Modeling Soot in Coal Systems

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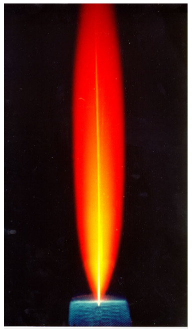
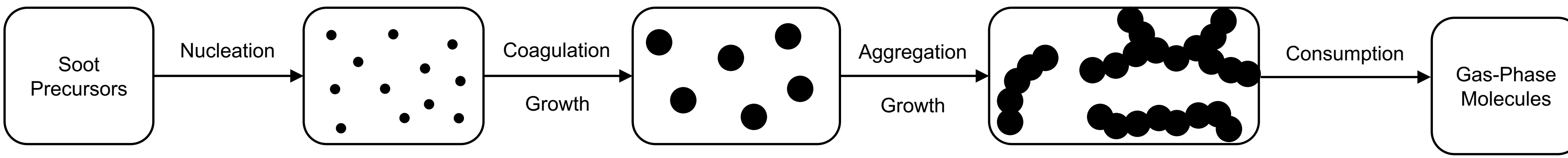
Introduction



Soot

- Particles heavily impact radiative heat transfer
- Changes flame chemistry
- Health and environmental impacts

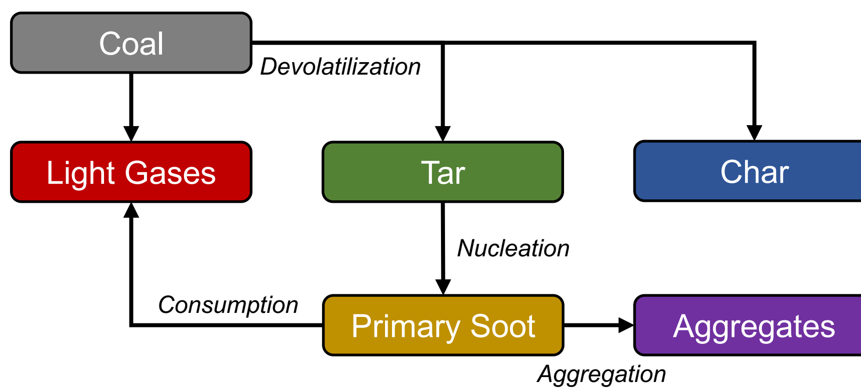
Gaseous Fuels



- Rate largely determined by formation of precursors and time in fuel-rich environment
- Soot precursors are PAHs

Solid Fuels

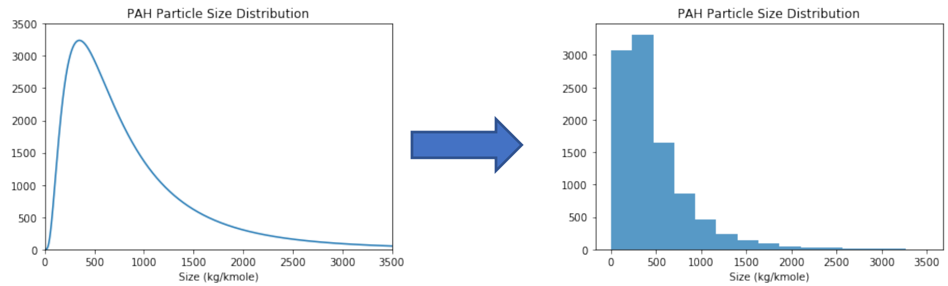
- Coal gives off tar during primary pyrolysis
- Tar is primary soot precursor



Model Overview

PAH Molecules

- Transport PAH PSD using a discrete bin approach



- Bin sizes determined by CPD model (~6 bins)
- Transport includes 4 source terms:
  - PAH creation
  - Surface Reactions
  - Thermal Cracking
  - Soot Nucleation

<u>Bin Species Number Density</u>

$$\frac{\delta \bar{\rho} N_i}{\delta t} + \nabla \cdot (\bar{\rho} \tilde{v} N_i) + \nabla \cdot \left(\widetilde{\bar{\rho} v'' N_i''} \right) = S_{N_i}$$

$$S_{N_i} = r_{create} + r_{growth} - r_{crack} - r_{nucl}$$

Soot Particles

- Transport soot PSD using method of moments

$$M_r = \int_0^{\infty} m_i^r N_i(m) dm$$

- Interpolative closure for source terms

$$M_p = L_p \left(M_0, M_1, \ldots M_r \right)$$

- Transport includes 3 source terms:
  - Soot Nucleation
  - Particle Coagulation
  - Surface Reactions

