

# Large Eddy Simulation of Soot Formation in Oxy-Coal Combustion

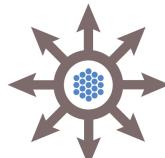
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*Brigham Young University, University of Utah*

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**Salt Lake City Utah**

*November 1, 2017*



CARBON CAPTURE  
MULTIDISCIPLINARY  
SIMULATION CENTER



# Acknowledgements



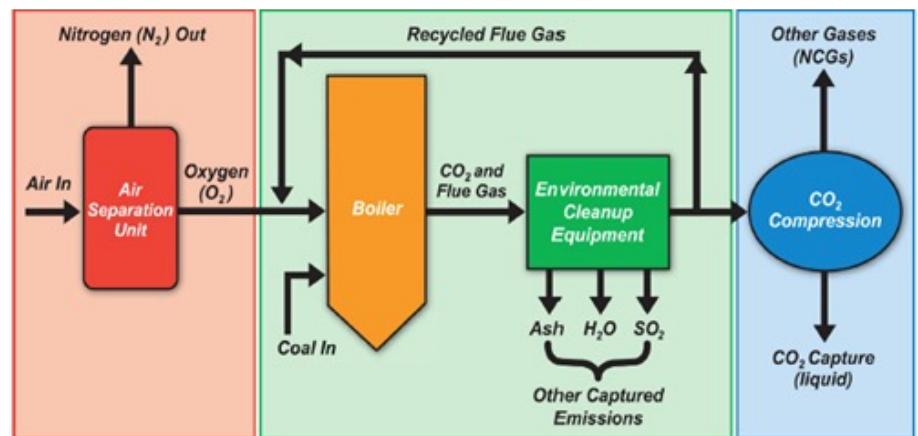
National Nuclear Security Administration



- 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

# Oxy-Coal Combustion

- Coal remains an important source of power generation in the world.
- Increased concern over CO<sub>2</sub> has led to development of various carbon capture methods.
- Oxy-fuel was developed to allow affordable and simpler carbon capture.
- In order develop oxy-coal systems more quickly, computer simulations have rapidly increased in accuracy and capabilities



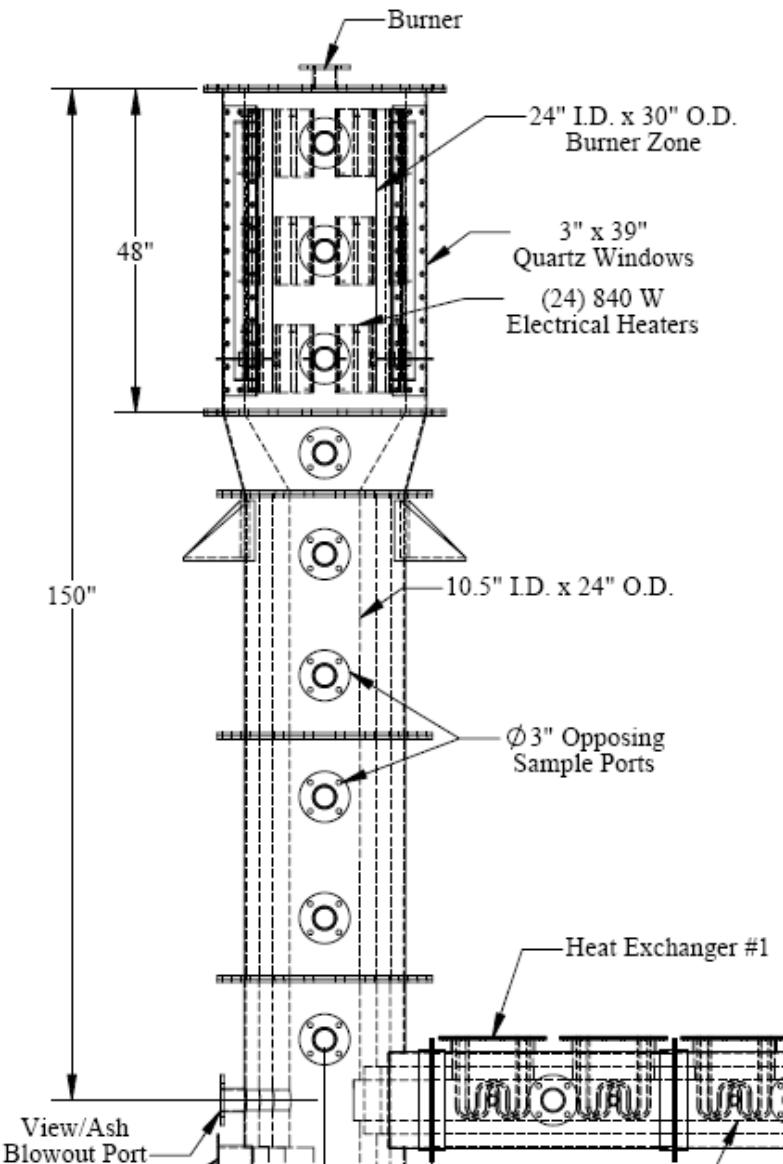
# Oxy-Fuel Combustor (OFC)

