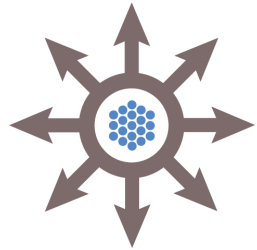


Soot Nucleation and Consumption in Oxy-Coal Systems

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Acknowledgements



CARBON CAPTURE
MULTIDISCIPLINARY
SIMULATION CENTER



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- This material is based upon work supported by the Department of Energy, National Nuclear Security Administration, under Award Number(s) DE-NA0002375
- Support is acknowledged from the University of Utah, and Brigham Young University
- This work is part of a larger work performed by the CCMSC, a tri-university center with oversight and collaboration with three national labs.

Oxy-Coal Combustion

- Due to the increasing concern of impending CO₂ regulations, research into various carbon capture technologies has increased.
- Oxy-fuel combustion allows for easy separation of CO₂.
- 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



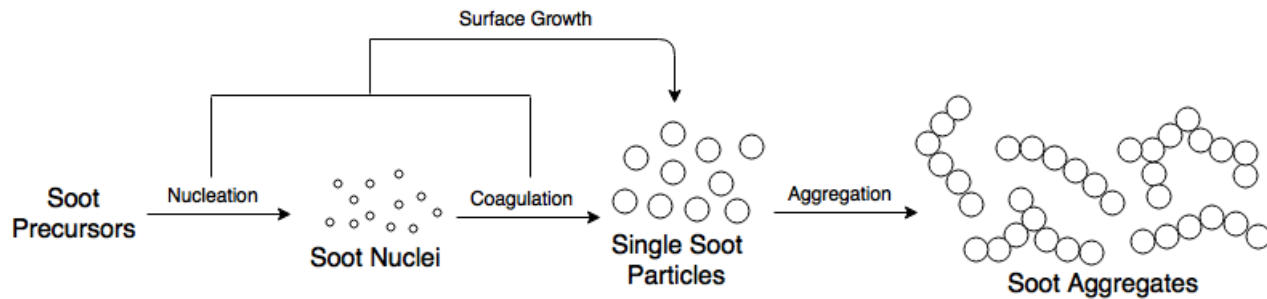
Soot

- 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.