<u>PSD Moment Density</u>

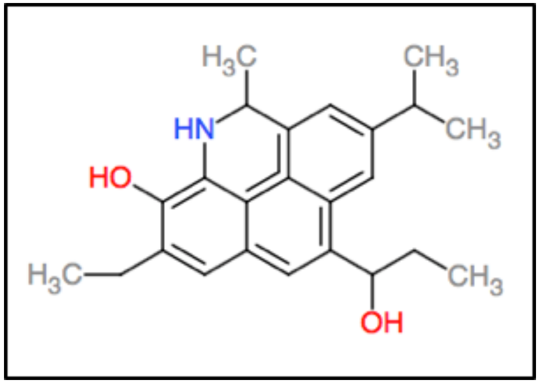
$$\frac{\delta \bar{\rho} M_r}{\delta t} + \nabla \cdot (\bar{\rho} \tilde{v} M_r) + \nabla \cdot \left(\widetilde{\bar{\rho} v'' M_r''} \right) = S_{M_r}$$

$$S_{M_r} = r_{nucl} + r_{growth} + r_{coag} - r_{consume}$$

PAH Model - Creation

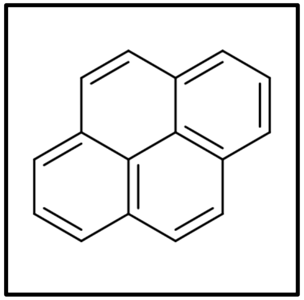
PAH molecules creation from two sources:

Hypothetical Tar Molecule



1. Release of tar molecules by parent fuel
   - Rate determined from results of CPD model (Fletcher, 1992)
   - PSD spans broad range (~150 kg/kmole – 3000 kg/kmole)
   - Lognormal PSD (median ~350 kg/kmole, small variance)
     - Varies over time, shifts to higher MWs.

