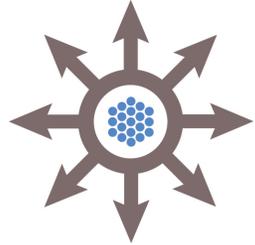


# Soot Nucleation and Consumption in Oxy-Coal Systems

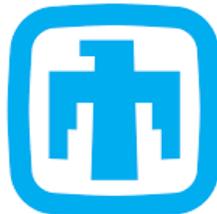
Alexander Josephson, Neal Gaffin, and David Lignell



# Acknowledgements



CARBON CAPTURE  
MULTIDISCIPLINARY  
SIMULATION CENTER



Sandia  
National  
Laboratories



Lawrence  
Livermore  
National  
Laboratory

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# Oxy-Coal Combustion

- Due to the increasing concern of impending CO<sub>2</sub> regulations, research into various carbon capture technologies has increased.
- Oxy-fuel combustion allows for easy separation of CO<sub>2</sub>.
- For the foreseeable future we are, both national and internationally, still largely dependent on coal for energy.
- Coal presents unique challenges:
  - Complex fuel
    - Chemical structure
    - Dynamic morphology throughout combustion
  - Multi-phase flows
  - Diverse reaction rates



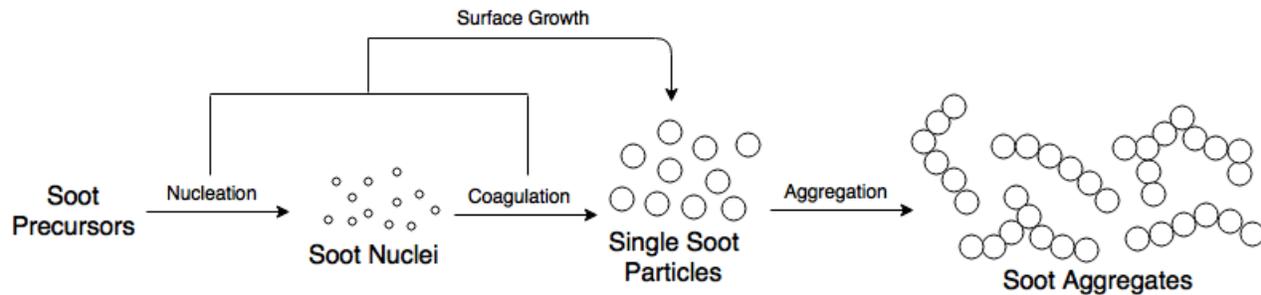
# Soot

- Soot is a carbonaceous particle formed in flames' fuel-rich areas.
- Highly influences radiative heat transfer to boiler walls. (If available include Ben's studies here.)
- Can act as a nitrogen sink.
- If not fully consumed, can pose significant health risks.



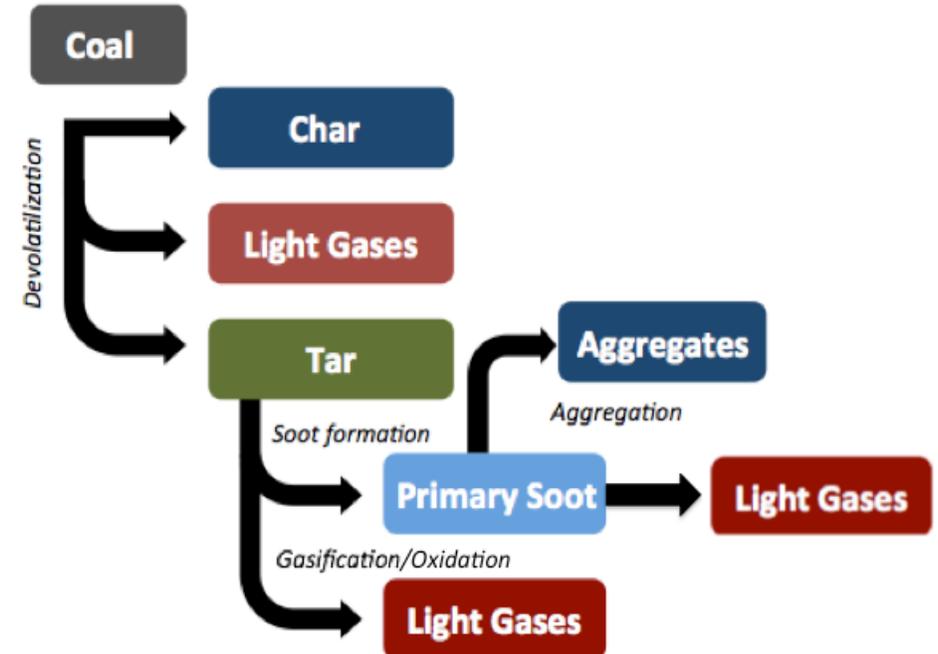
# Coal-derived Soot

## Soot Formation (Gaseous Fuel)



- Soot particles primary source are PAH (polycyclic aromatic hydrocarbons) that are formed in the fuel-rich region of the flame.
- Creation and growth of PAHs to a critical size is the limiting step in soot formation

