Detailed Modeling of Soot Formation from Solid Fuels

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Acknowledgements/Background

- Work began as part of the CCMSC's PSAAP II project
  - Demonstrate exascale computing with V&V/UQ to more rapidly deploy new technologies for providing low cost, low emission electric power generation
  - Full-scale simulation of an oxy-coal boiler
  - Work supported by the Department of Energy, National Nuclear Security Administration, under Award Number(s) DE-NA0002375

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- Work continued through the EES division at LANL
  - HIGRAD/FIRETEC- combines physics models that represent combustion, heat transfer, aerodynamic drag and turbulence. Designed to simulate the constantly changing, interactive relationship between fire and its environment.
  - Predicting solid particle emissions from wildfires
  - Work supported by

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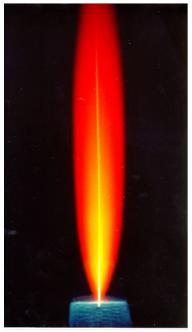
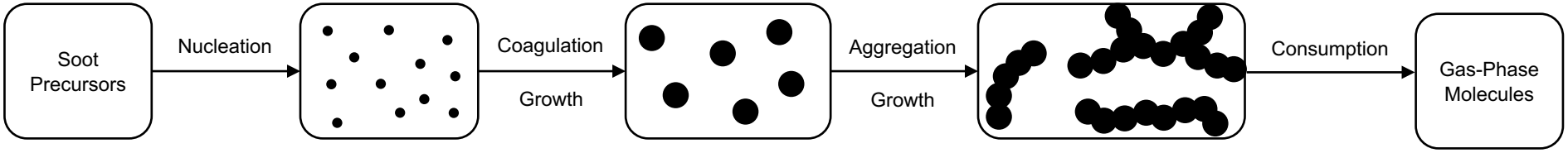
Soot Introduction



Soot

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

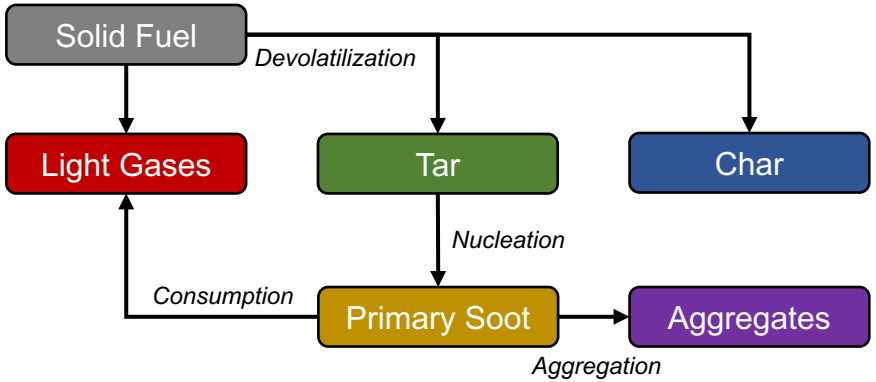
Gaseous Fuels



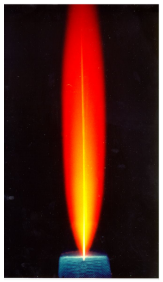
- Rate largely determined by formation of precursors and time in fuel-rich environment
- Soot precursors are PAHs

Solid Fuels

- Parent fuel gives off tar during primary pyrolysis
- Tar is primary soot precursor



Soot Challenges



Validation Data

- Difficulties in physical collections
- Optical measurements
- Very few standards in experimentation or data reporting

Particle Size Distributions

- Particles form a broad distribution with a very large number of particles
- Characterization of the distribution (assumed shape, method of moments, discrete bin, etc.)
  - Assumed shape:
    - Typical- mono-dispersed or log-normal distributions

$$N_i(m) = \frac{1}{m\sigma\sqrt{2\pi}} \exp\left[-\frac{(ln\ m - \mu)^2}{2\sigma^2}\right]$$

  - Discrete bin
    - Possible distribution too broad

$$N = \sum_{k=0}^{n_i} \delta(m) N_i(m)$$

  - Method of moments
    - Closure
    - Configuring the PSD from the moments

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

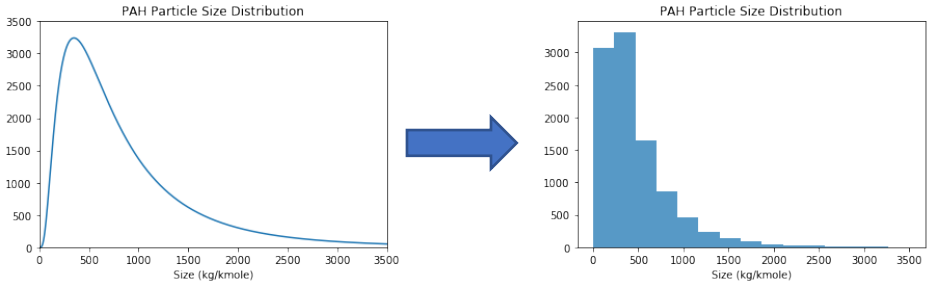
Modeling

- Numerical stiffness and stability
- Chemistry complications (equilibrium vs flamelet)
- Particle morphology during agglomeration
- System priorities (particle and system composition)