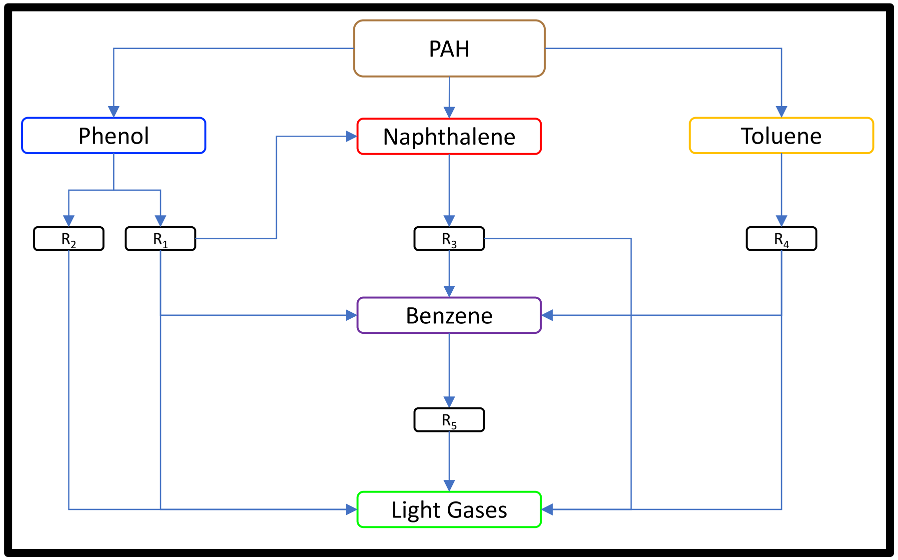
Pyrene Molecule

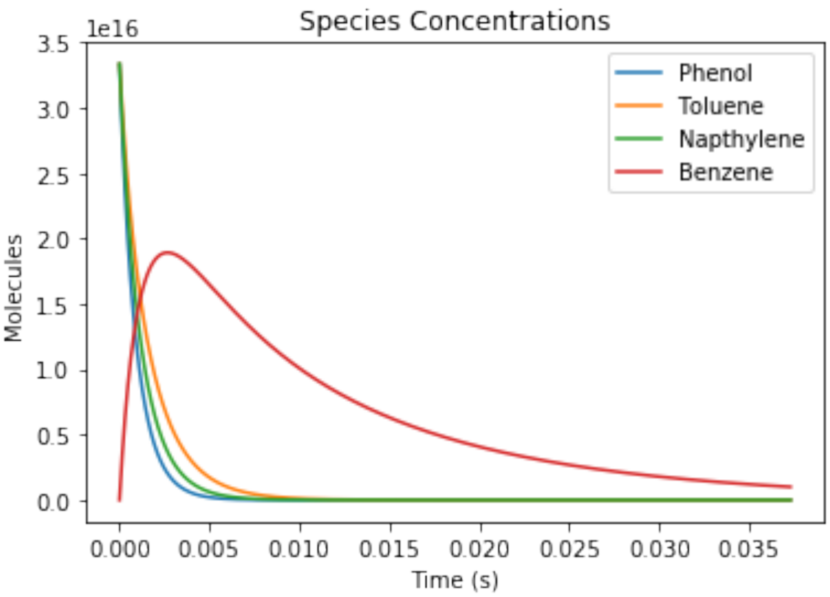


2. Formation of aromatic rings from the gas-phase
   - Rate determined by ABF mechanism (Appel, 2000)
   - Creation of pyrene added to the PAH bins
   - Usually insignificant source of PAH (But not always, Zeng, 2011)

PAH Model – Thermal Cracking

- Thermal cracking scheme originates from work done by Marias, et al (2016)
- Four types of PAH molecules
- Cracking reactions determine amount of mass lost
- Initial fraction estimation done
  - Maximum tar concentration used
  - Equal parts phenol, naphthalene, and toluene
  - Phenol and toluene branches established by CNMR and Elemental analyses of parent coal
  - Cracking scheme applied over time with soot nucleation until 99% PAH consumed
  - Average species fraction computed and used as constants over long simulation





PAH/Soot Model – Soot Formation

Based on work presented in *Soot Formation in Combustion*
(Bockhorn 1991)

Change in PAH species

$$r_i = \sum_{j=j_0}^{\infty} \beta_{i,j} N_i^{PAH} N_j^{PAH}$$

Change in soot moments

$$r_r = \sum_{i=i_0}^{\infty} \sum_{j=i}^{\infty} \beta_{i,j} (m_i + m_j)^r N_i^{PAH} N_j^{PAH}$$

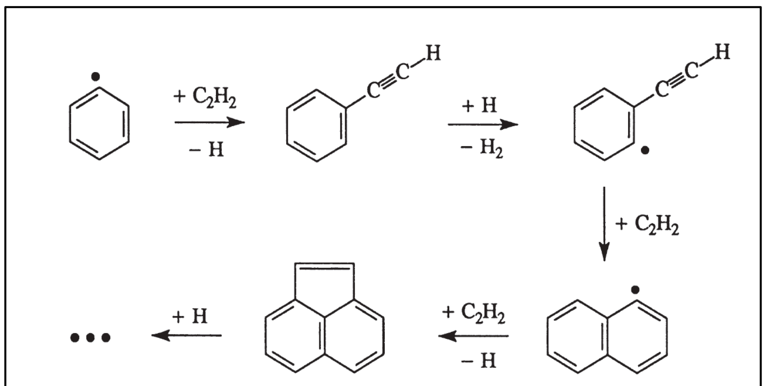
β represents the frequency of collision between different PAH molecules computed using the kinetic theory of gases.