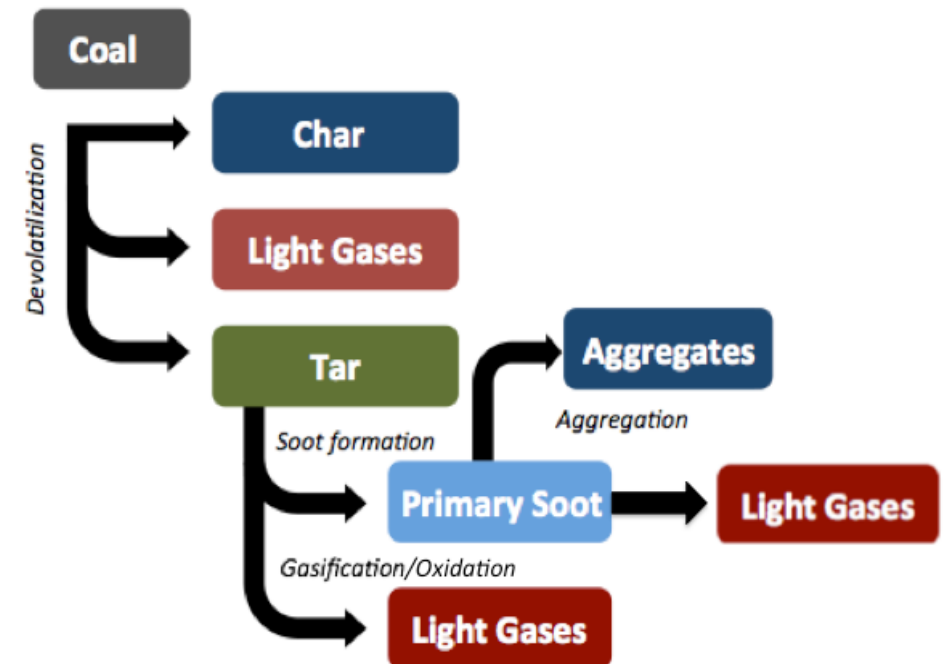
Coal-derived Soot

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

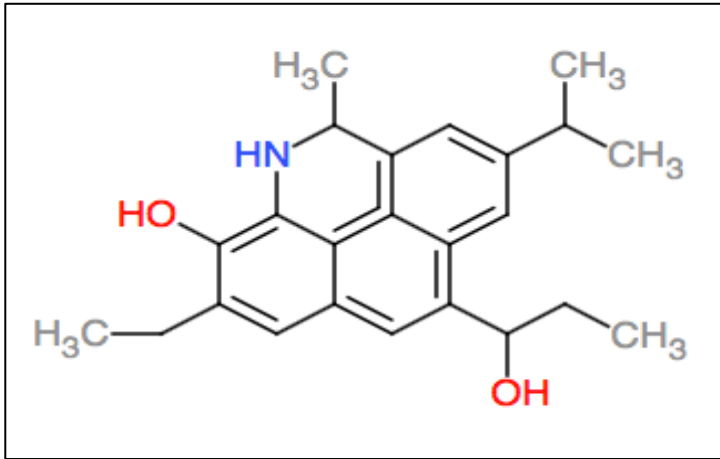
Soot Formation (Solid Fuel)



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

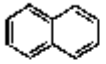
Nucleation

Tar Molecule

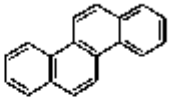


Common PAH Molecules

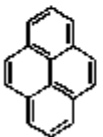
Polycyclic Aromatic Hydrocarbons



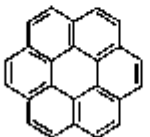
Naphthalene
C₁₀H₈



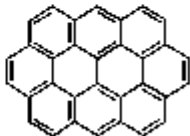
Chrysene
C₁₈H₁₂



Pyrene
C₁₆H₁₀



Coronene
C₂₄H₁₂



Ovalene
C₃₂H₁₄

- 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

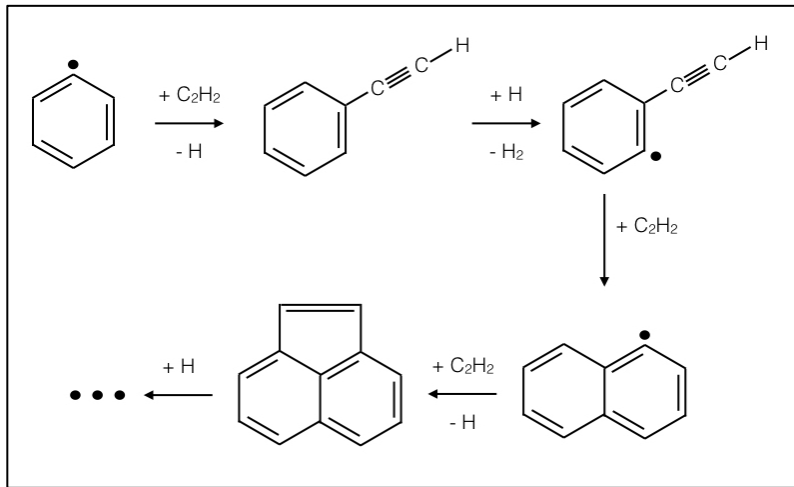


Tar NMR Parameters



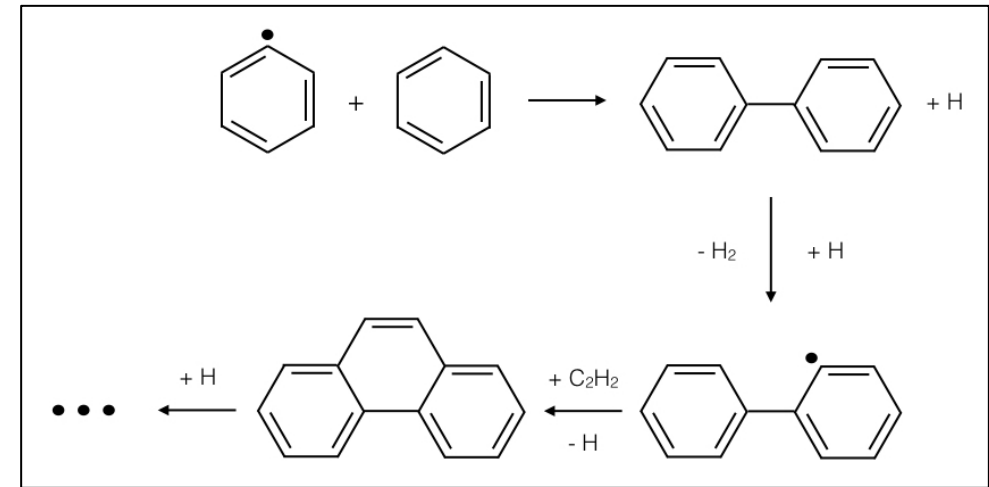
Hydrogen Abstraction and Carbon Addition

