On the Effect of Pressure on Black Liquor Pyrolysis and Gasification

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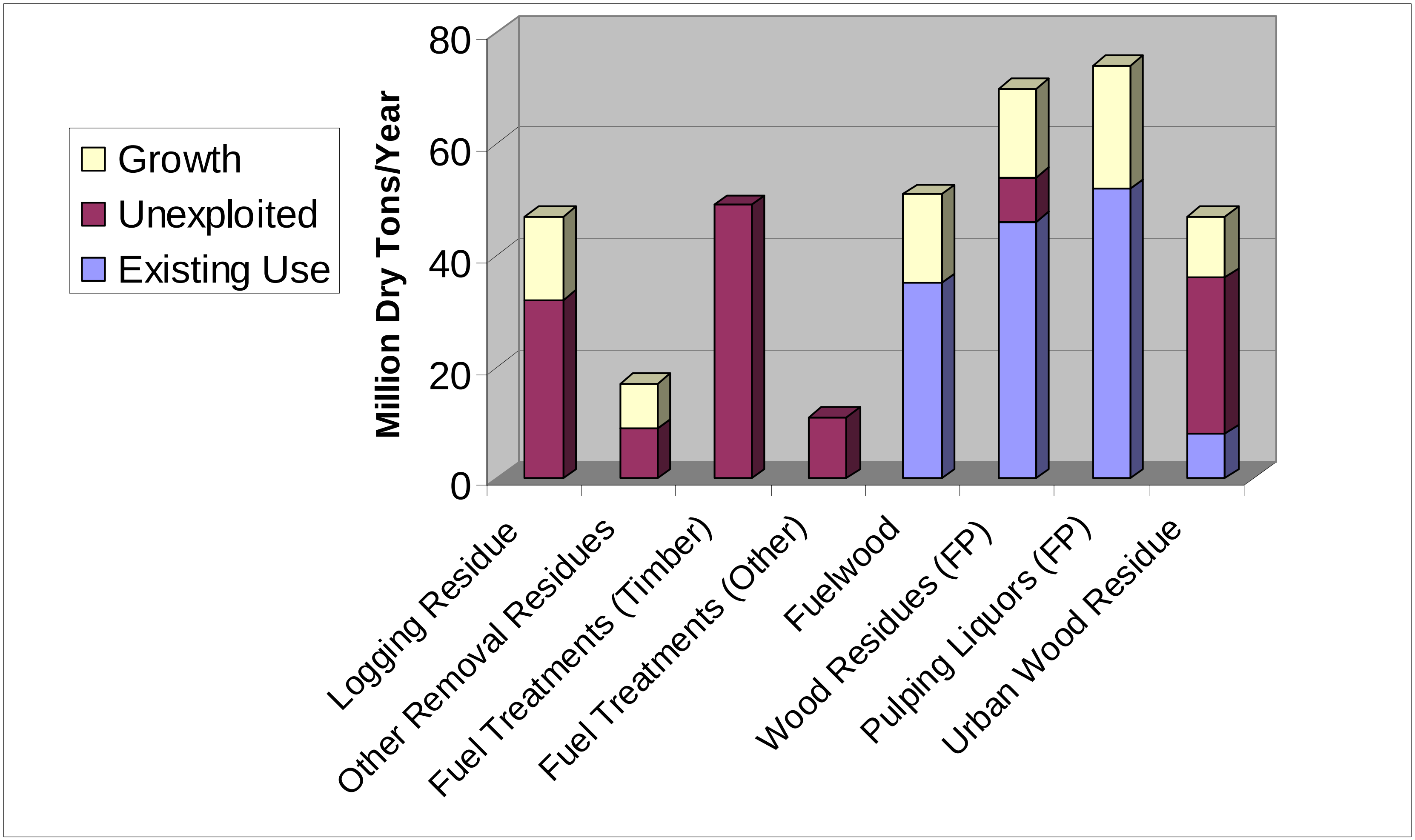
US Forest Biomass Availability



Source: Billion ton biomass report

Black Liquor

- By-product from kraft pulping of wood
- Contains dissolved organics from wood and inorganic cooking chemicals ($NaOH$, Na_2S)
- A liquid with 15-30% water content
- Currently burnt to recover cooking chemicals and produce steam/electricity

Typical Black Liquor Composition	
C	37%
H	4%
Na	20%
S	4%
K	0.5%
Cl	0.5%
O	34%

Black Liquor Gasification

- Being developed to improve efficiency
  - Higher electricity generation
  - Production of fuels or chemicals from syngas
  - More efficient pulping
    - Separation of sulfur and sodium during gasification enables liquor recovery for several high-yield pulping processes

Black Liquor Gasification Technologies

- Low-temperature gasification
  - Below inorganic melting temperature (~600°C)
  - Fluidized bed technology
  - Atmospheric
- High-temperature gasification
  - Above inorganic melting temperature (900-1000°C)
  - Entrained-flow reactors
  - Atmospheric and pressurized

Objectives of Current Work

- To evaluate the impact of pressure on
  - black liquor char characteristics
  - the rate of carbon conversion
  - the fate of sulfur in black

  at conditions relevant to high-temperature black liquor pyrolysis and gasification
  - high heating rate
  - temperature ~900-1000C