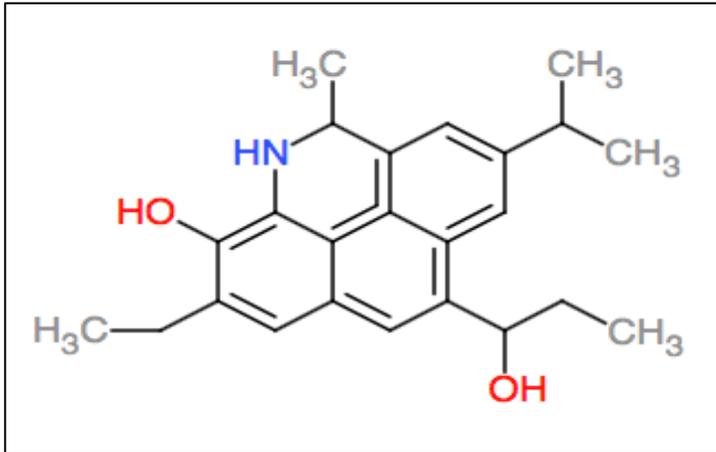
## Soot Formation (Solid Fuel)



- Soot particles primary source are tars, that are released from the coal particle during devolatilization.
- Tends to have higher sooting potential than gaseous fuels.

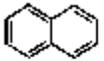
# Nucleation

Tar Molecule

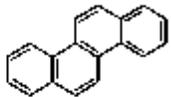


Common PAH Molecules

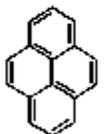
## Polycyclic Aromatic Hydrocarbons



Naphthalene  
C<sub>10</sub>H<sub>8</sub>



Chrysene  
C<sub>18</sub>H<sub>12</sub>



Pyrene  
C<sub>16</sub>H<sub>10</sub>



Coronene  
C<sub>24</sub>H<sub>12</sub>



Ovalene  
C<sub>32</sub>H<sub>14</sub>

- In traditional soot models, PAH is the building block of soot nucleation
  - PAH molecules form and grow through various mechanisms to form soot particles
- Coal systems contain tars, which are essentially PAH molecules with a few differences:
  - Elemental analysis of tar reveals composition similar to parent coal
  - Molecule is made up of aromatic clusters with potentially large amounts of aliphatic side chains
  - Average tar molecular weight: ~350 amu
- In coal-derived soot models, tar is the building block of soot nucleation
- Complete model must include the evolution of tars in a system along

# Tar Cracking

- Tar molecules have a tendency to undergo a secondary pyrolysis and shed its aliphatic parts
- Atoms in rings tend not be removed as easily, nitrogen of particular importance
- Results in aromatic clusters very similar to the more common PAHs
- It is possible that not all aliphatic portions are consumed
- Cracking happens in parallel with surface growth but tends to happen at a much faster rate