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

Bin Species Number Density

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

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

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

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

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

PSD Moment Density

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

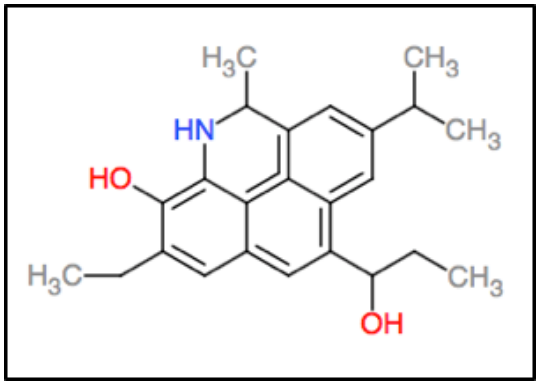
$$S_{M_r} = r_{nucl} + r_{growth} + r_{coag} - r_{consume}$$

PAH Model - Creation

PAH molecules creation from two sources:

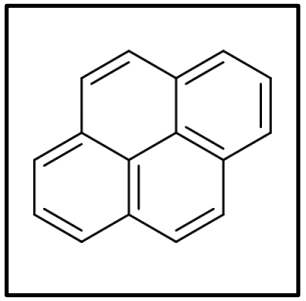
1. Release of tar molecules by parent fuel
   - Rate determined from results of CPD model (Fletcher, 1992)
   - PSD spans broad range (~150 kg/kmole – 3000 kg/kmole)
   - Lognormal PSD
     - Coal (median ~350 kg/kmole, small variance)
     - Biomass (median ~225 kg/kmole, larger variance)
     - Varies over time, shifts to higher MWs.

Hypothetical Coal Tar Molecule

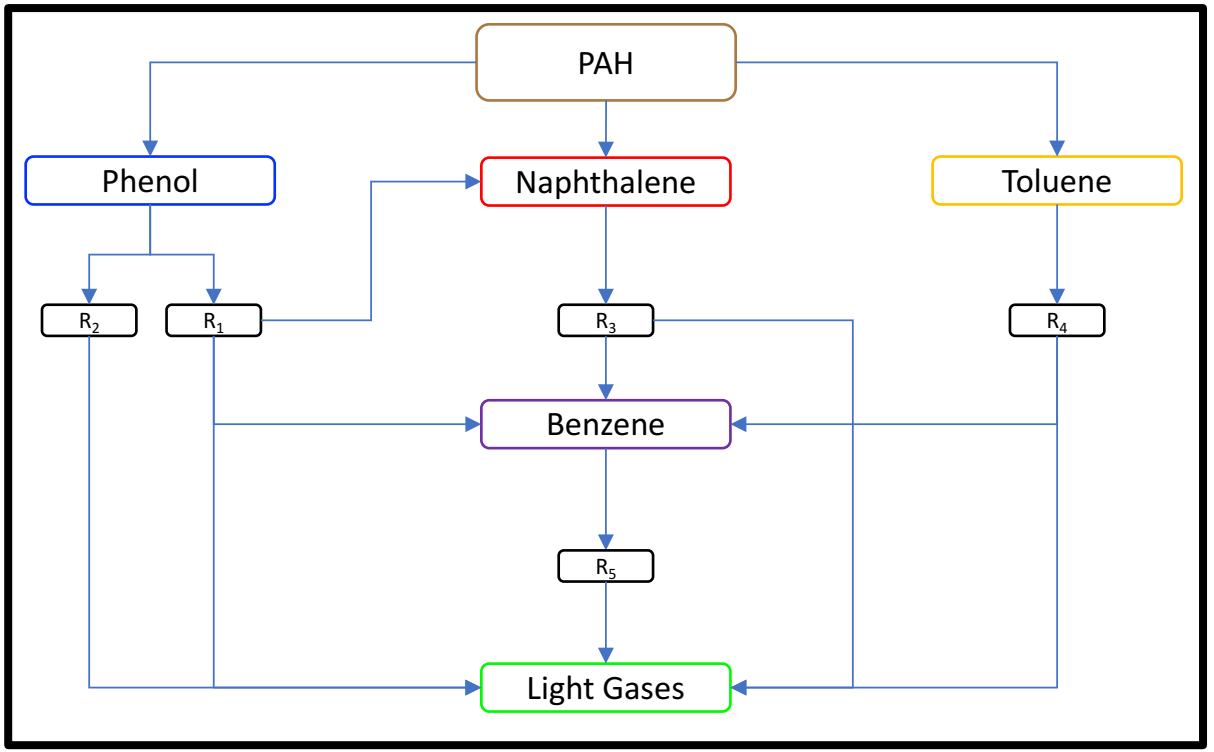


2. Formation of aromatic rings from the gas-phase
   - Rate determined by ABF mechanism (Appel, 2000)
   - Creation of pyrene added to the PAH bins
   - Usually insignificant source of PAH (But not always, Zeng, 2011)