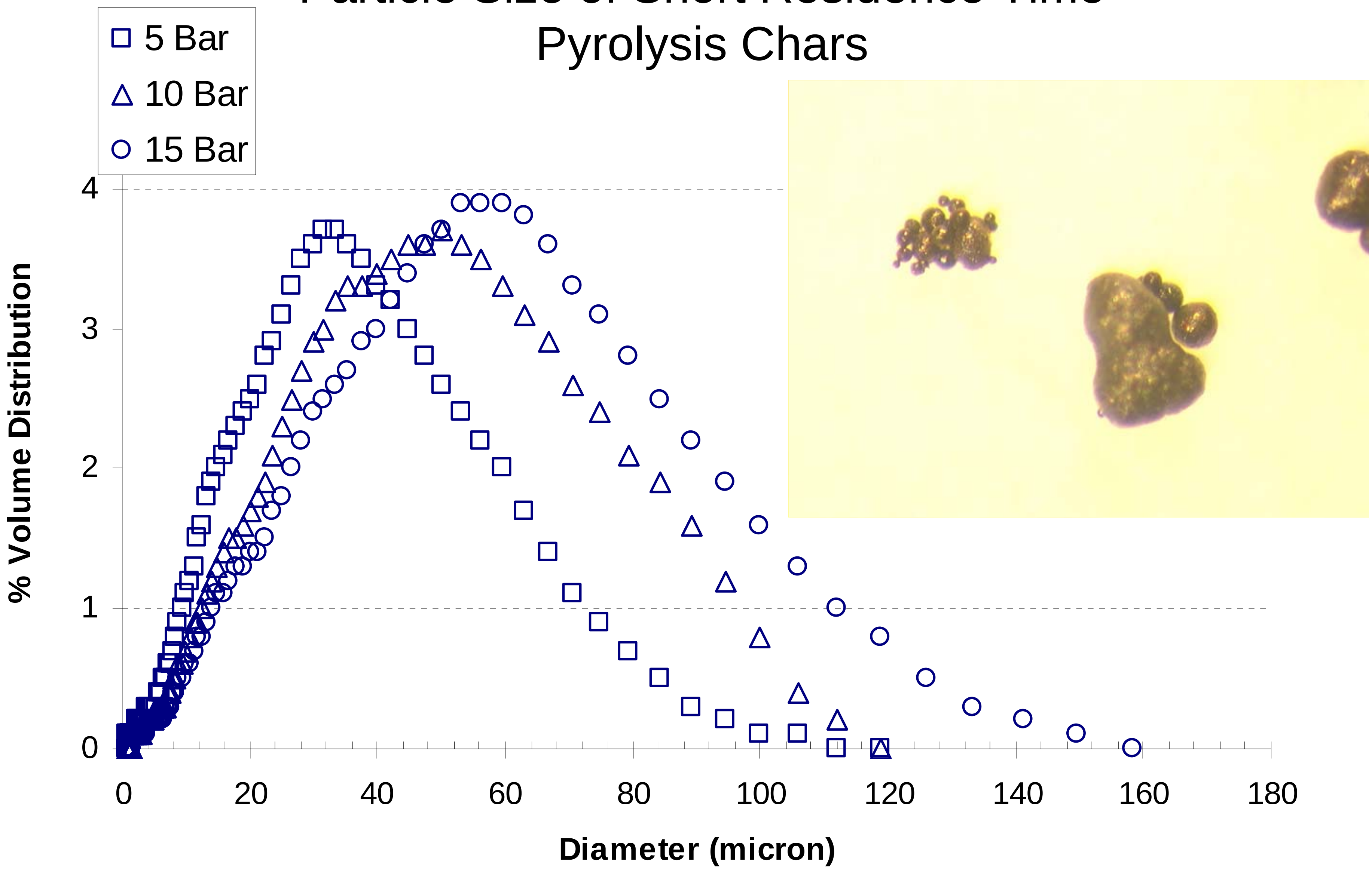
Experimental

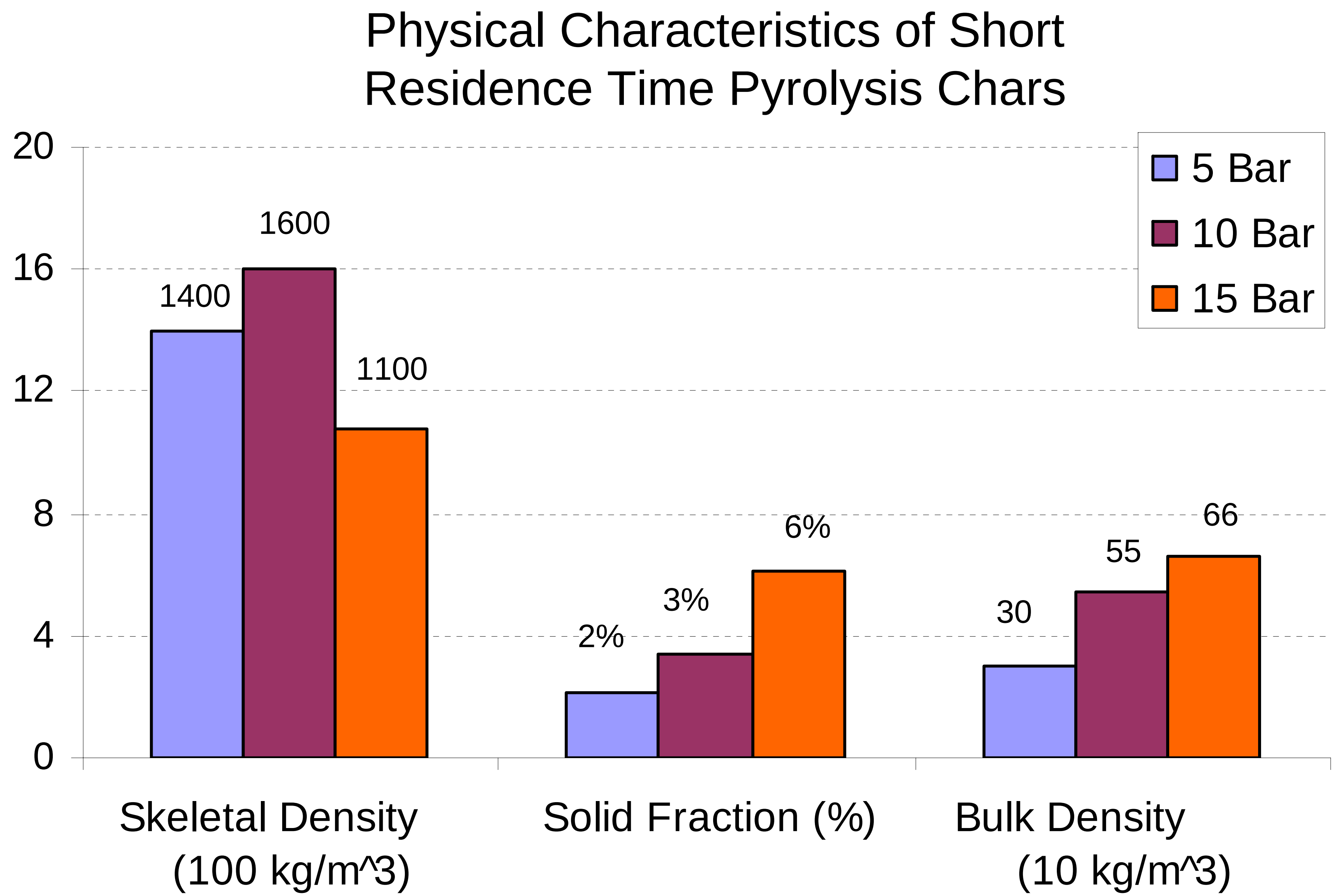
- Dried black liquor particles pyrolyzed or gasified in a pressurized entrained-flow reactor (PEFR)
- Carbon gasification rate and distribution of sulfur between gas and condensed phase measured
- Char properties evaluated by
  - SEM, optical microscopy for morphology
  - Mercury porosimetry for pore size distribution and porosity
  - N_2 absorption for surface area measurements
  - Light scattering for particle size distribution measurements