- Lab-scale combustor
- University of Utah
- 100 kW
- Down fired
- Refractory-lined
  - 3 inch,  $k=0.15 \text{ W/m}^*\text{K}$
- No swirl



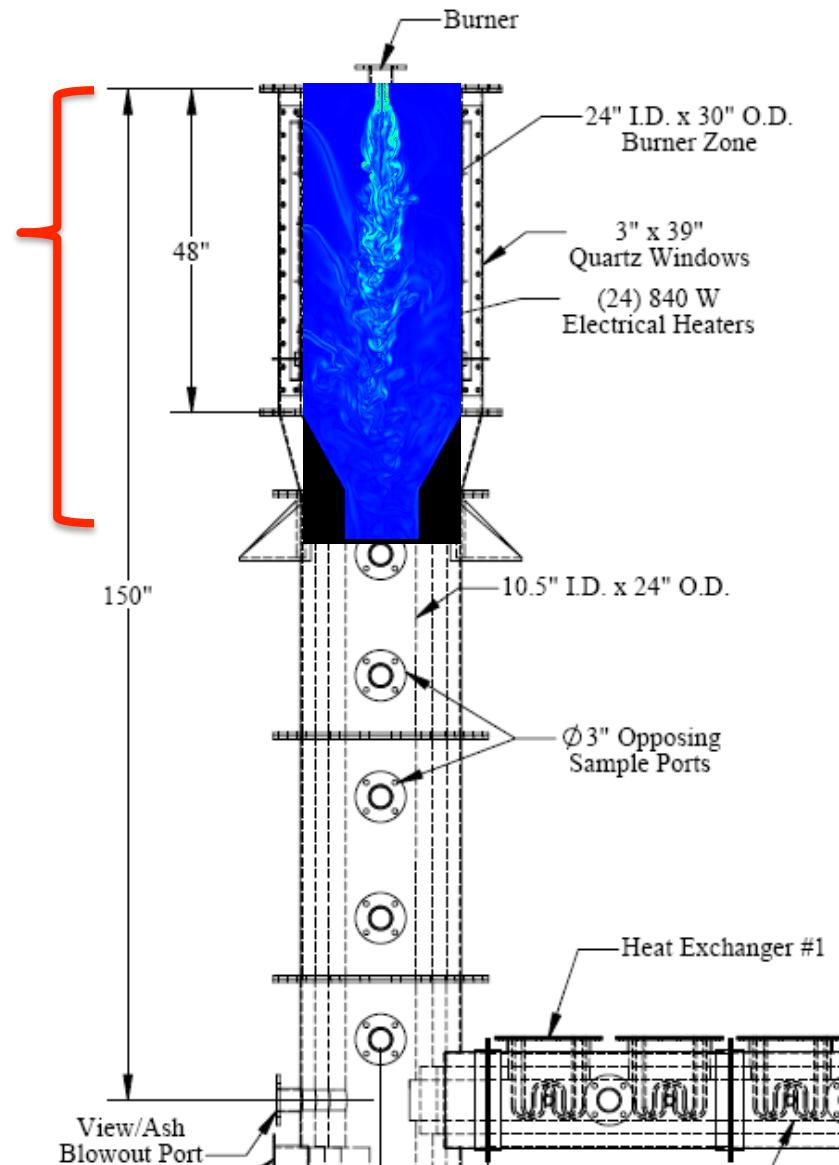
# OFC

- Diameter = 0.6 m
- Simulation length = 1.7 m
- 100 kW capacity
- Streams
  - Primary
  - Secondary
  - Purge
- $D_p=1.6 \text{ cm}$ ,  $D_s=3.5 \text{ cm}$