Pyrene Molecule



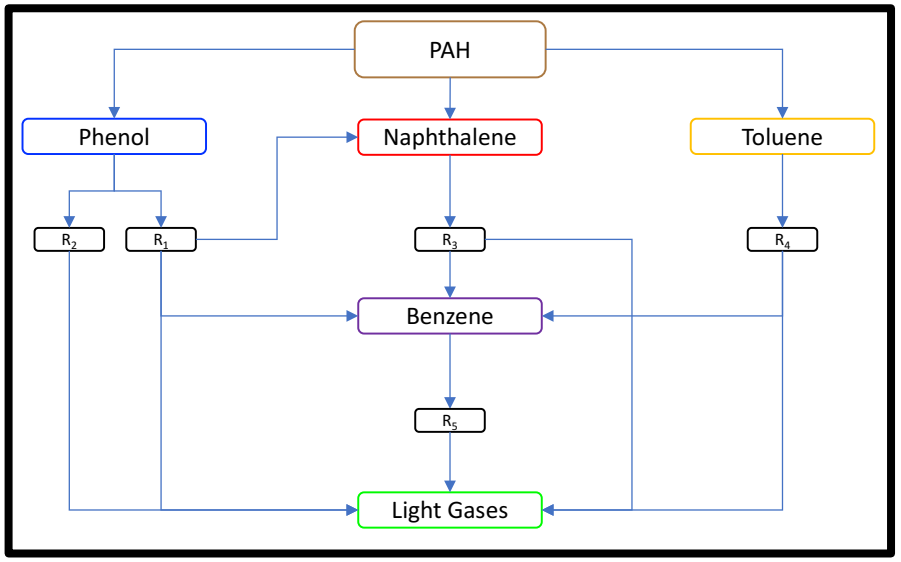
PAH Model – Thermal Cracking

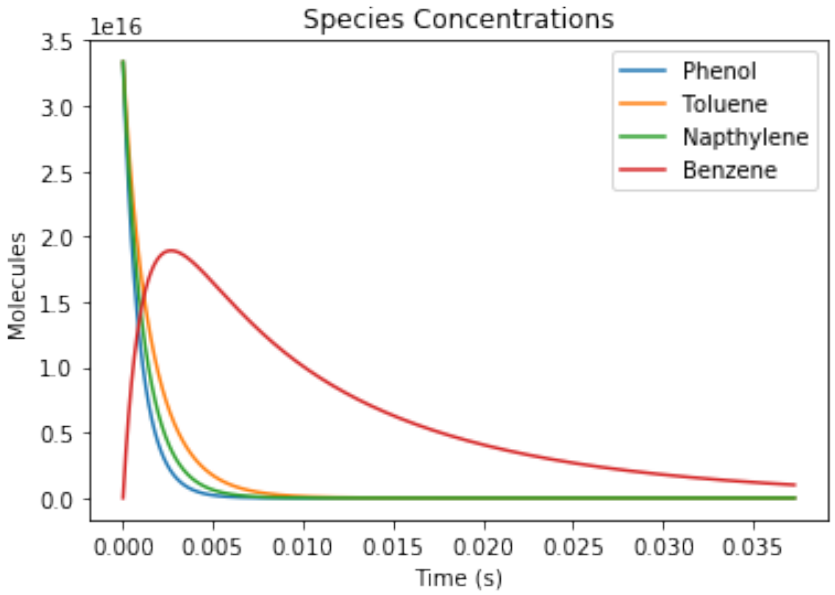


- Thermal cracking scheme originates from work done by Marias, et al (2016)
- Four types of PAH molecules
- Cracking reactions determine amount of mass lost
- All reactions are simple Arrhenius equations with fitted parameters

PAH Model – Thermal Cracking

- It is undesirable to transport four species for each PAH bin
- Fraction of each species assumed to be constant
- Fraction estimation
  - Maximum tar concentration used
  - Equal parts phenol, naphthalene, and toluene
  - Phenol and toluene branches established by CNMR and Elemental analyses of parent fuel
  - 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

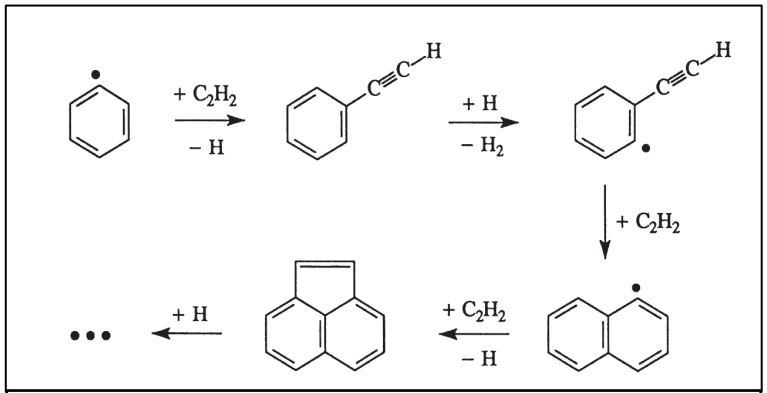
$$r_r = \sum_{i=i_0}^{\infty} \sum_{j=i}^{\infty} \beta_{i,j} (m_i + m_j)^r N_i^{PAH} N_j^{PAH}$$