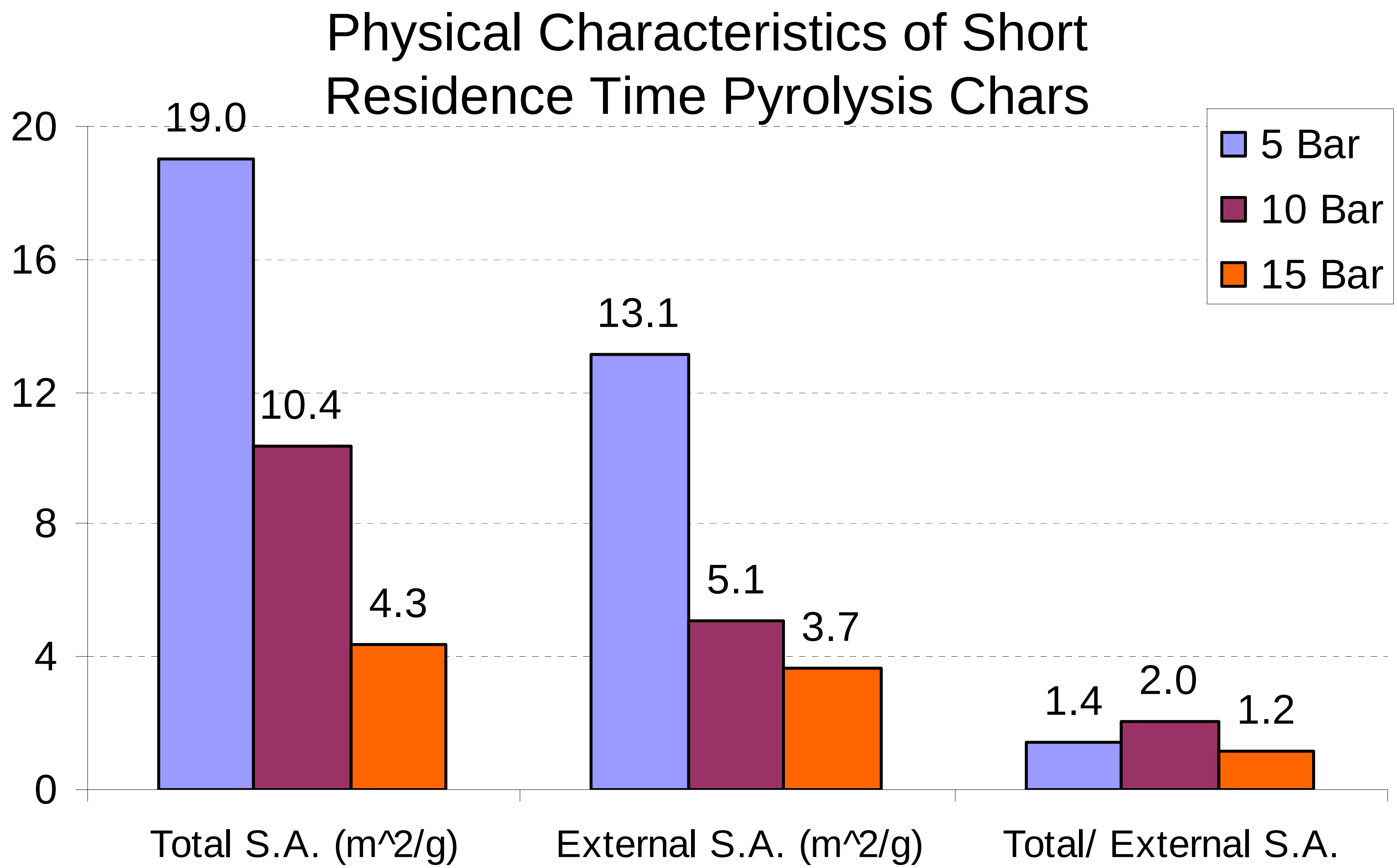
Experimental Conditions

Pyrolysis	10, 15 bar, 900°C 100% N_2 0.9 - 3.5 s
Constant Partial Pressure Gasification	5, 10, 15 bar, 900°C 0.25 bar H_2O, 0.5 bar CO_2 in N_2 0.6 - 3.5 s
Constant Mole Fraction Gasification	10, 15 bar, 900°C 10% CO_2, 2% H_2O, 1.7% CO, 0.3% H_2 in N_2 0.9 - 3.5 s