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:

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

- 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:

$$R_{T Aro} = ST_{Tar} \cdot f_a$$

- 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^\cdot , O^\cdot , 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.



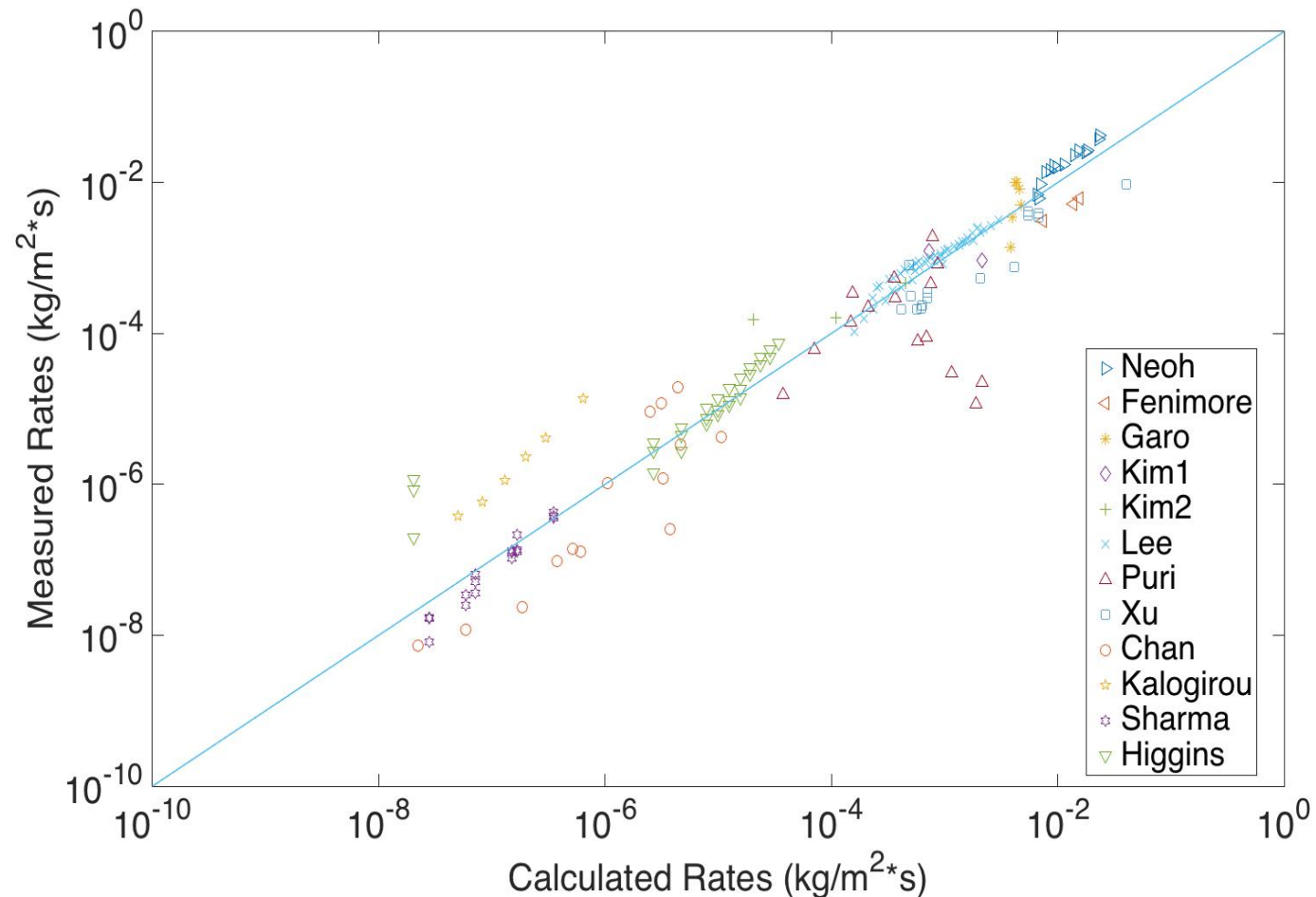
Oxidation

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

- 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

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

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



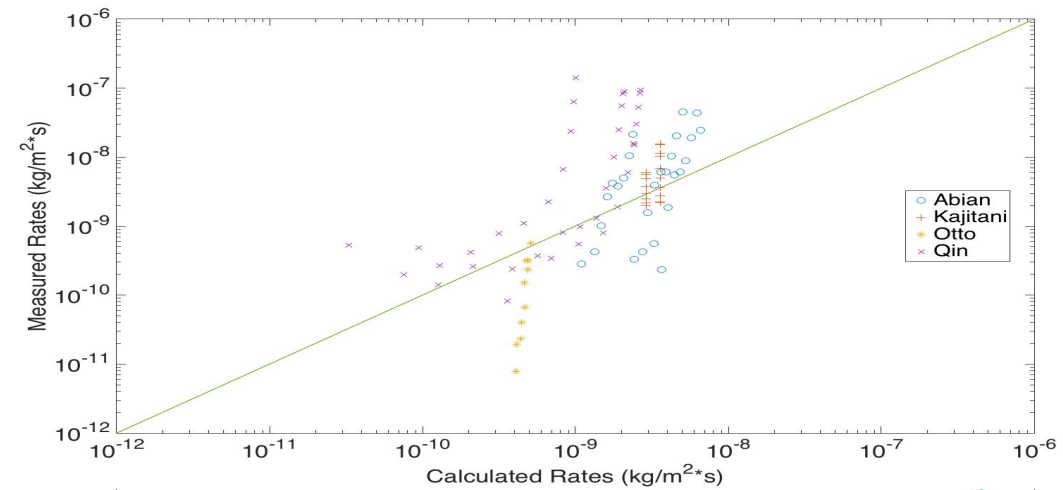
Gasification