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

PAH/Soot Model – Gas Phase Kinetics

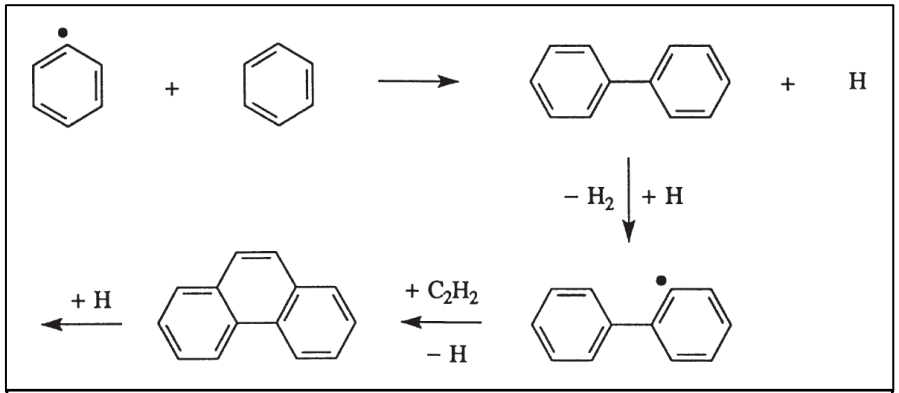
Growth of soot particles:

1. HACA (Frenklach, 1994)



HACA

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

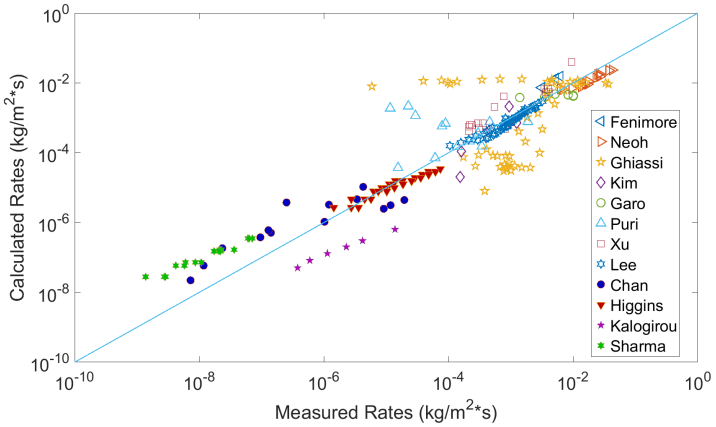


Aromatic Combination (Deposition)

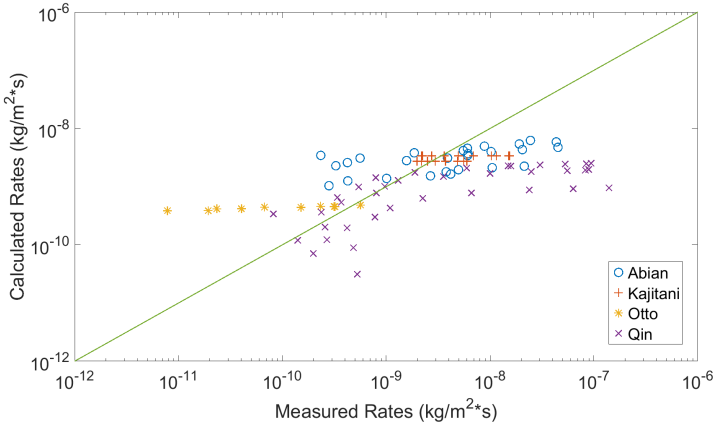
PAH/Soot Model – Gas Phase Kinetics

Two mechanisms for consumption simplified: $r_{consume} = r_{oxi} + r_{gas}$

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



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



PAH Model – Coagulation

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

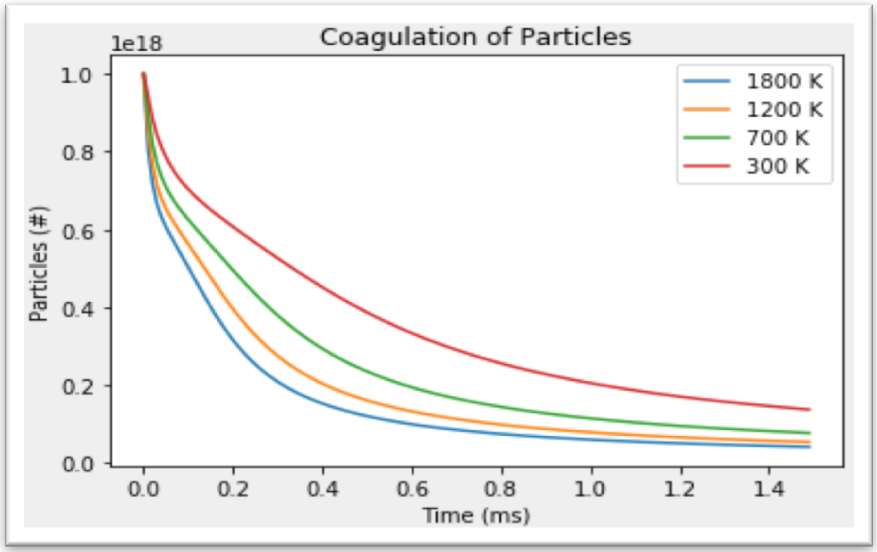
$$Kn = 2\lambda_f / d$$

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

- Continuum and free molecular rates are calculated as follows:

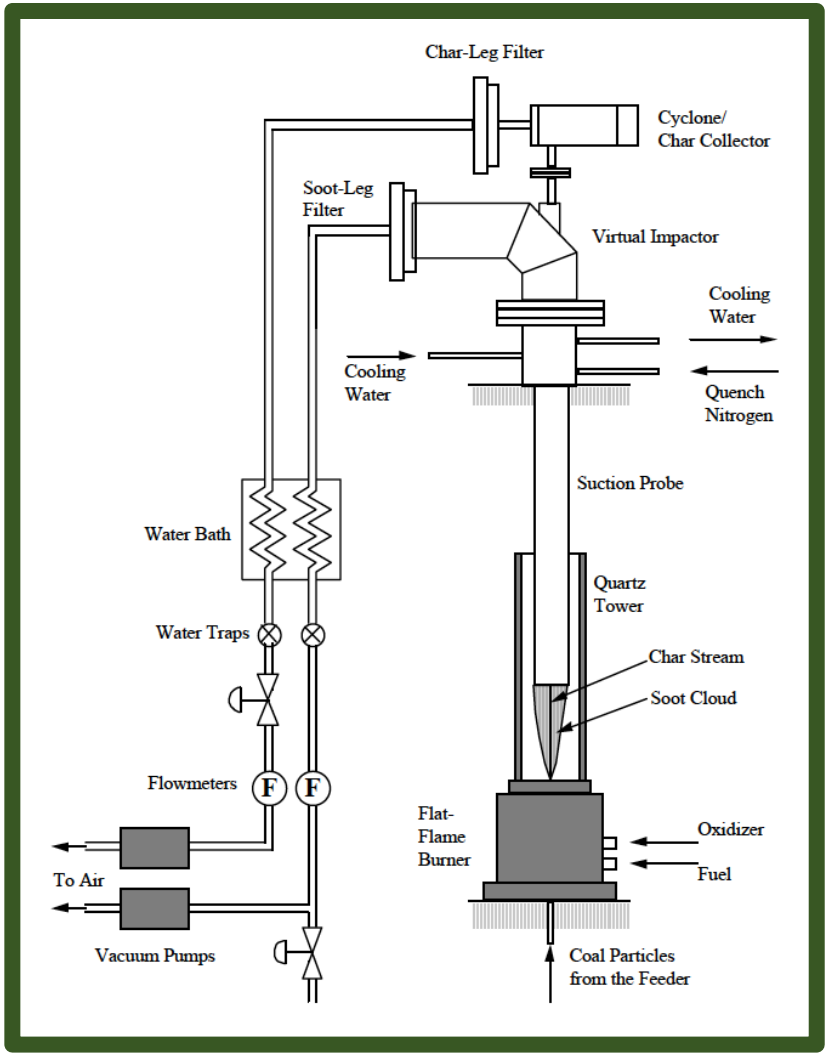
$$G_r = \frac{1}{2} \sum_{k=1}^{r-1} \binom{r}{k} \left(\sum_{i=1}^{\infty} \sum_{j=1}^{\infty} m_i^k m_j^{r-k} \beta_{ij} N_i N_j \right)$$