PAH/Soot Model – Gas Phase Kinetics

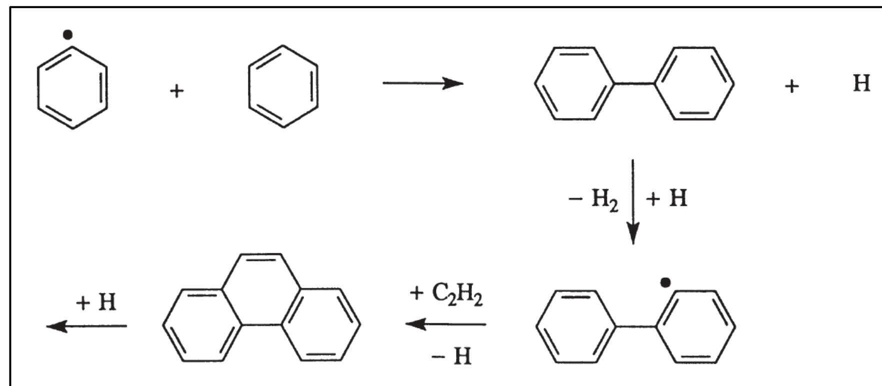
Three major types of mechanisms:

1. Surface Growth, accomplished through HACA (Frenklach, 1994)

2. PAH deposition onto a soot particle surface (Frenklach, 1991)



HACA



Aromatic Combination (Deposition)

3. Consumption, through oxidation or gasification

$$r_{consume} = r_{oxi} + r_{gas}$$

$$r_{oxi} = \frac{1}{T^{1/2}}\left(A_{O_2}P_{O_2}\exp\left[\frac{-E_{O_2}}{RT}\right] + A_{OH}P_{OH}\right)$$

$$r_{gas} = A_{CO_2}P_{CO_2}^{1/2}T^2\exp\left[\frac{-E_{CO_2}}{RT}\right] + A_{H_2O}P_{H_2O}^{1.21}T^{-1/2}\exp\left[\frac{-E_{H_2O}}{RT}\right]$$

Soot Model – Coagulation

- Based on work done by Frenklach (Frenklach 2002)
- Knudsen number defines continuum vs free molecular

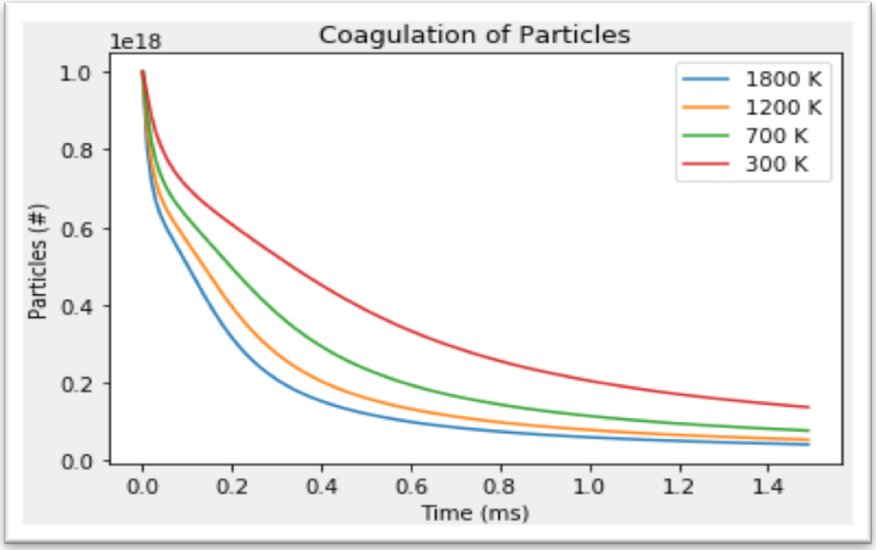
$$Kn = 2\lambda_f/d$$

$$G_r = \frac{G_r^f}{1+1/Kn} + \frac{G_r^c}{1+Kn}$$

- Continuum and free molecular rates are calculated as follows:

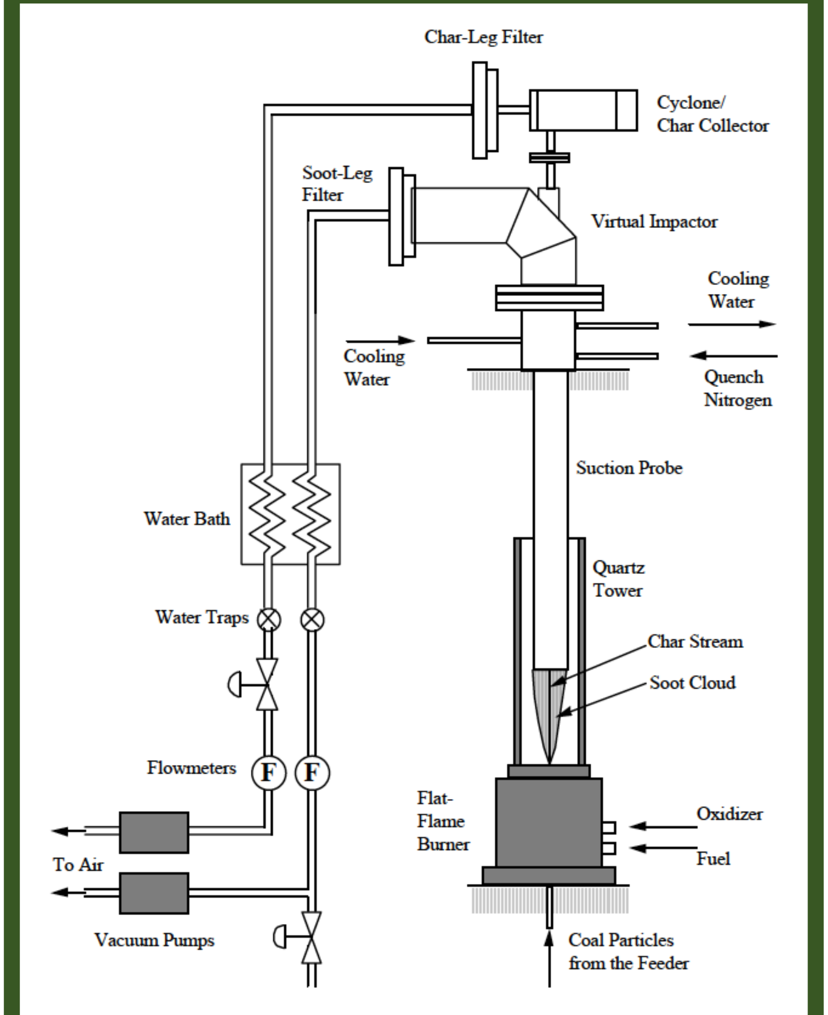
$$G_r = \frac{1}{2}\sum_{k=1}^{r-1}\binom{r}{k}\left(\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} m_i^k m_j^{r-k}\beta_{ij}N_iN_j\right)$$

- β are calculated differently for free molecular vs continuum (Seinfeld 1998)