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

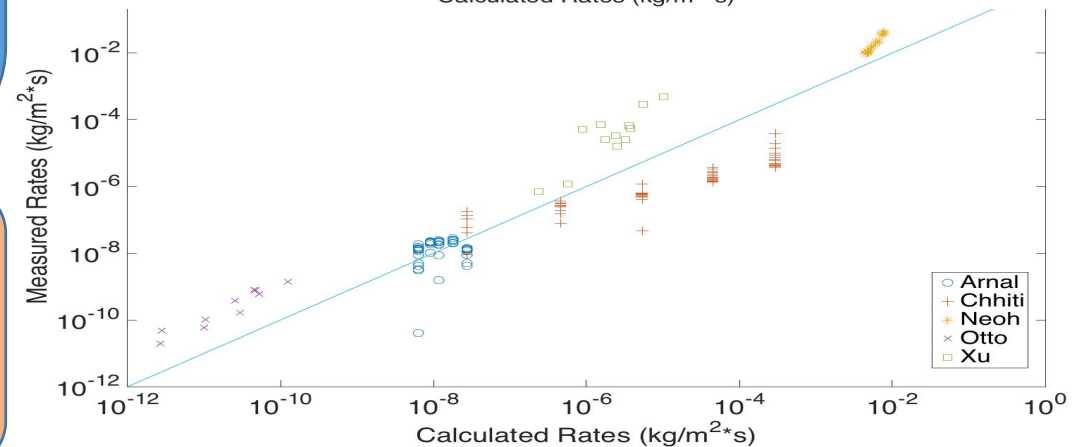
- Modified Arrhenius model with temperature dependence decoupled from Arrhenius constant
- Reaction orders determined through numerical experimentation
- Experimentation was done for CO₂ and H₂O independently so analysis for different terms could be done separately
- Tunable parameters are the two Arrhenius constants, two activation energies, and the H₂O reaction order

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

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



CO₂ Data Fit



H₂O Data Fit

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

