly below 10^4 K/s



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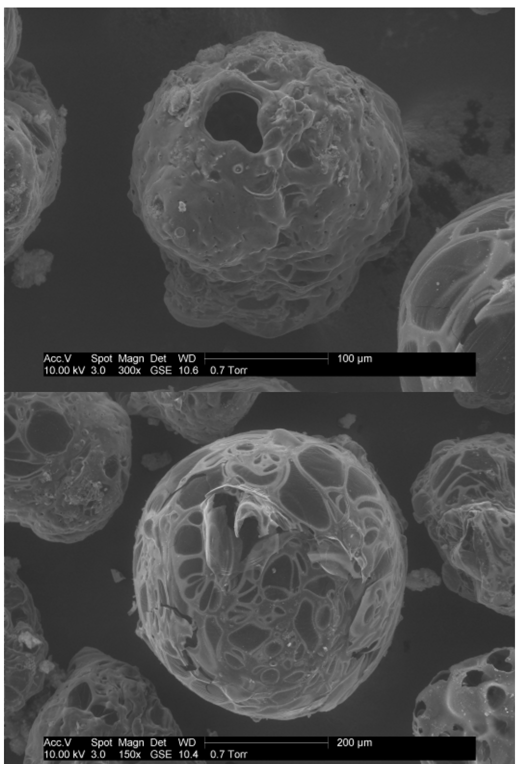
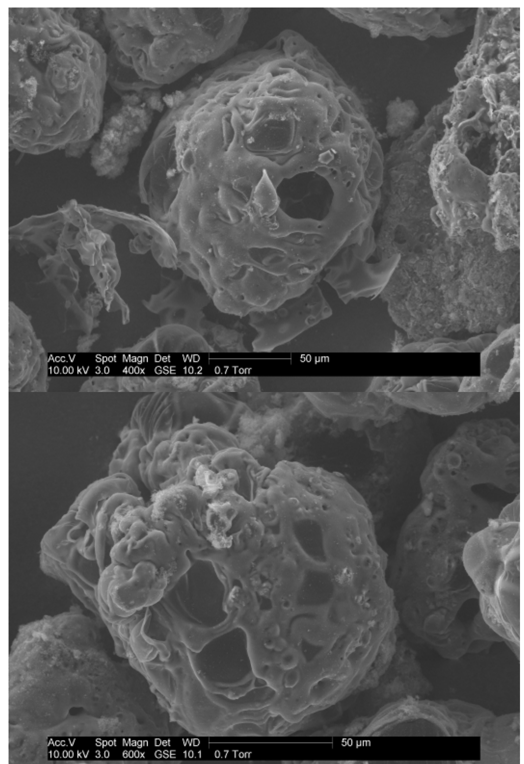
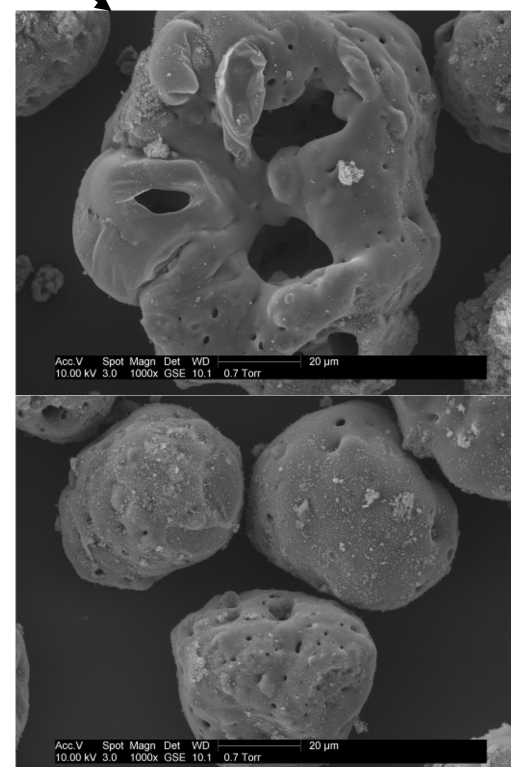
U.S. Bituminous Coal A Swelling

(0.85 atm)