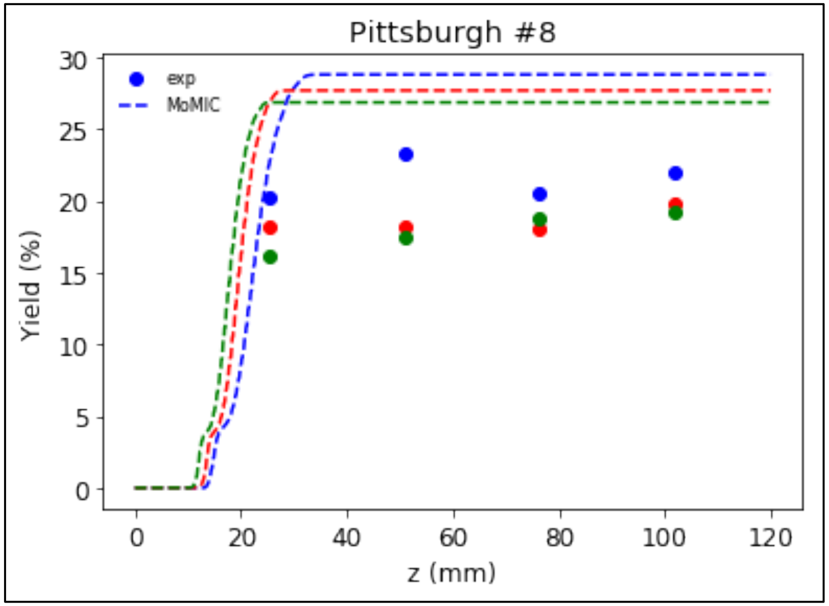
Note the temperature dependence

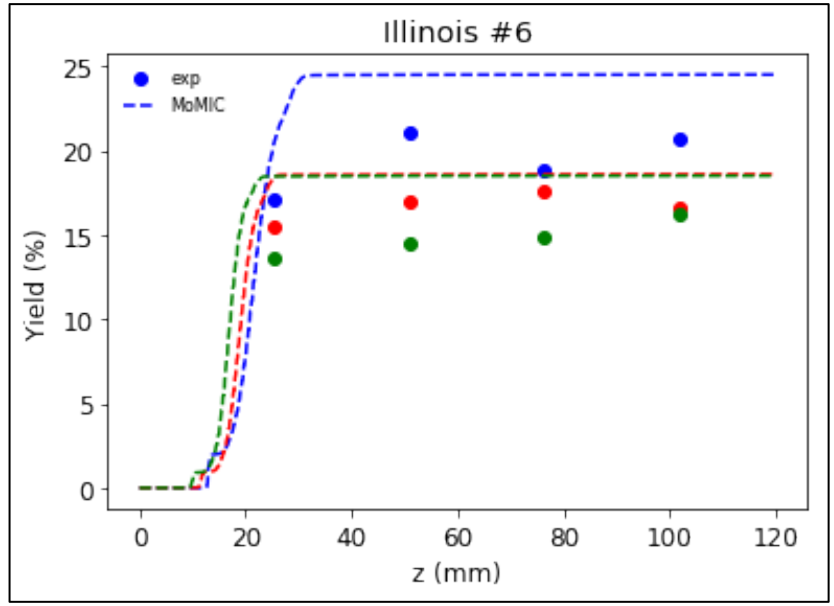
Validation



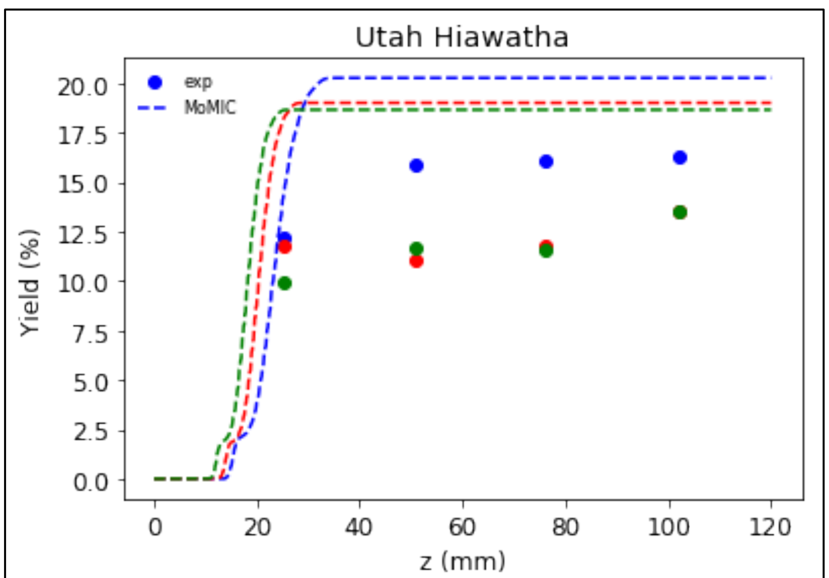
- Experiment conducted by Jinliang Ma at BYU (Ma, 1998)
- Laminar flat flame burner
- Separation system collects soot, char and ash particles
- 6 coal types
- 3 flame temperatures
- Equilibrium chemistry profile ABF mechanism

Validation (Soot Mass)