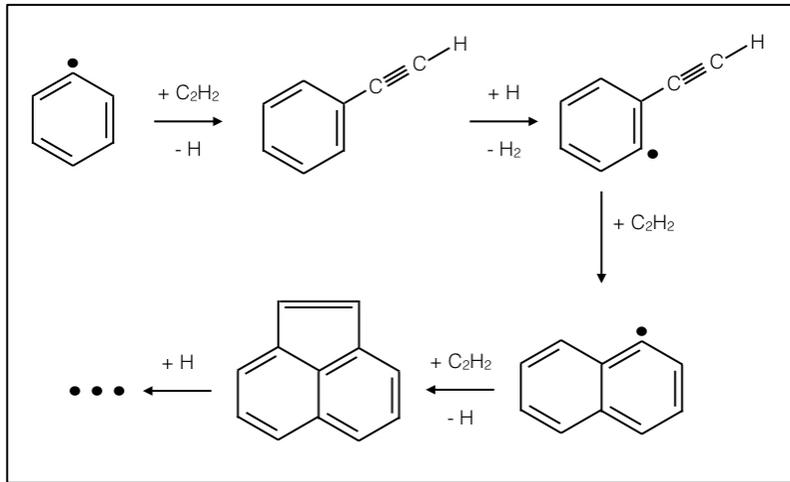


# Tar NMR Parameters



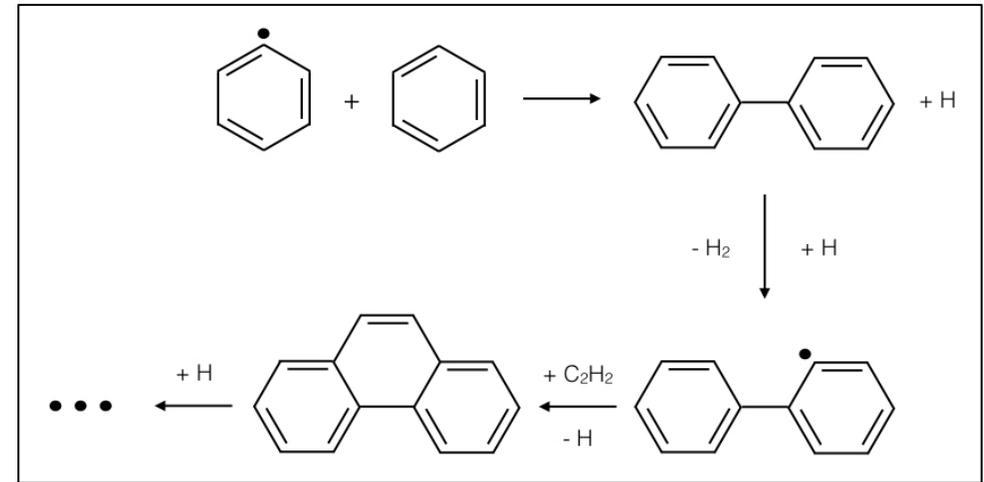
# Hydrogen Abstraction and Carbon Addition

## Surface Growth via Acetylene Addition



- Starting benzene ring is radicalized usually by reaction with the hydrogen radical.
- Mechanism is dependent on mostly on concentrations of the H radical and acetylene.
- Propagation reaction.

## Surface Growth via PAH Condensation



- Starting benzene ring is radicalized similarly.
- Mechanism is dependent on mostly on concentrations of the H radical, acetylene, and PAH.
- PAH can vary in size as long as the geometry of the molecule permits the site reactions.
- Propagation reaction.

# Nucleation Model

- Model will transport two internal coordinates:
  - Aliphatic tar mass, with two source terms:
    - Production of mass based off tar product from devolatilization:

$$R_{T Ali} = S T_{Tar} \cdot (f_{al} + f_a^C)$$

- For its consumption based off secondary pyrolysis:

$$R_{TP} = A \cdot T^n \exp \left[ \frac{-E_a}{RT} \right]$$

- PAH the following source terms:
  - Production of mass based off tar product from devolatilization:

$$R_{T Aro} = S T_{Tar} \cdot f_a$$

- Surface growth of aromatics:
    - Dr. Frenklach's growth by HACA
  - PAH condensation:
    - Growth again by HACA
  - PAH to soot particles:
    - Assume a log-normal distribution of tar and a certain % of tar becomes soot based off of 2000 amu.



# Consumption

## Oxidation

- Dominates traditional combustion
- Occurs by the attack of oxidizing agents
  - $O_2$ ,  $OH^-$ ,  $O^-$ , etc
- Products are oxidized carbon species
  - $CO_2$ ,  $CO$ , etc
- Strongest at the high temperature and fuel-lean areas
- Occurs at on the particle surface

## Gasification

- Negligible in traditional combustion
- Occurs by the attack of high energy molecules
  - $CO_2$ ,  $H_2O$ , etc
- Products are fractured species
  - $H_2$ ,  $CH$ ,  $CO$ , etc
- Occurs at the particle surface but reactions can penetrate deeper
- Rates dependent on temperature and species concentrations.