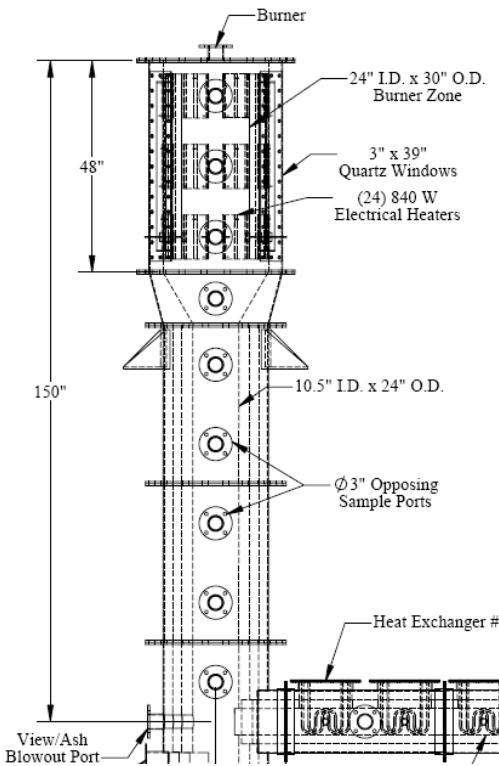
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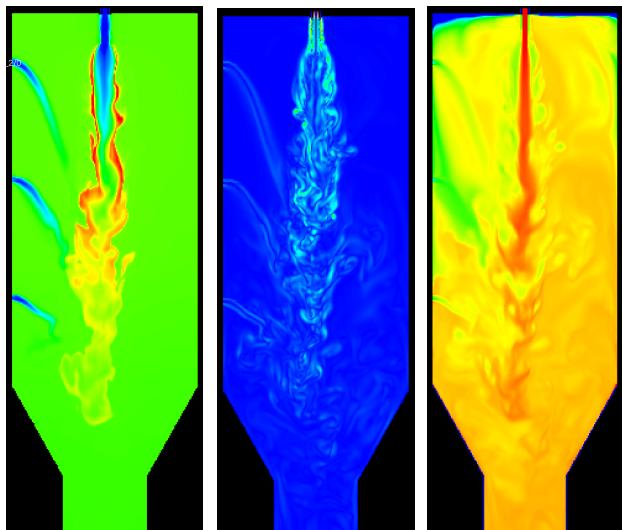
# OFC

## Stream Properties



SUFCO Bituminous Coal	SKYLINE Bituminous Coal
<ul style="list-style-type: none"> <li>• Primary           <ul style="list-style-type: none"> <li>• Coal: 3.81 kg/hr</li> <li>• <math>CO_2</math>: 5.40 kg/hr</li> <li>• <math>O_2</math>: 1.04 kg/hr</li> <li>• <math>T=300\text{ K}</math></li> </ul> </li> </ul>	<ul style="list-style-type: none"> <li>• Coal: 4.47 kg/hr</li> <li>• <math>CO_2</math>: 7.48 kg/hr</li> <li>• <math>O_2</math>: 1.22 kg/hr</li> <li>• <math>T=366\text{ K}</math></li> </ul>
<ul style="list-style-type: none"> <li>• Secondary           <ul style="list-style-type: none"> <li>• <math>O_2</math>: 7.48 kg/hr</li> <li>• <math>T = 489\text{ K}</math></li> </ul> </li> </ul>	<ul style="list-style-type: none"> <li>• <math>O_2</math>: 10.23 kg/hr</li> <li>• <math>T = 529\text{ K}</math></li> </ul>
<ul style="list-style-type: none"> <li>• Purge           <ul style="list-style-type: none"> <li>• <math>CO_2</math>: 3.08 kg/hr (total)</li> <li>• <math>T=300\text{ K}</math></li> <li>• 3 radiometer inlets</li> </ul> </li> </ul>	<ul style="list-style-type: none"> <li>• <math>CO_2</math>: 3.85 kg/hr (total)</li> <li>• <math>T=294\text{ K}</math></li> <li>• 3 radiometer inlets</li> </ul>