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



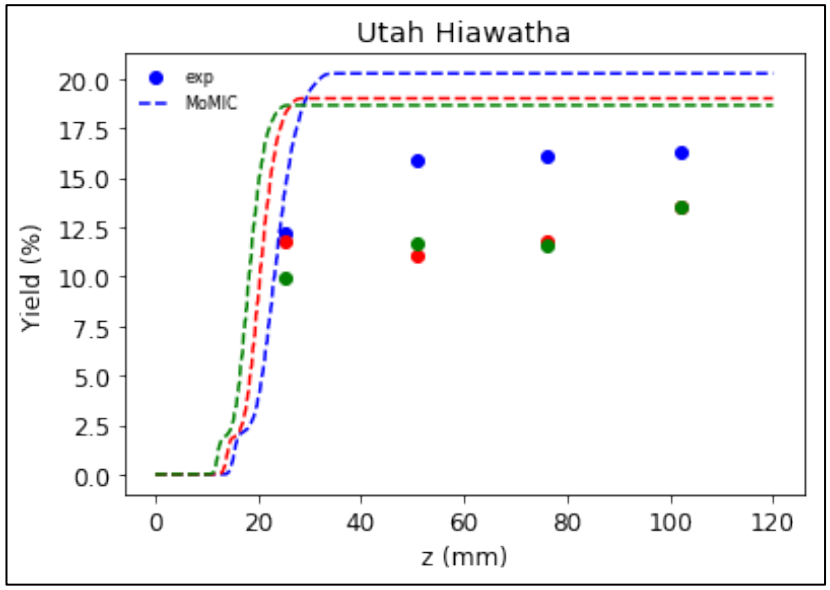
Note the temperature dependence

Coal 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

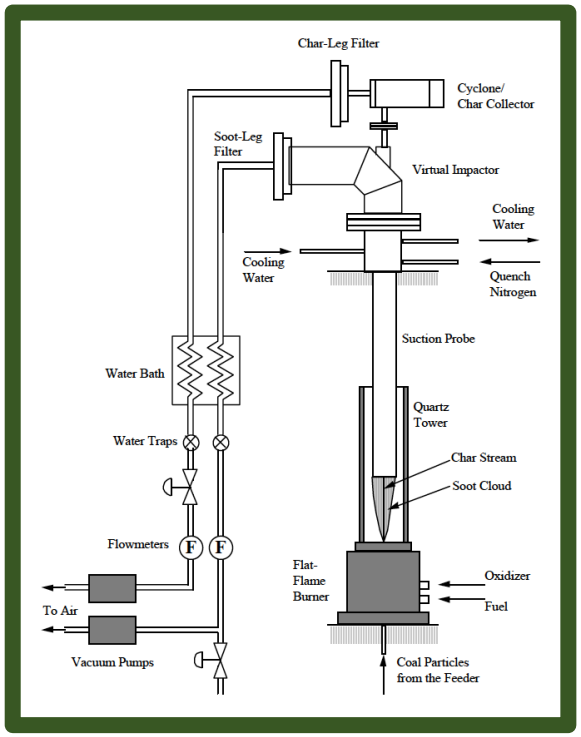
Coal Validation (Soot Mass)

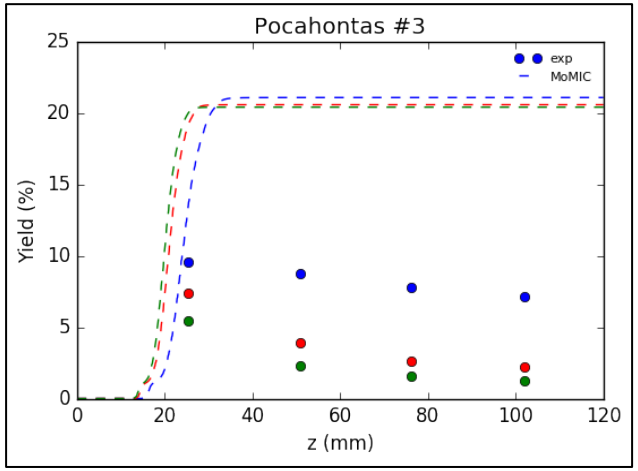


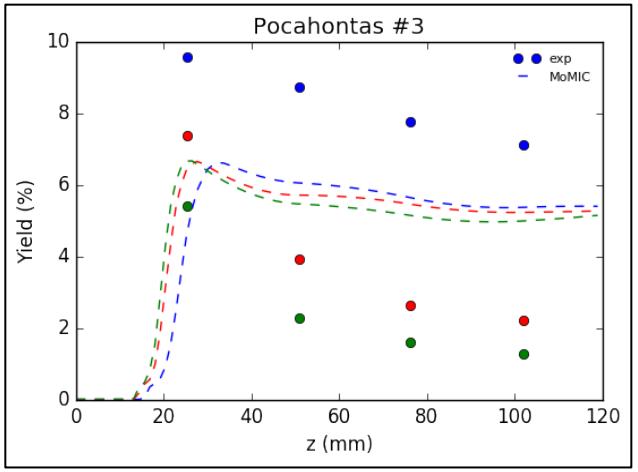
----- 1650 K
----- 1800 K
----- 1900 K
●● Experiment

- 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

Coal Validation (Particle Size)