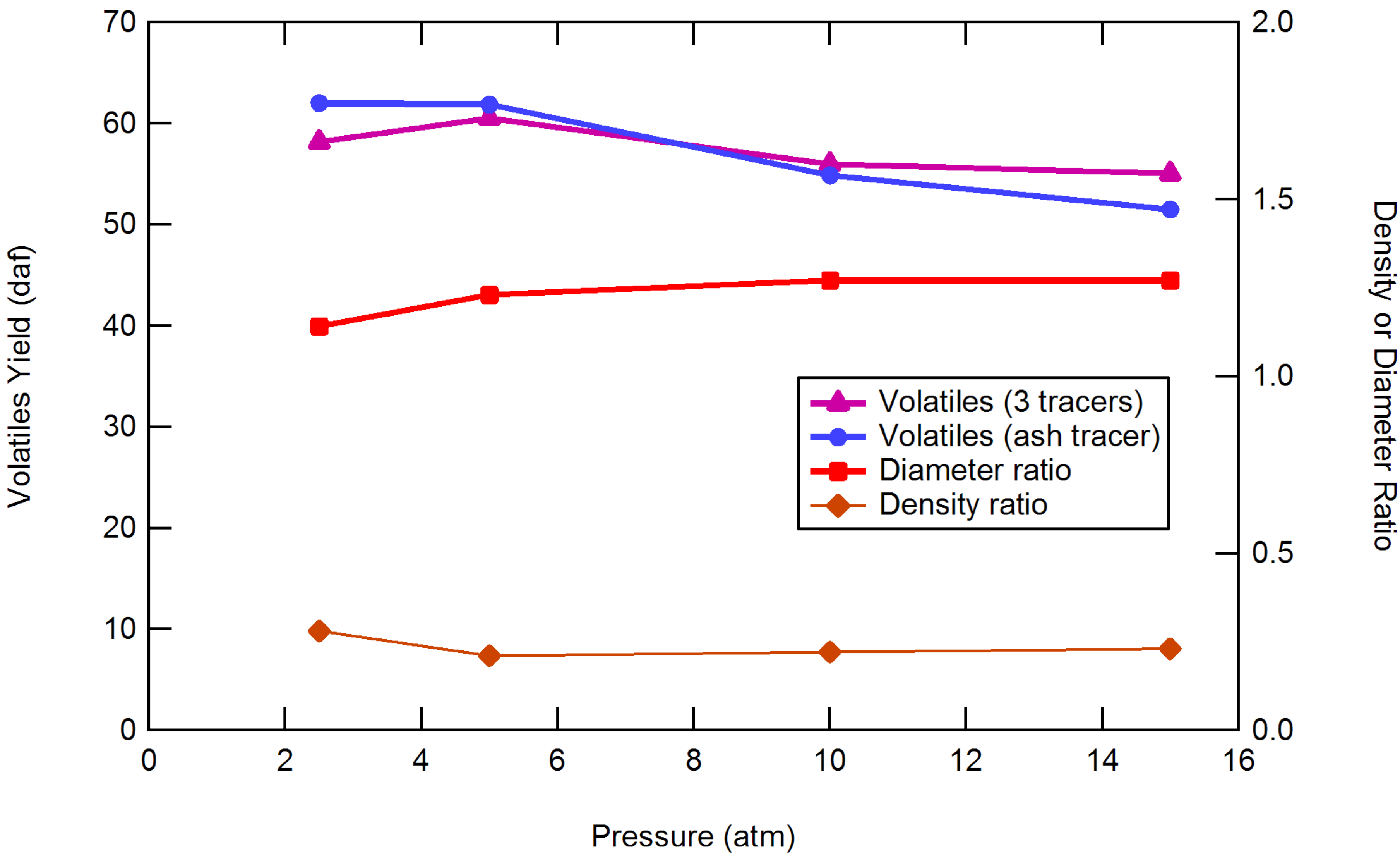
Particle Size (μm)	**149-177**	**88-105**	**53-66**
Heating Rate (K/s)	$4.1 \cdot 10^4$	$7.2 \cdot 10^4$	$2.0 \cdot 10^5$
MR (% daf)	60.29	63.25	61.44
ρ/ρ_0	0.24	0.39	0.53
d/d_0	1.22	1.00	0.93