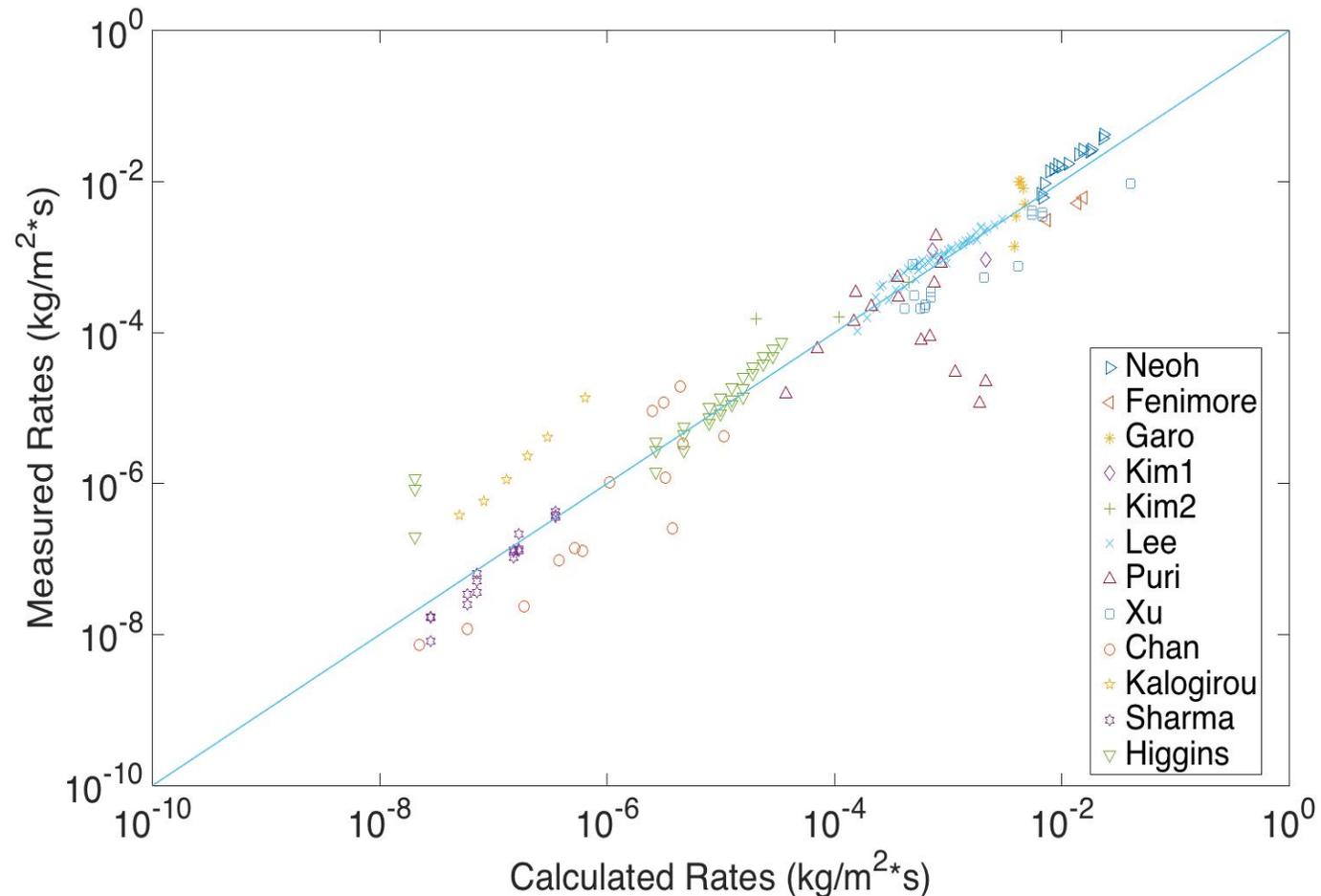


# Oxidation

$$R_{oxi} = \frac{1}{T^{0.5}} \left( A_{O_2} P_{O_2} \exp \left[ \frac{-E_{O_2}}{RT} \right] + A_{OH} P_{OH} \right)$$

- This is a modified Arrhenius model with the temperature dependence decoupled from the Arrhenius constant and reaction orders determined through numerical experimentation
- Couples oxidation by the  $O^-$  radical with oxidation by OH or  $O_2$
- Activation energy for the OH is considered significantly small to be negligible
- Tunable parameters are the two Arrhenius constants and the one activation energy