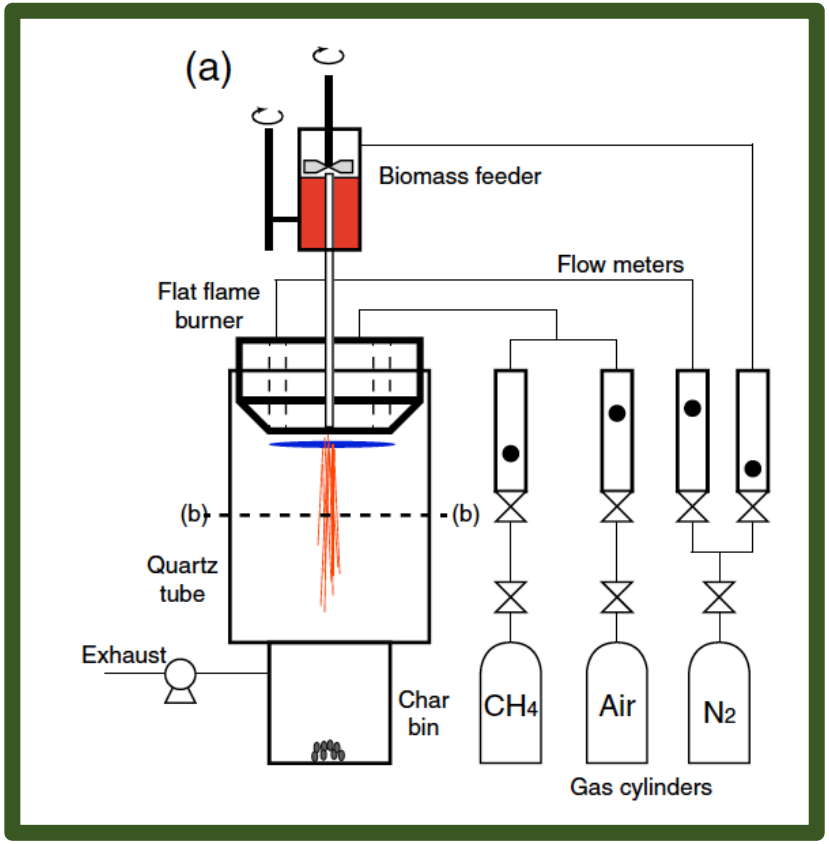






- Better agreement with the particle sizes
- Needs some refinement
  - Morphology of the soot

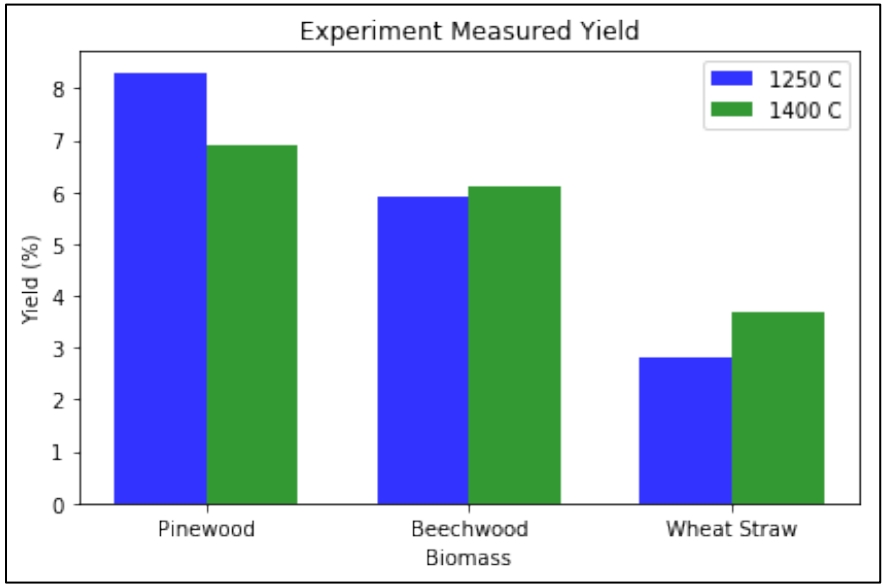
Biomass Validation

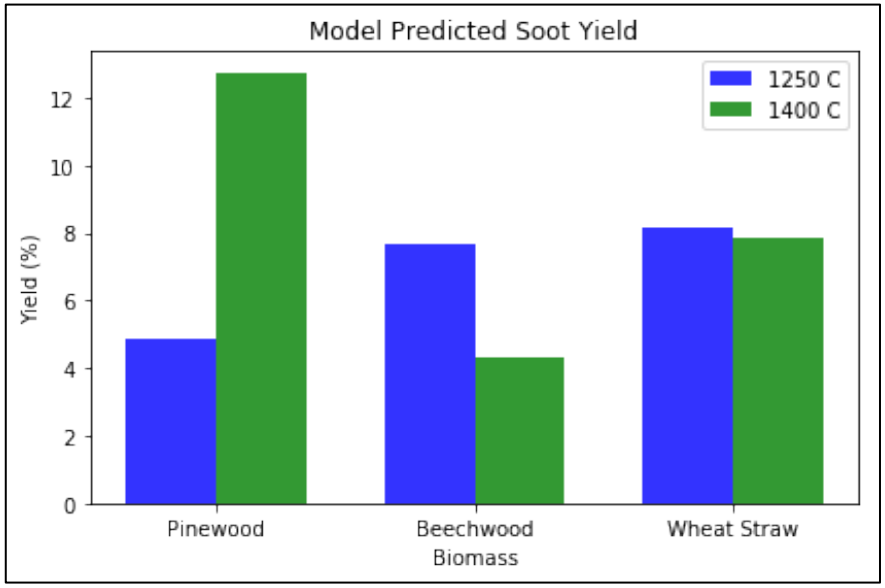


Burak Goktepe, Kentaro Umeki, Rikard Gebar, *Does distance among biomass particles affect soot formation in an entrained flow gasification process?,* Fuel Processing Technologies, 2016

- Experiment conducted in collaboration between Technical University of Denmark and Lulea University of Technology (Trubetskaya, 2016)
- Drop tube reactor
- Biomass gasification
- Soot collected as deposits from drop tube products
- 3 biomass types
- 2 reactor temperatures