Particle Size of Short Residence Time Pyrolysis Chars

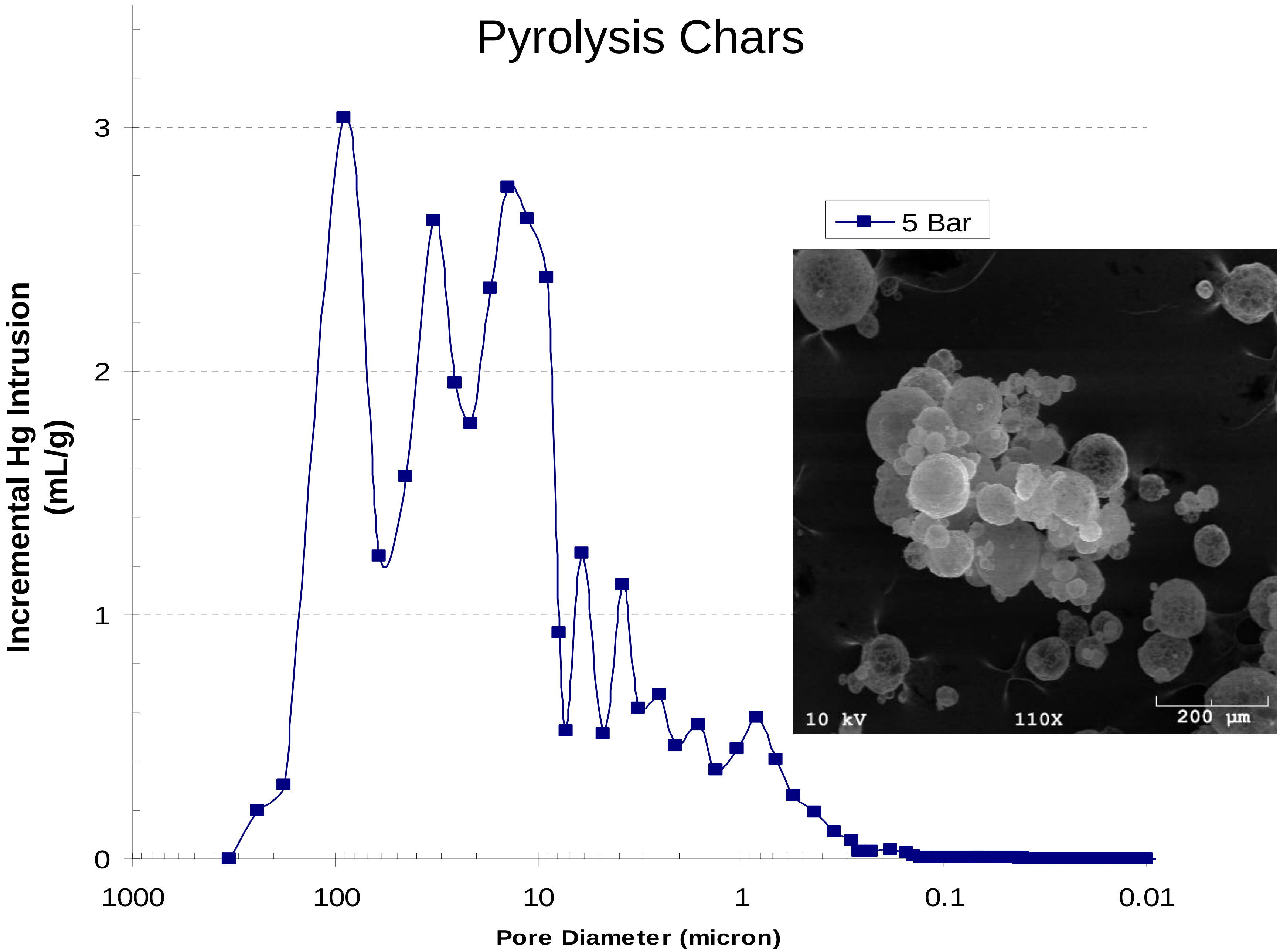



Physical Characteristics of Short Residence Time Pyrolysis Chars
20
16
12
8
4
0
5 Bar
10 Bar
15 Bar
1400
1600
1100
2%
3%
6%
30
55
66
Skeletal Density (100 kg/m^3)
Solid Fraction (%)
Bulk Density (10 kg/m^3)

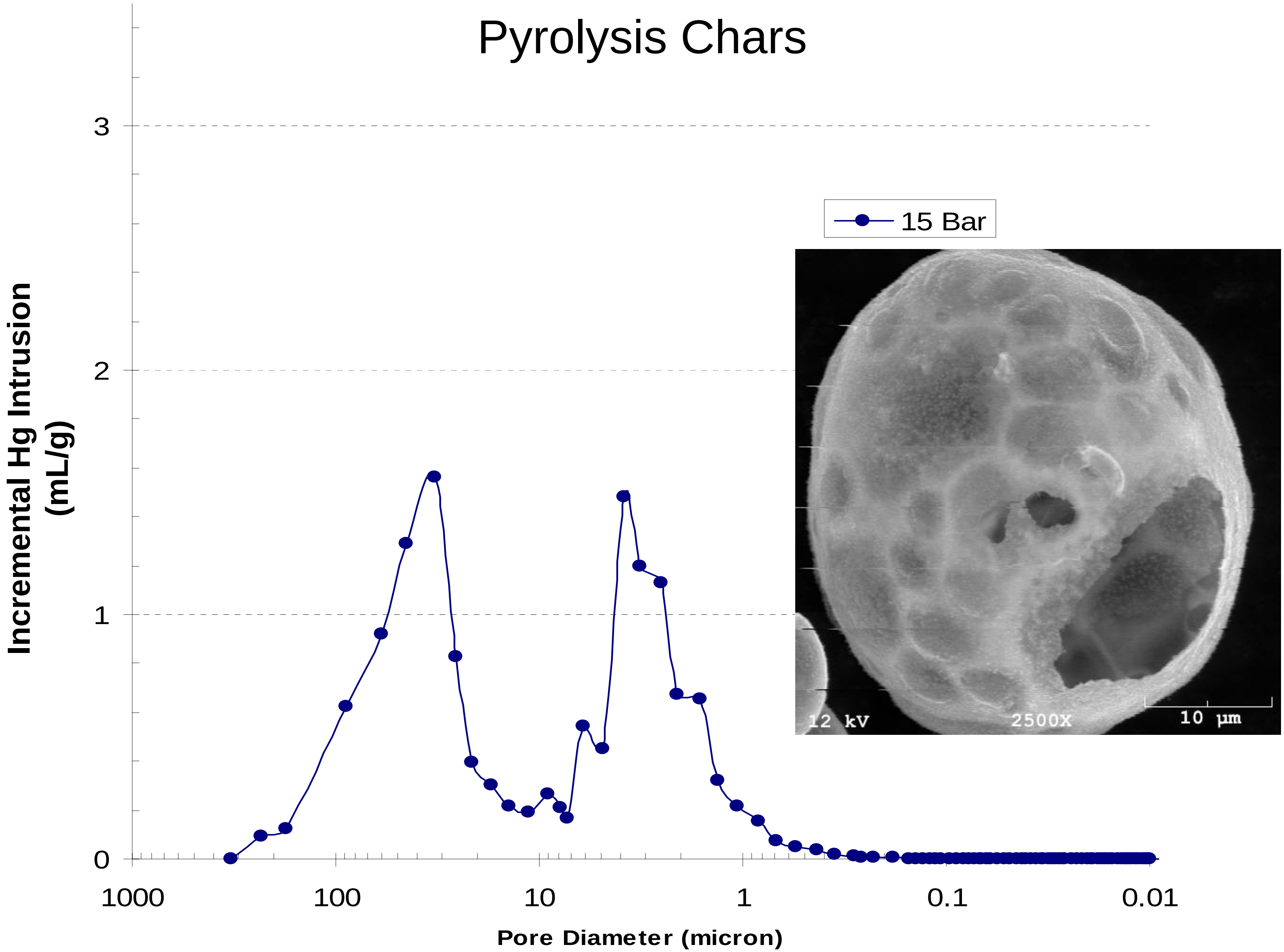


Physical Characteristics of Short Residence Time Pyrolysis Chars
20
16
12
8
4
0
19.0
10.4
4.3
13.1
5.1
3.7
1.4
2.0
1.2
5 Bar
10 Bar
15 Bar
Total S.A. (m^2/g)
External S.A. (m^2/g)
Total/ External S.A.