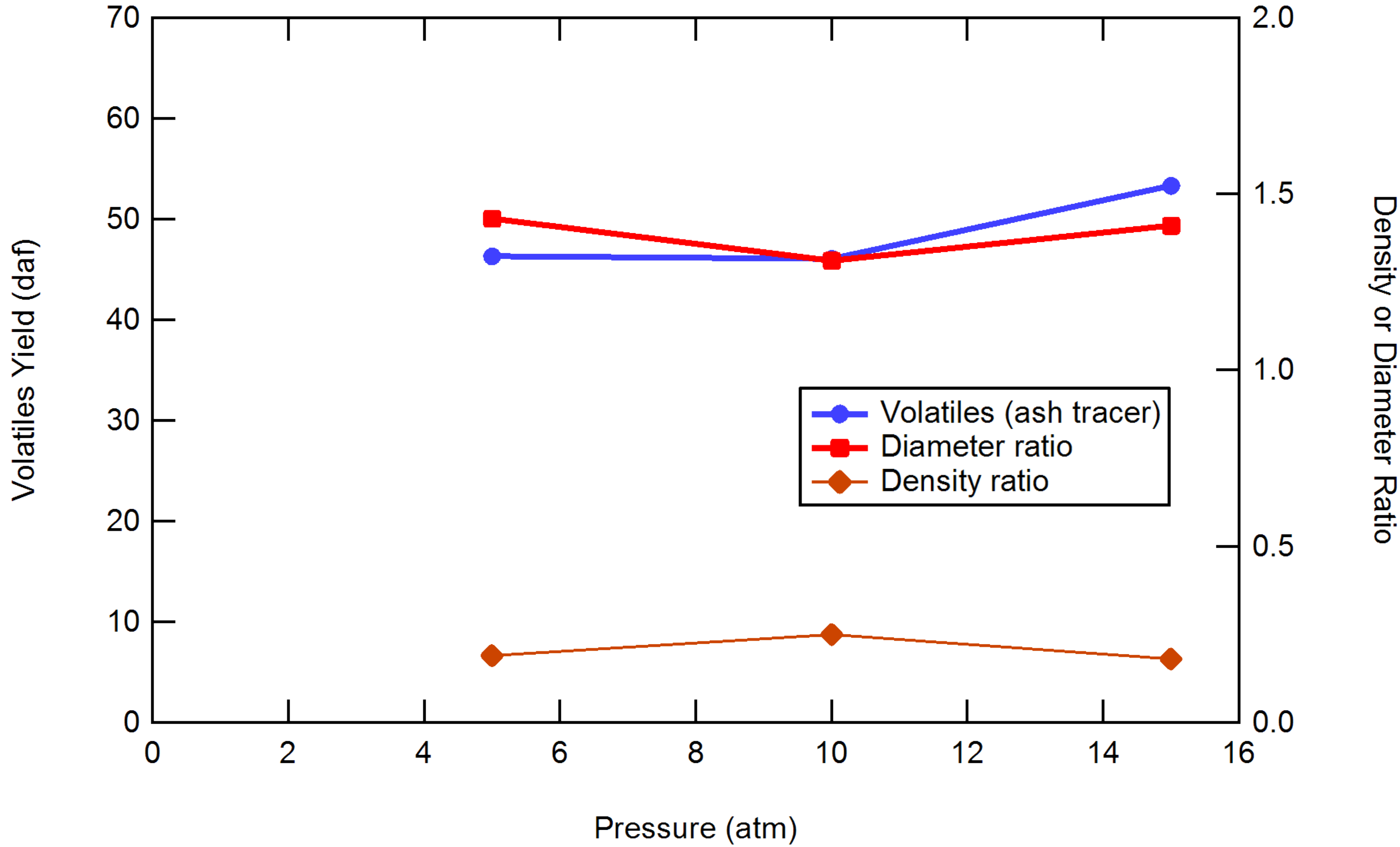




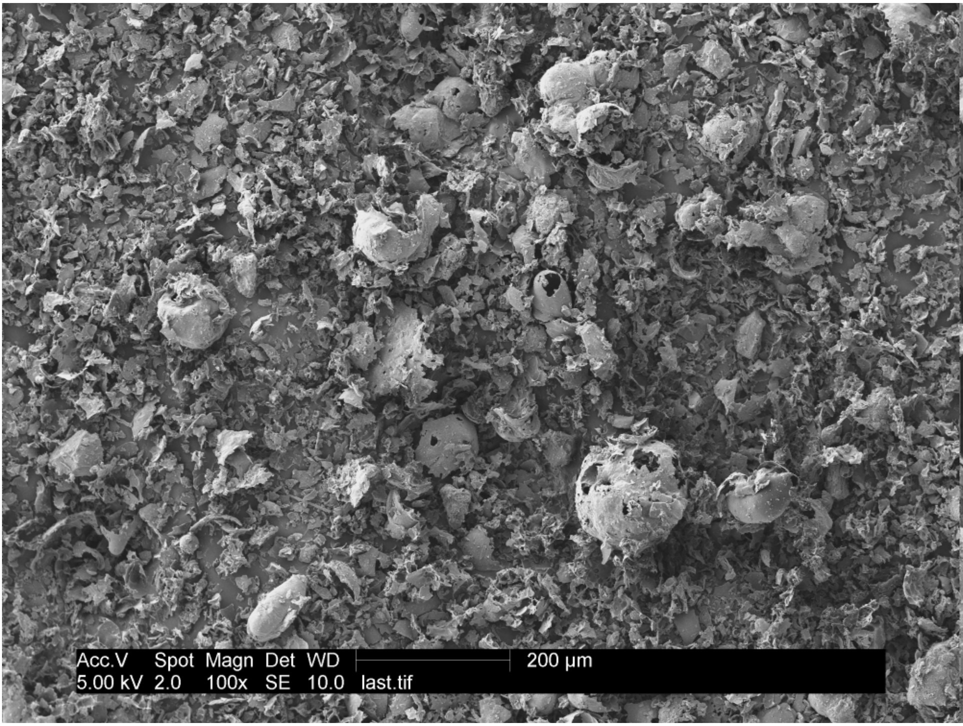
E Bitum A Coal Pyrolysis (40 ms)



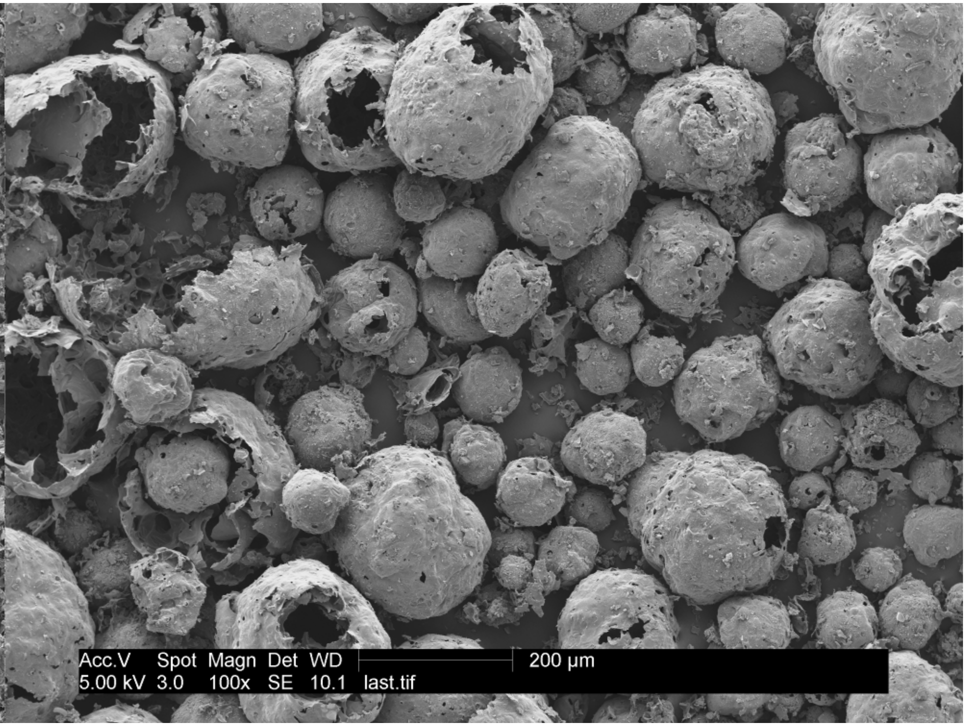
E Bitum B Coal Pyrolysis (40 ms)