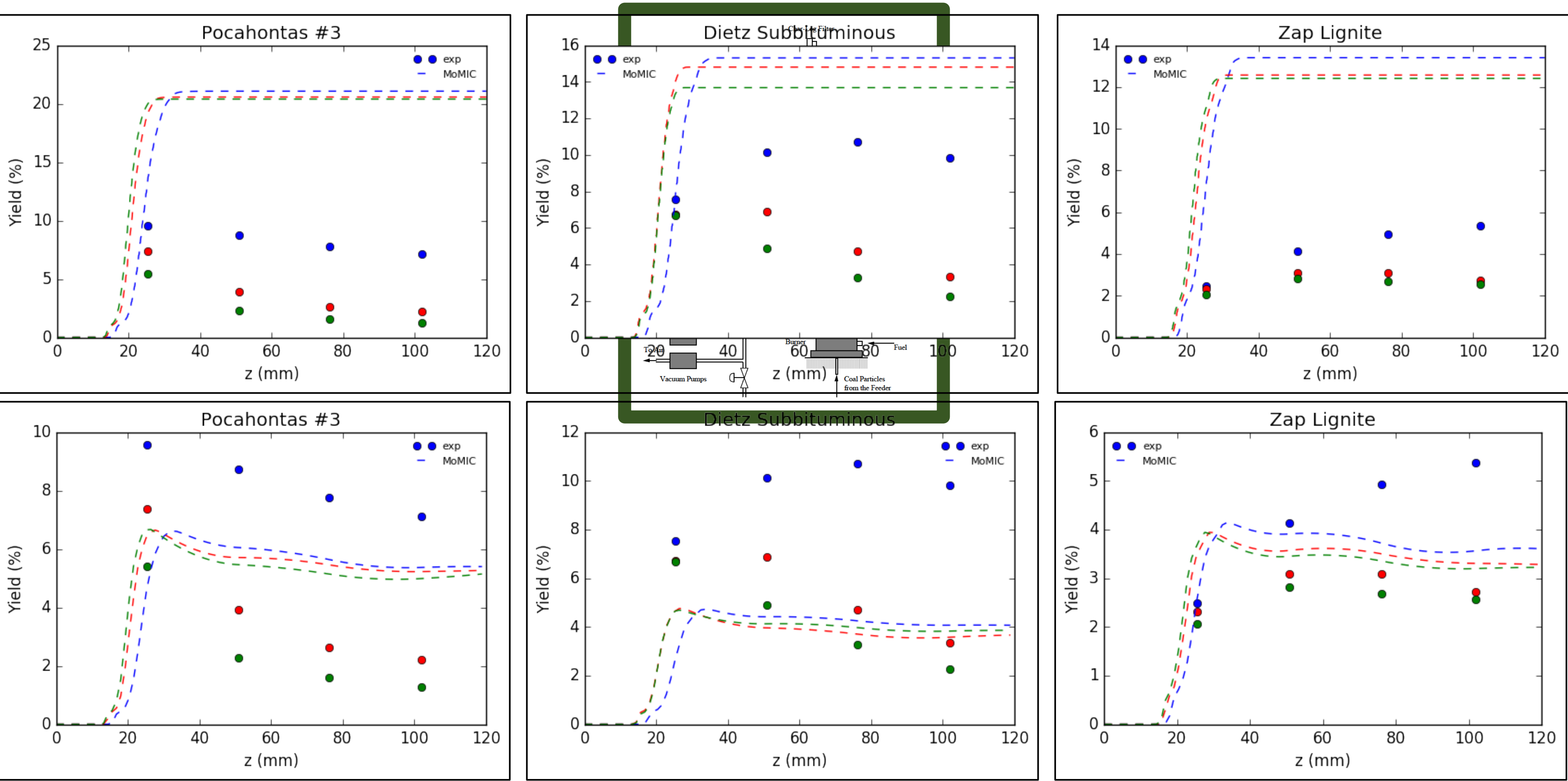
----- 1650 K
----- 1800 K
----- 1900 K
●● **Experiment**



- Model predicts consistent results with the experimented data
- Model results 'over predict' experimental results
    - Experimental mass loses:
        - Soot not captured by suction probe
        - Deposits in collection system
        - Filter pore size 1 micron
        - Sieve loses
- Concentrations level off
    - Little to no gas phase reactions

Validation (Particle Size)

- Better agreement with the particle sizes
- Needs some refinement
    - Morphology of the soot



Conclusions

- Detailed model for coal-derived soot presented
- Model evaluates evolution of two species: PAH and soot
- PAH PSD- discrete bin approach
- Soot PSD- method of moments with interpolative closure
- Validation work presented with good agreement

Ongoing Work

- Further detailing of evolving particle size in Ma's soot collection system
- Aggregate evaluation
- Application of model to biomass
- Surrogate model creation in computationally expensive systems