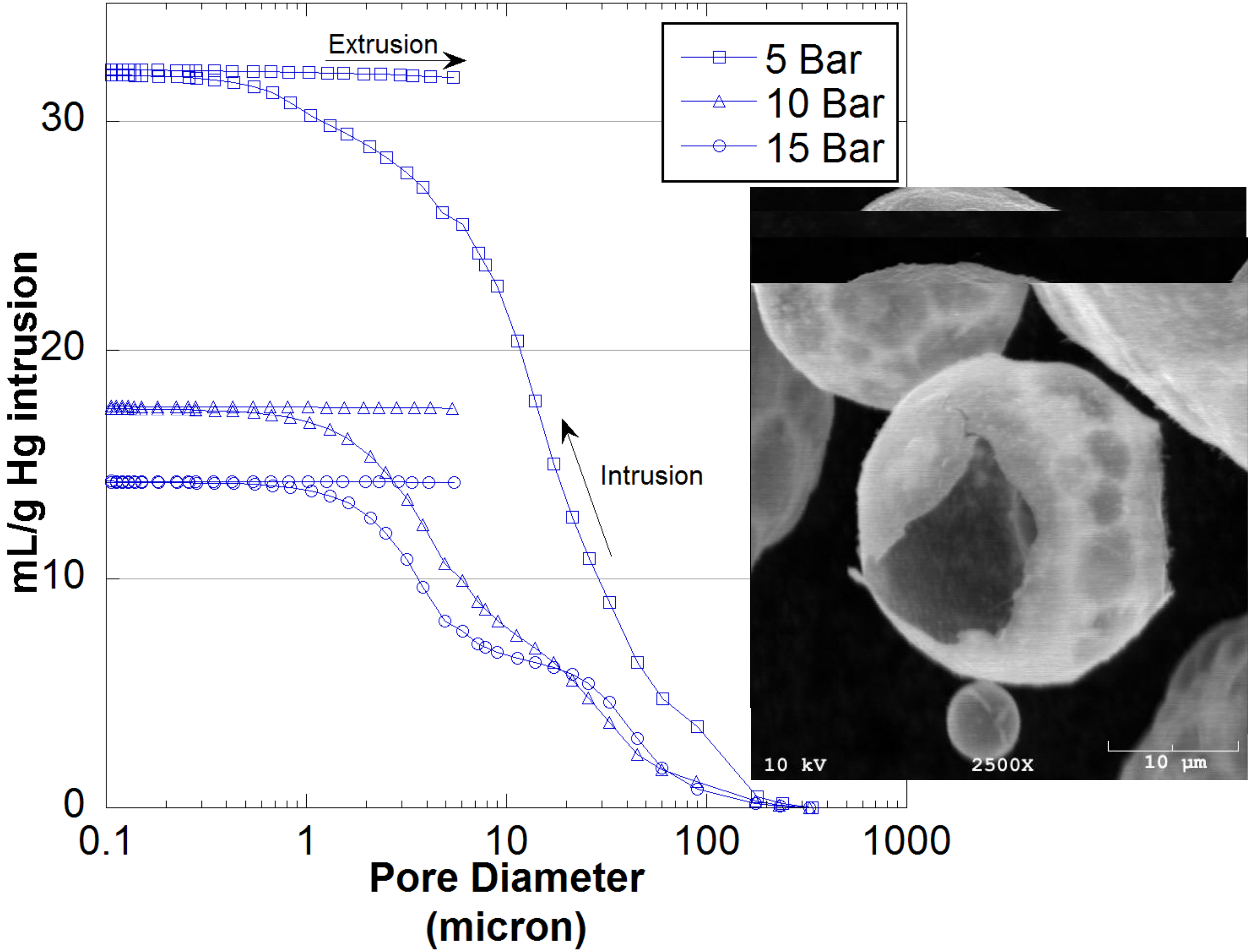
Pore Sizes of Short Residence Time Pyrolysis Chars

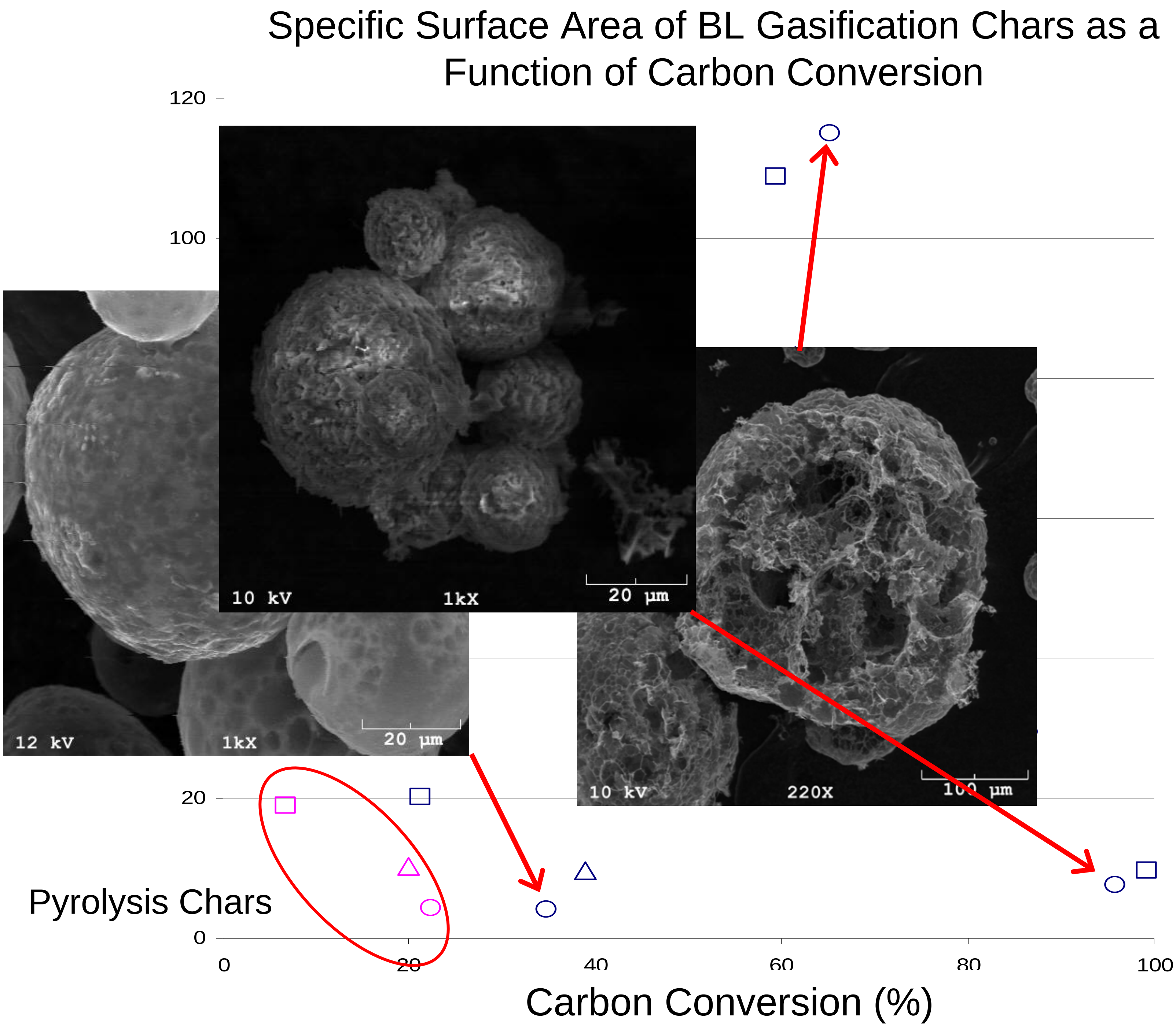


Pore Sizes of Short Residence Time Pyrolysis Chars



Cumulative Hg Data for Short Residence Time Pyrolysis Chars





Specific Surface Area of BL Gasification Chars as a Function of Carbon Conversion
120
100
20
0
0
20
40
60
80
100
Carbon Conversion (%)
Pyrolysis Chars
12 kV
1kX
20 µm
10 kV
1kX
20 µm
10 kV
220X