Char Fragmentation

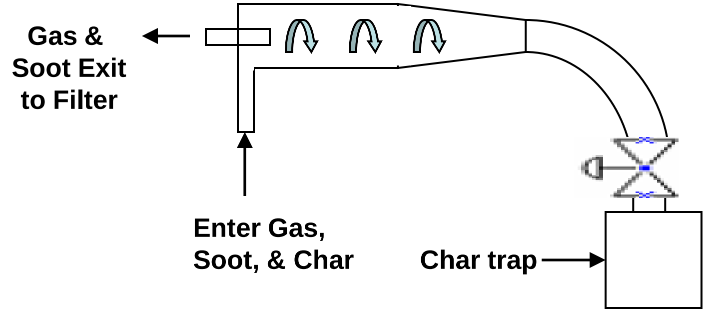


1.1 gram coal fed



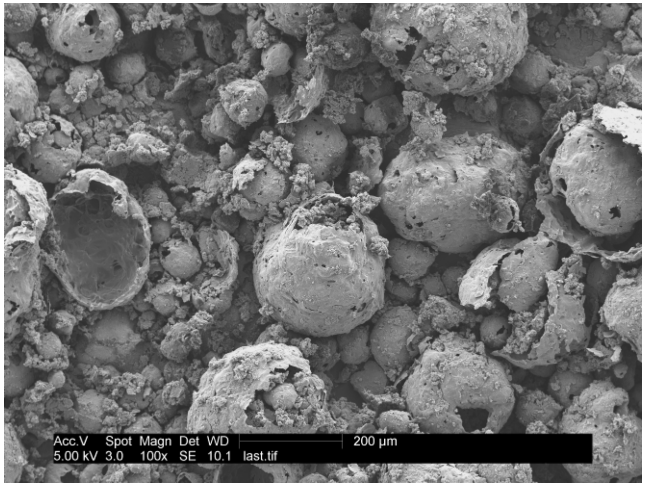
0.4 gram coal fed

- 10 atm Char, U.S. Bituminous Coal B
    - Freshly pyrolyzed, 1700 K
- Cenospheric char particles fragile
- Char accumulates in horizontal cyclone
    - – Must empty cyclone frequently and carefully to avoid fragmentation

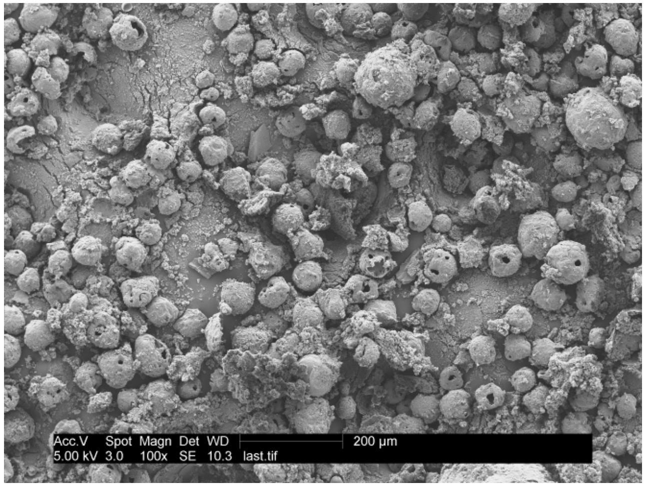


Large and Medium Particle Sizes

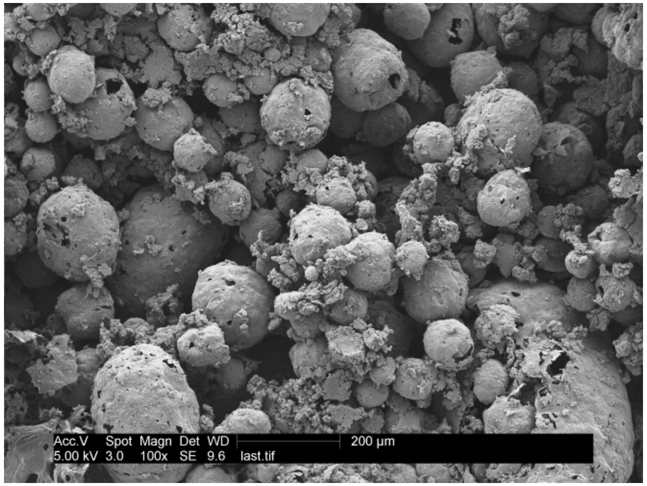
U.S. Bituminous Coal B, 5 atm, 1700 K, 750 ms