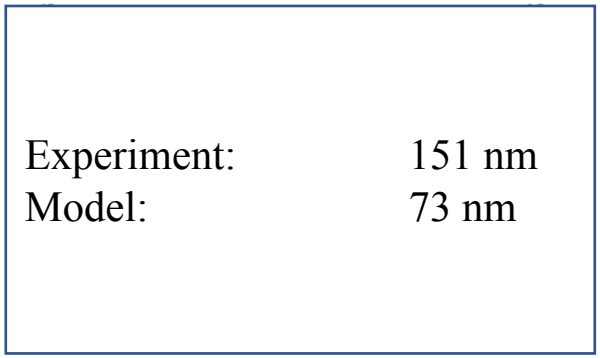
Biomass Validation (Soot Mass)



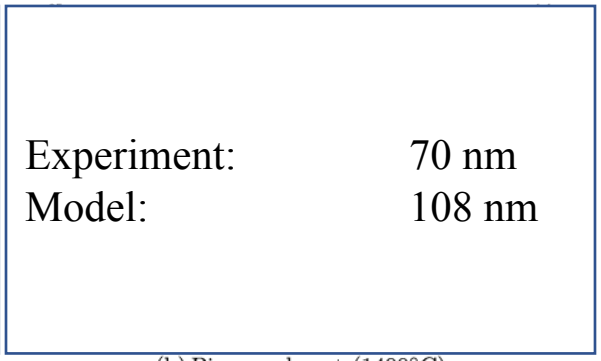


Biomass	Temperature (C)	Measured Yield (%)	Predicted Yield (%)
Pinewood	1250	8.3	4.8
Pinewood	1400	6.9	12.7
Beechwood	1250	5.9	7.7
Beechwood	1400	6.1	4.3
Wheat Straw	1250	2.8	8.1
Wheat Straw	1400	3.7	7.9

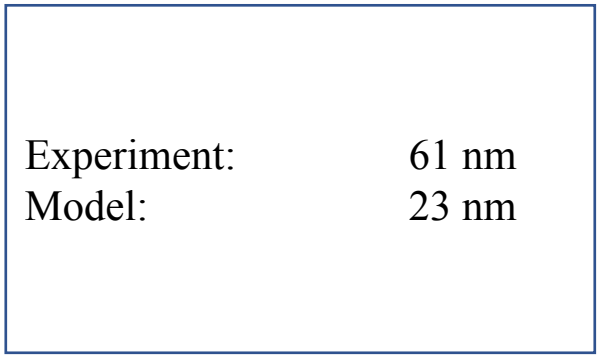
Biomass Validation (Particle Size)



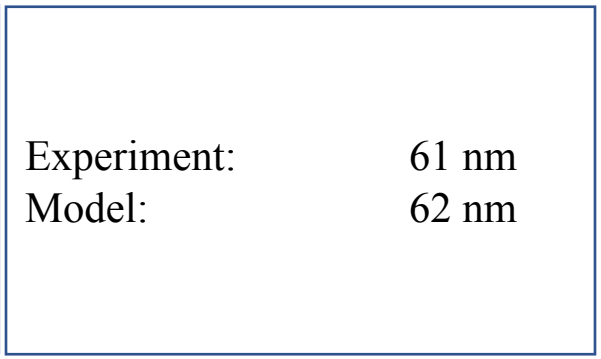
(a) Pinewood soot (1250°C)



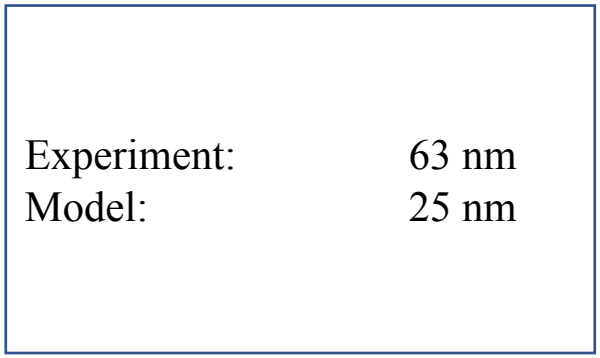
(b) Pinewood soot (1400°C)



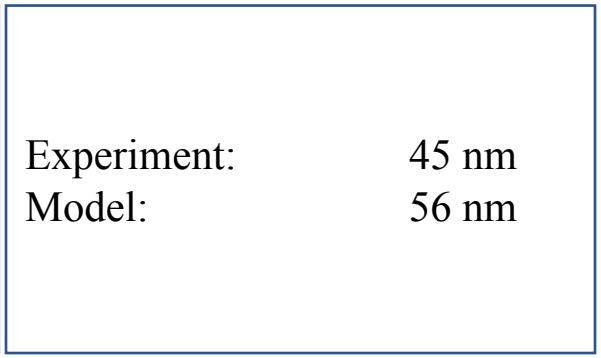
(c) Beechwood soot (1250°C)



(d) Beechwood soot (1400°C)



(e) Wheat straw soot (1250°C)



(f) Wheat straw soot (1400°C)

Conclusions

- Detailed soot model for complex solid fuels 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 for both coal and biomass systems

Ongoing Work

- Aggregate evaluation
- Surrogate model creation for use in computationally expensive systems