Conclusions

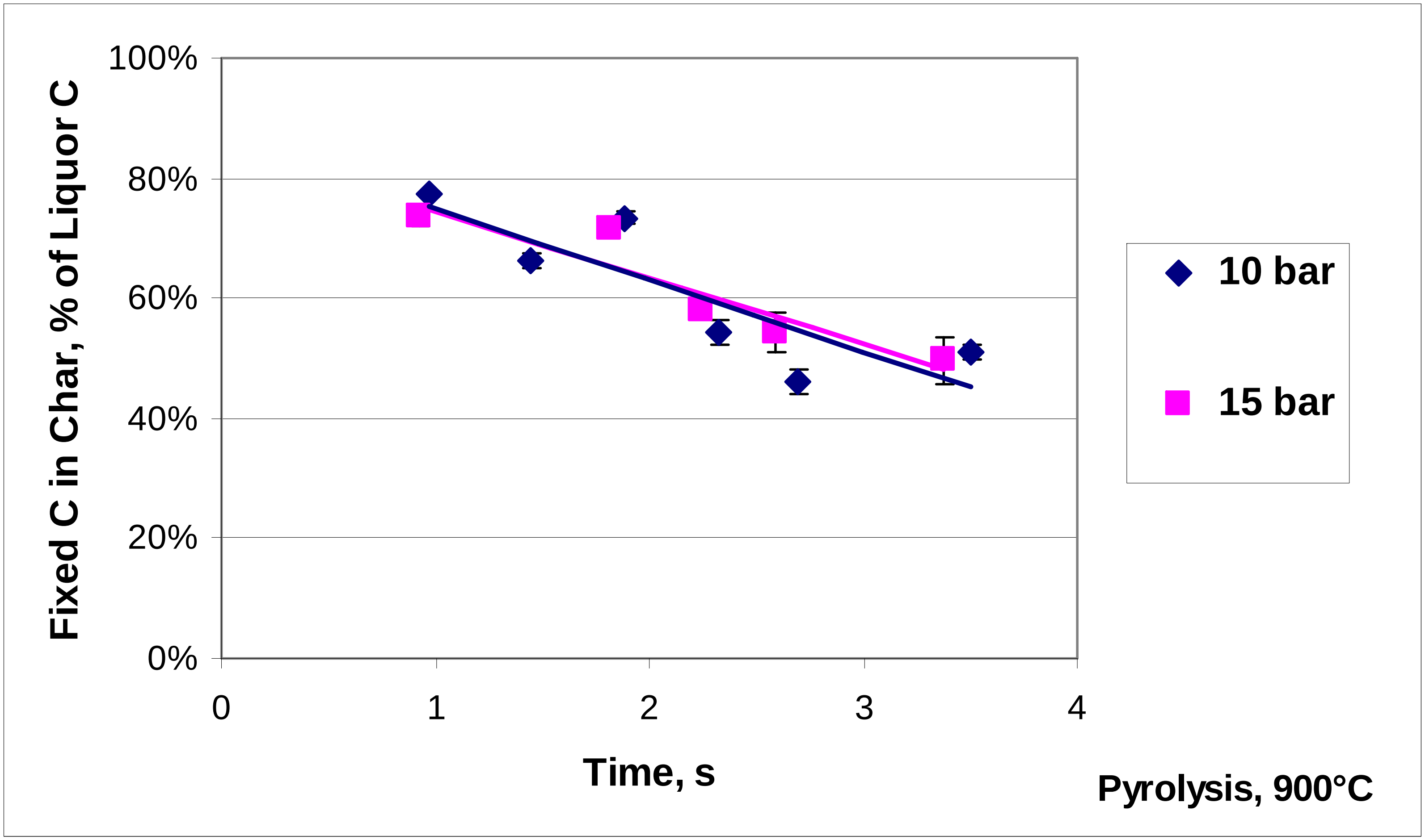
- Cenospheric chars (hollow spheres)
- Char from pyrolysis
  - Increasing pressure decreases porosity
  - Increasing pressure increases agglomeration of particles
- Char from gasification
  - Surface area as function of carbon conversion goes through maximum
  - Surface area not dependent on pressure at carbon conversions >40%
  - Gasification rate not proportional to surface area

Black Liquor Carbon Gasification: Langmuir-Hinshelwood Kinetics:

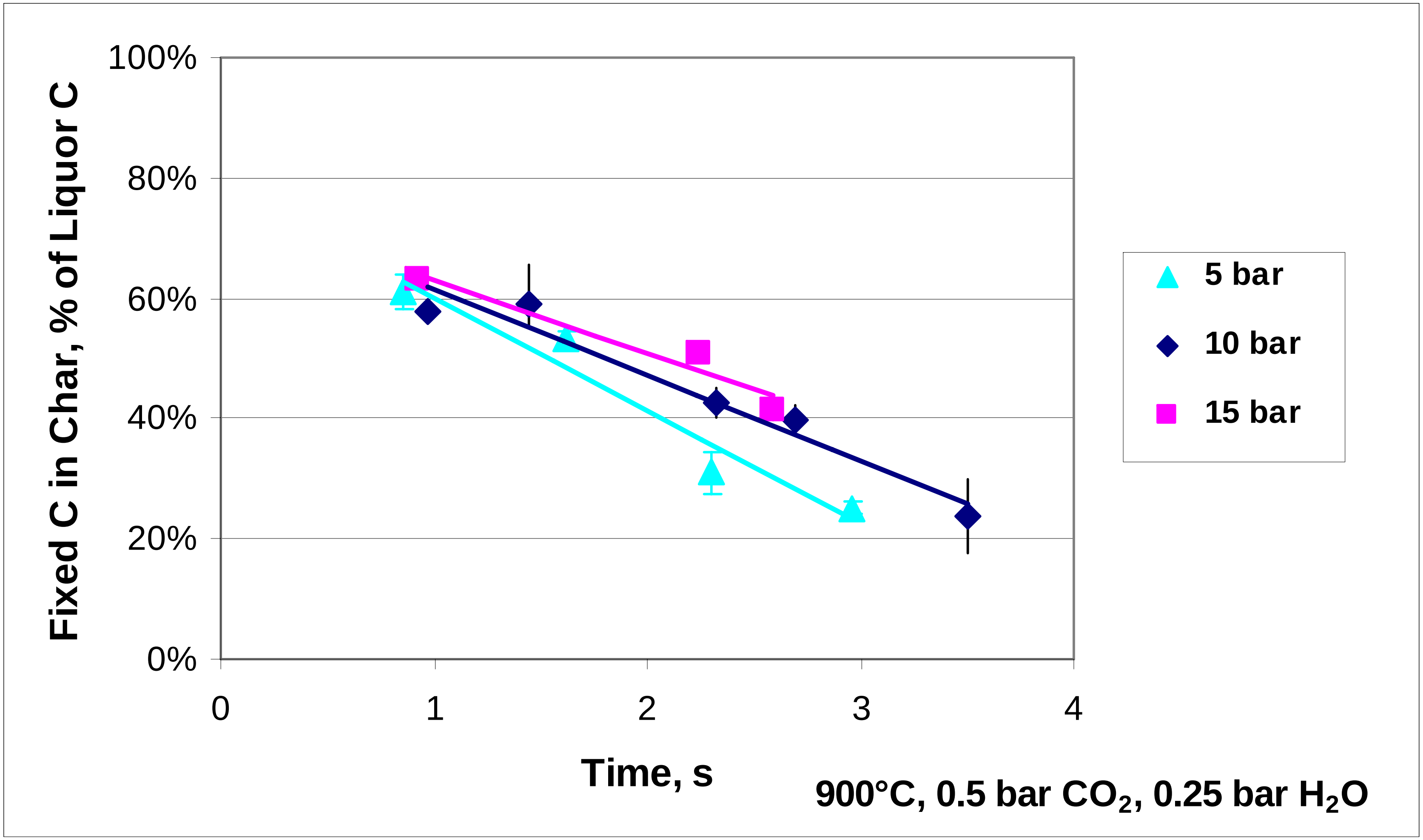
$$-r = \frac{kP_{CO_2}}{1 + aP_{CO} + bP_{CO_2}}$$