Large cenospheric shells present



Large shells aerodynamically separated

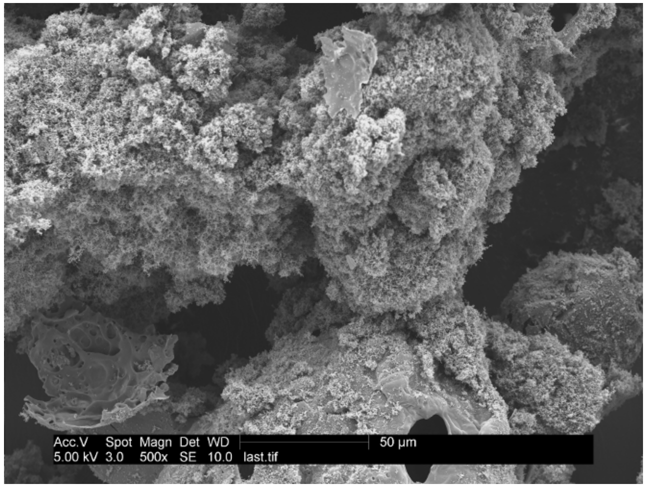


U.S. Bituminous Coal B, 15 atm, 1700 K, 124 ms

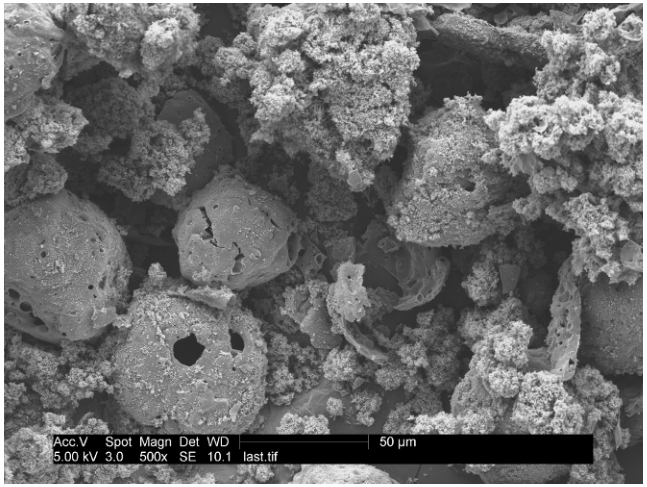
Large cenospheric char particles carried onto soot filter

Soot with Char

- High yield of large soot agglomerates
  - Not separating from char
  - Hinders determination of mass release, swelling, surface area
- Gasification implications
  - Soot radiates lots of heat due to high surface area
  - Kinetics of soot gasification largely unexplored
  - Conversion of volatiles to soot slows total carbon burnout



Bituminous Coal A, 5 atm, 1900 K, 750 ms



Bituminous Coal B, 5 atm, 1700 K, 750 ms

Next Steps

- Does swelling decrease with heating rate at elevated pressures?
  - Bituminous coals
- Extend swelling correlations to account for this decrease in swelling at elevated pressures and heating rates
- Fit gasification data to kinetic parameters in a gasification model
  - Follow approach similar to CBK/G*
    - Also try n^{th} order kinetics for comparison
  - Compare to PTGA data on PFFB chars

*Liu, G.-S. and S. Niksa, *Progress in Energy and Combustion Science,* **30**(6), 679-717 (2004).

Summary and Conclusions

- Modified HPFFB suitable for gasification studies
  - Heating rates of ~10^5 K/s at up to 15 atm
  - Gas composition, residence time more flexible
  - Initial studies in high H_2 flames
  - Currently working with CO flames to eliminate burner pre-heating
  - One-inch diameter burner at high pressure

- Preliminary steam gasification experiments
  - Subbituminous coal in Zone II conditions
  - High surface area and porosity

- Atmospheric swelling experiments
  - Confirms previous trends
  - Reinforce suggestion of swelling ratio < 1 at heating rates of ~10^6 K/s
  - Proceeding with pressurized experiments
    - Taking care to avoid soot and fragmentation

Acknowledgments

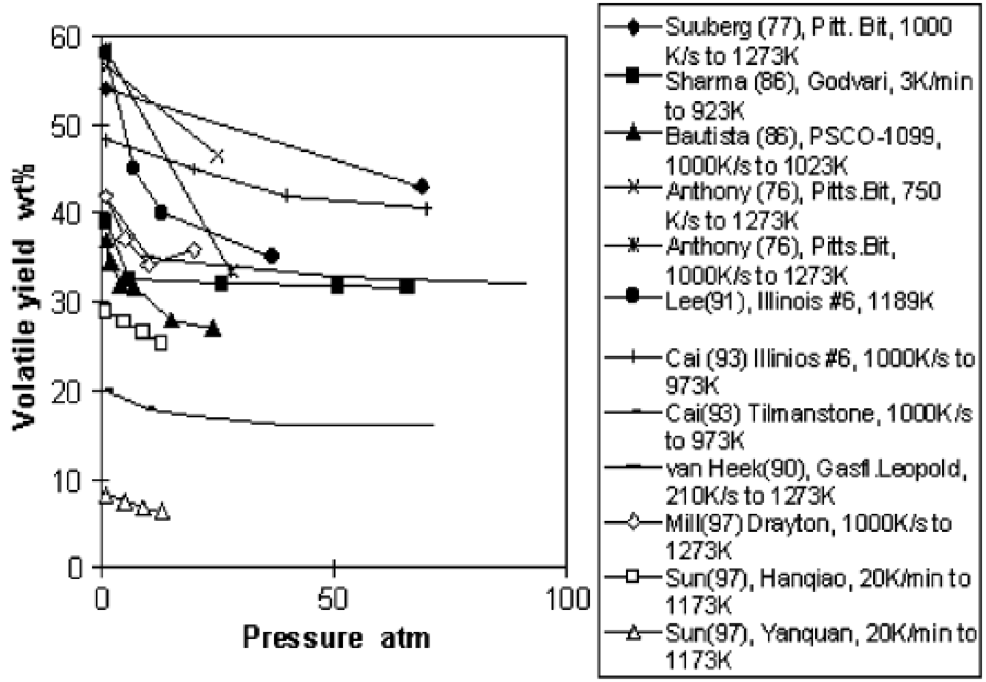
- Funding: DOE through the Utah Clean Coal Program and GE Global Research