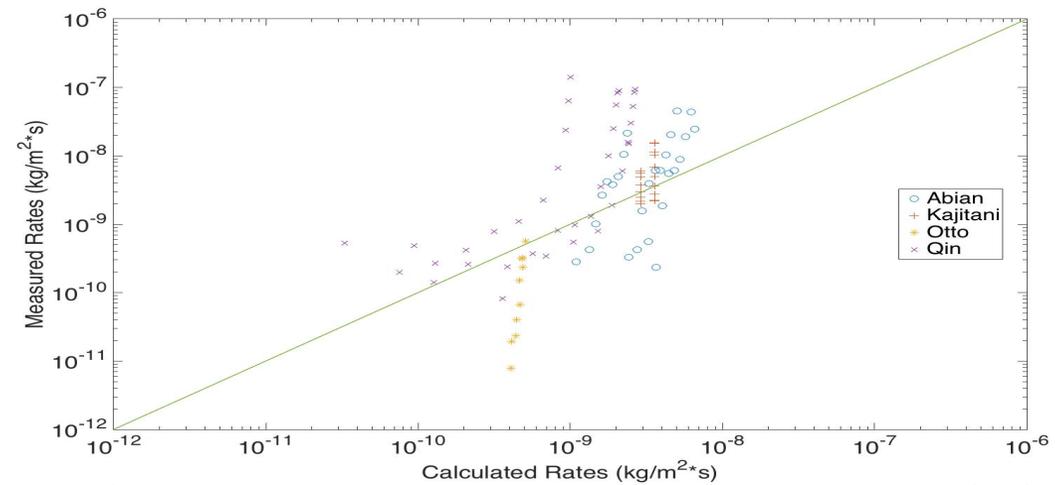
$$A_{O_2} = 1.92 \cdot 10^{-3} \frac{kgK^{1/2}}{Pam^2s}$$
$$A_{OH} = 2.93 \cdot 10^{-3} \frac{kgK^{1/2}}{Pam^2s}$$



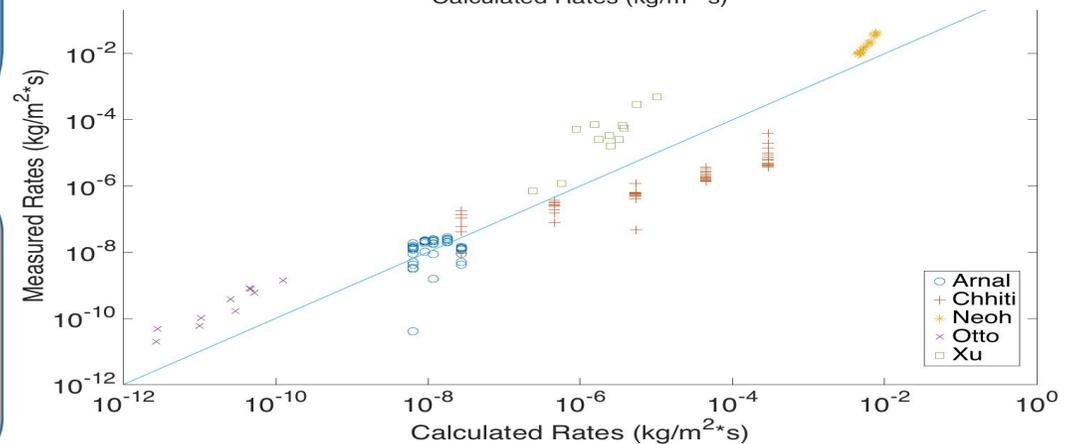
# Gasification

$$R_{gas} = A_{CO_2} P_{CO_2}^{0.5} T^2 \exp \left[ \frac{-E_{CO_2}}{RT} \right] + \frac{A_{H_2O} P_{H_2O}^n}{T^{1/2}} \exp \left[ \frac{-E_{H_2O}}{RT} \right]$$

- Modified Arrhenius model with temperature dependence decoupled from Arrhenius constant
- Reaction orders determined through numerical experimentation
- Experimentation was done for CO<sub>2</sub> and H<sub>2</sub>O independently so analysis for different terms could be done separately
- Tunable parameters are the two Arrhenius constants, two activation energies, and the H<sub>2</sub>O reaction order



CO<sub>2</sub> Data Fit



H<sub>2</sub>O Data Fit

$$A_{H_2O} = 1.86 \cdot 10^6 \frac{kgK^{1/2}}{Pa^n m^2 s} \quad A_{CO_2} = 1.31 \cdot 10^{-17} \frac{kg}{Pa^{1/2} K^2 m^2 s}$$

$$E_{H_2O} = 4.17 \cdot 10^5 \frac{J}{mole} \quad E_{CO_2} = 5.55 \cdot 10^3 \frac{J}{mole}$$

# Model Calibration

Bayes' Theorem

$$P(x_i|y) = \frac{P(x_i)P(y|x_i)}{P(y)}$$

$P(x_i)$  - 'Prior', incorporates prior knowledge into a pdf

$P(y)$  - Data uncertainty

$P(y|x_i)$  - 'Likelihood', taken from a Gaussian pdf

$P(x_i|y)$  - 'Posterior', resultant pdf for parameter estimation



# Conclusion