$$-r = \frac{k'}{1 + \frac{P_{H_2}}{a' P_{H_2O}} + b' P_{CO}}$$

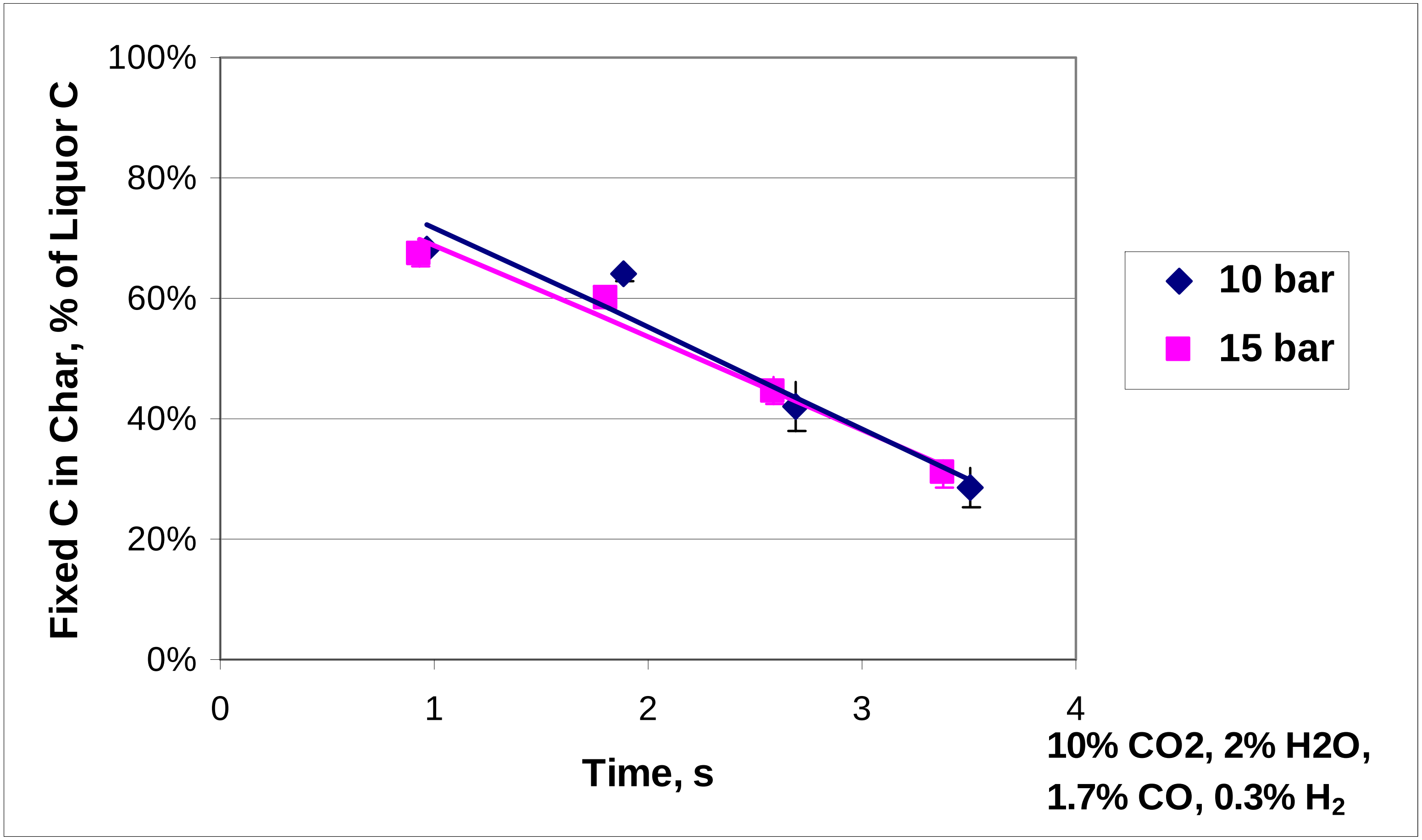
Release of Carbon during Pyrolysis at 10 and 15 bar