- Undergraduate Research Assistants
  - Greg Sorensen
  - Sam Goodrich
  - Jeff Van Wagoner
  - Dallan Prince

The End

Literature Review: Volatiles Yield

- Effect of increasing pressure
  - Inhibits release of tar
  - More light gases produced by cross-linking reactions
  - Net decrease in volatiles
- Effect of increasing heating rate
  - Causes devolatilization to occur at higher temperatures
  - Higher rate of devolatilization
  - Higher yield of volatiles, especially tar
- CPD model (and others) predicts experimental trends



Shan G. PhD thesis, Department of Chemical Engineering, University of Newcastle (NSW), Australia, 2000.

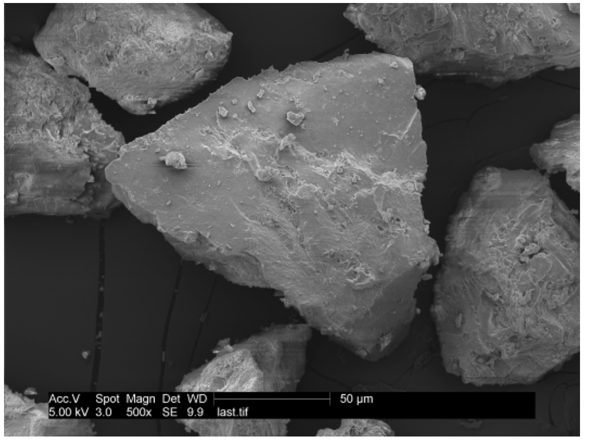
Yu, J., J. A. Lucas and T. F. Wall, Progress in Energy and Combustion Science, 33(2), 135-170 (2007).

Wyodak Ultimate Analysis

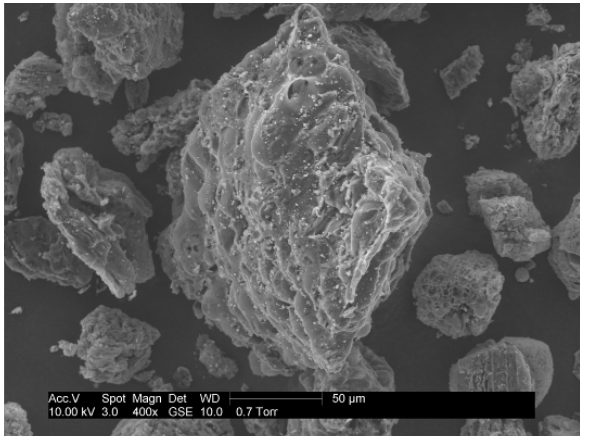
Sample	C	H	N	S	O (diff)
Wyodak Coal	72.25	5.30	0.94	0.50	21.01
90 ms char	91.14	1.11	1.06	0.27	6.42
208 ms char	92.50	1.16	0.86	0.39	5.10
868 ms char	92.69	1.22	0.94	0.53	4.62

- Increase in C
- Decrease in H and O after devolatilization
- N and S relatively constant

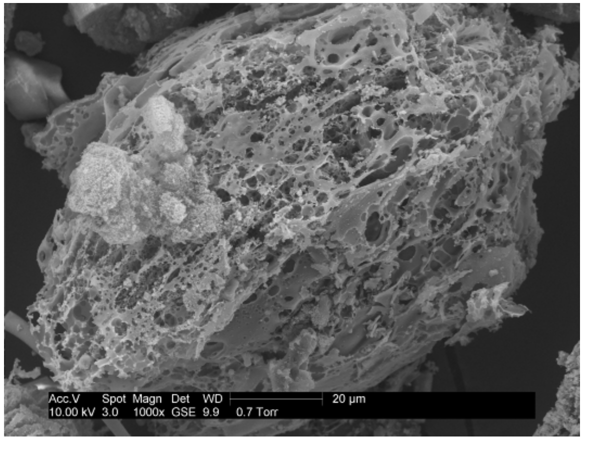
Steam Gasification of Wyodak Coal



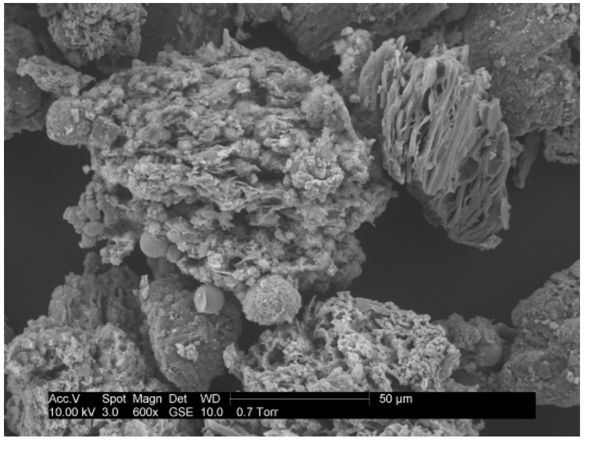
Raw coal (77 mm particles)



90 ms

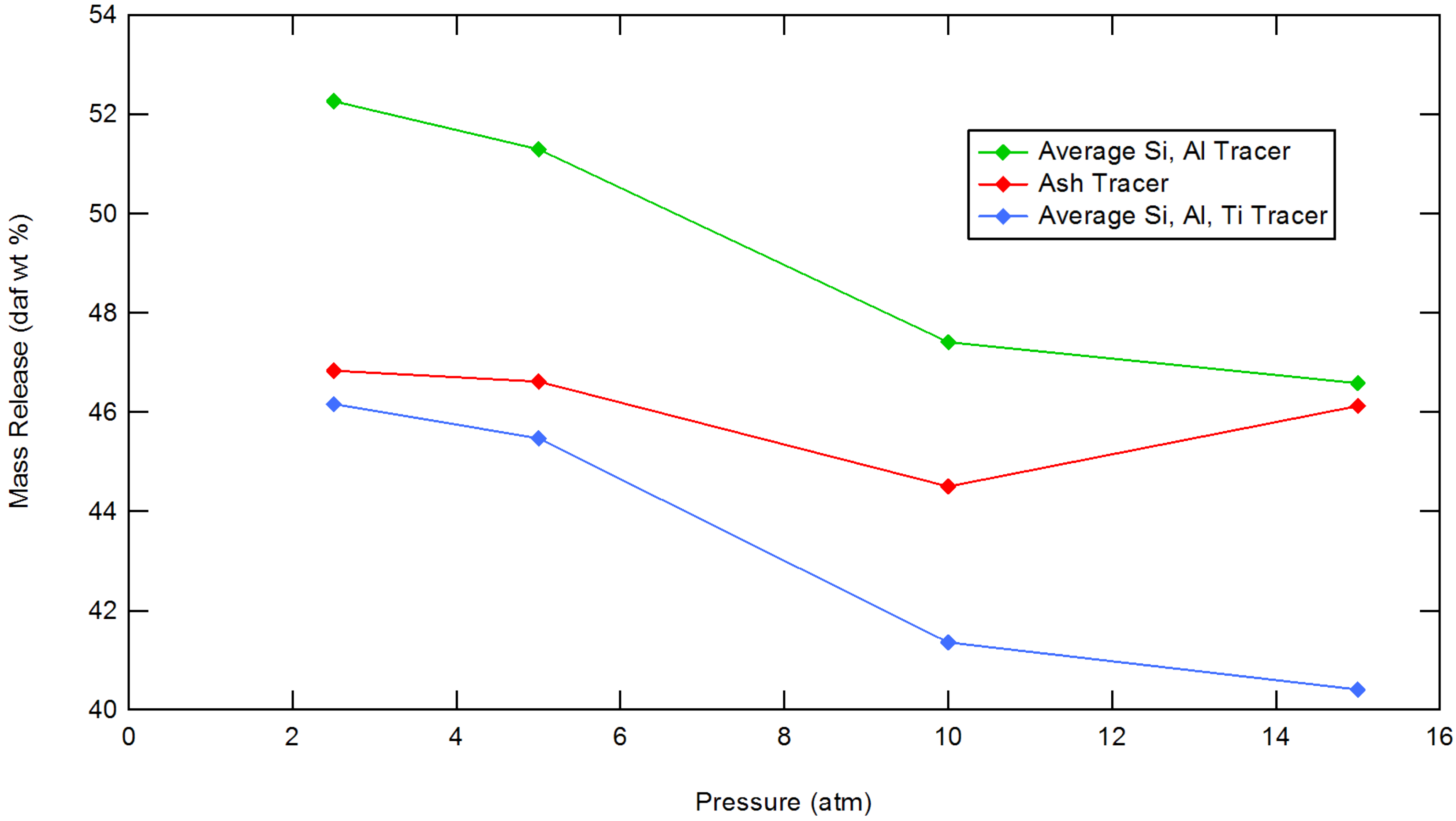


208 ms

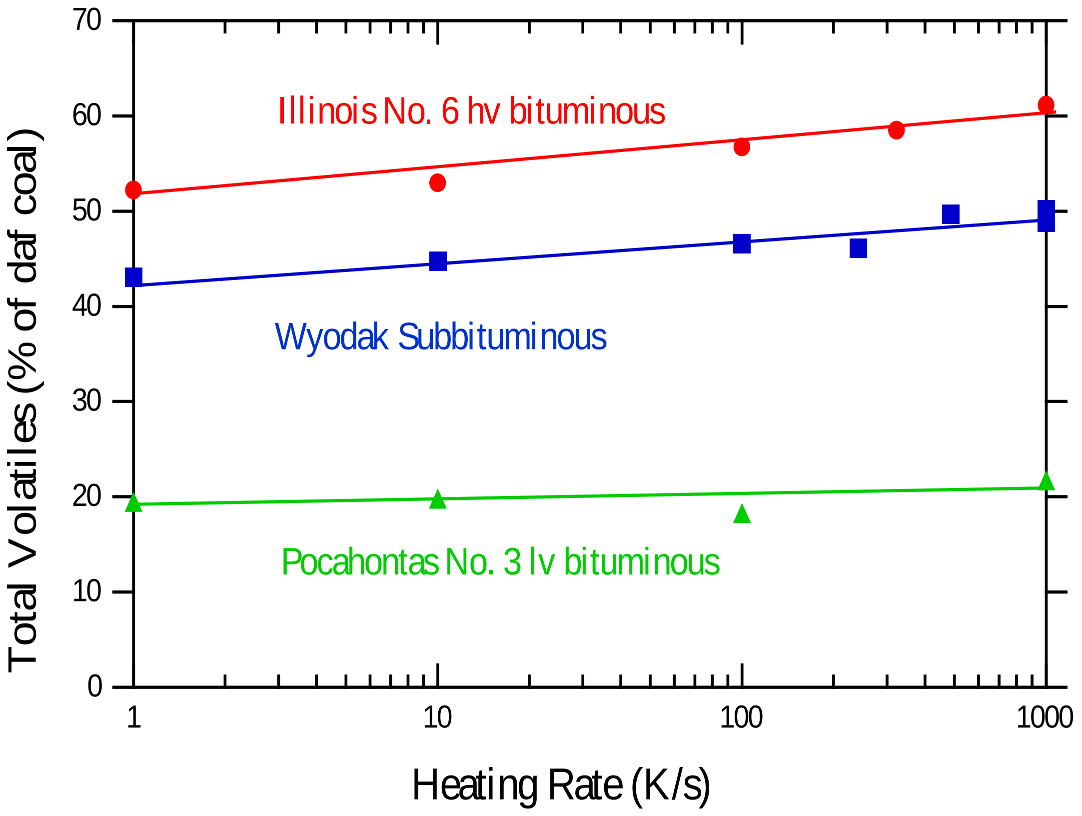


868 ms

Wyodak Pyrolysis at ~1700 K

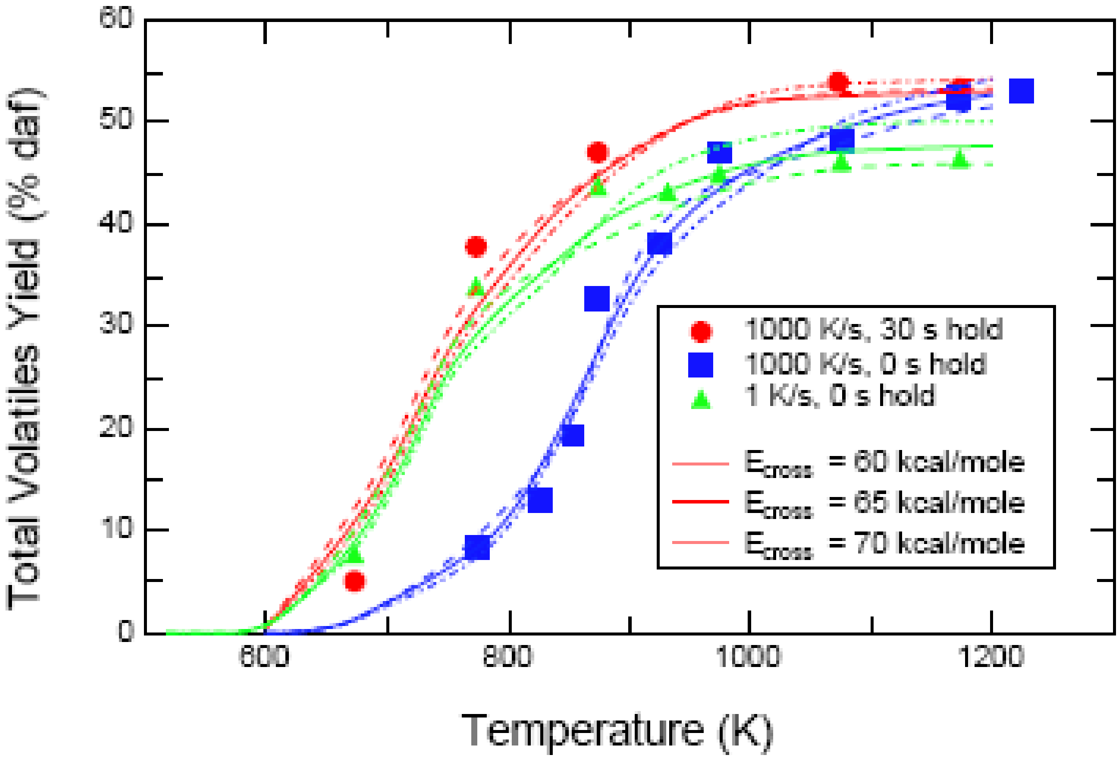


Total Volatile Yield Increases with Increasing Heating Rate



Argonne Premium coals heated to 700 ^oC in helium with 30 s hold (Gibbins and Kandiyoti, Energy & Fuels, 1989)

Reaction Temperature Increases with Increasing Heating Rate



Pittsburgh No. 8 hv bituminous coal in Helium (Gibbins and Kandiyoti, E&F, 1989). Lines are CPD model predictions (Fletcher, et al., E&F 1992)