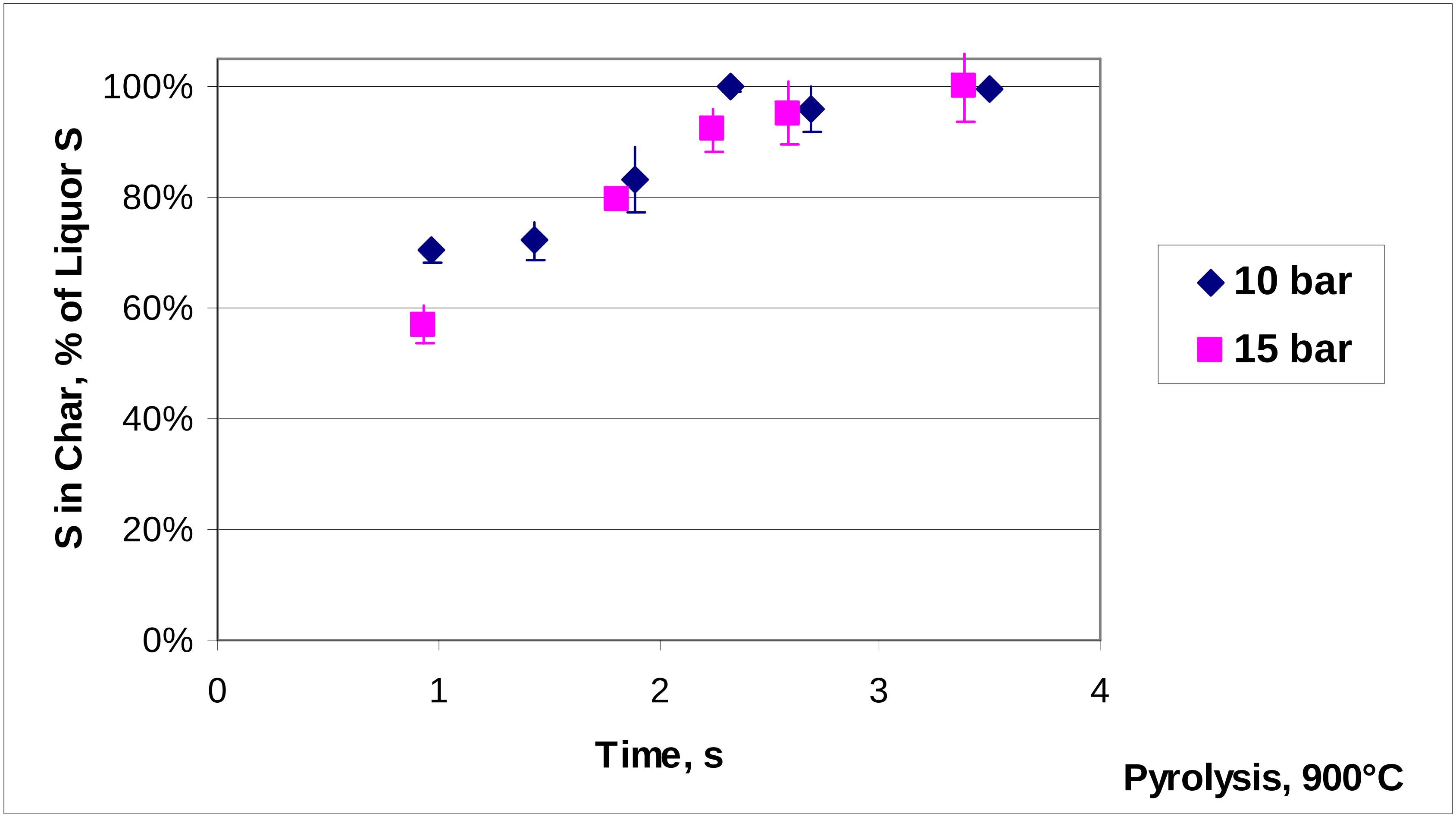
Constant Partial Pressure Gasification: Impact of Pressure



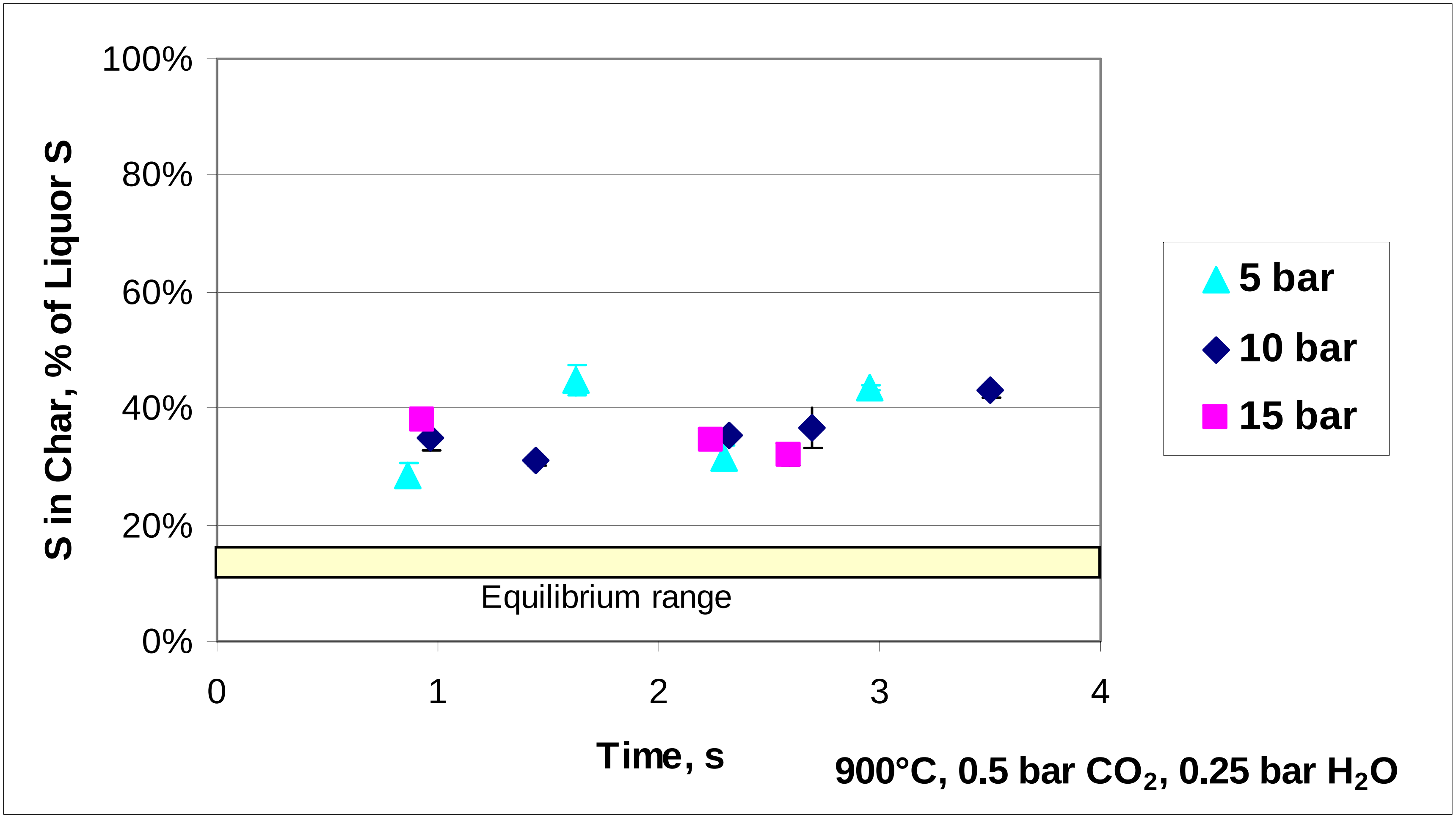
Constant Mole Fraction Gasification: Impact of Pressure



Fate of Sulfur during Pyrolysis



Fate of Sulfur during Gasification



Conclusions (I)

- Pressure did not impact carbon release carbon during pyrolysis
- During pyrolysis, sulfur was initially released, then recaptured in the char
  - Organic sulfur
  - Sulfide
- During gasification, S reaches constant distribution between gas/condensed phase fast

Conclusions (II)

- Gasification rates fairly constant in fixed carbon conversion range of 20-80%
- Constant mole fraction gasification
  - No impact of pressure on carbon gasification rate at gas concentrations studied
  - Experiments at higher CO/H_2 partial pressures ongoing
- Constant partial pressure gasification
  - Increasing pressure slightly decreased rate