# Simulation Parameters



- # grid cells = 9,562,500
- $\Delta x = \Delta y = \Delta z = 4$  mm
- $L_x = 1.7$  m (down),
  - $L_y = L_z = 0.6$  m
- Runtime  $\sim 10$  seconds.
- # processors: 1000-2000

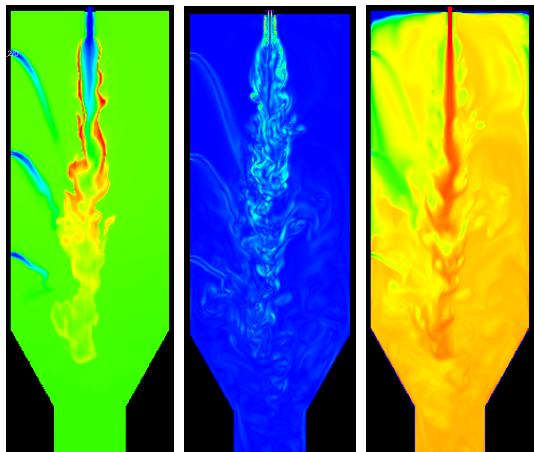
# Simulation: Models

Radiation

Gas Combustion

Particle Combustion

Soot formation



- Discrete Ordinates
- S<sub>8</sub> model (80 rays)
- Coal scattering
- Gray gases
- Boundaries
  - matching radiative and wall conductive heat fluxes

$$\epsilon(q_i - \sigma T_w^4) = k \frac{T_w - T_o}{\Delta x_w}$$

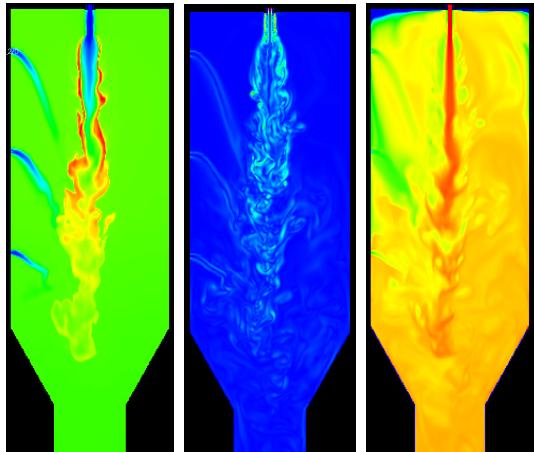
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Gas Combustion

Particle Combustion

Soot formation



- Transporting 2 mixture fraction variables
  - $\xi, \eta$
  - for mass fractions of primary gas and coal-off-gas.
- Lookup table
  - Equilibrium
  - Tabulated in terms of  $\xi, \eta$ , heat loss

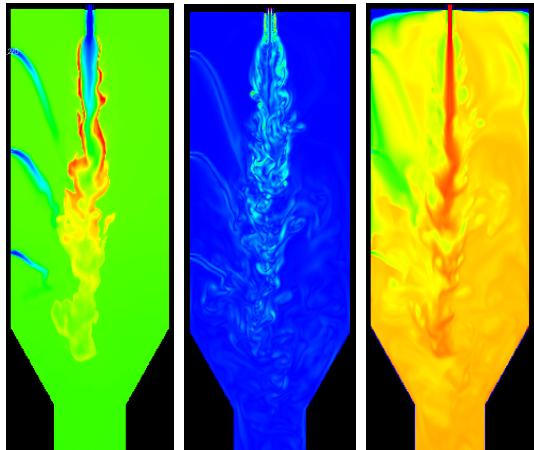
# Simulation: Models

Radiation

Gas Combustion

Particle Combustion

Soot formation



- **Coal Devolatilization**

- Yamamoto et al. PCI 32 (2011)
- Parameters tuned using CPD

- **Char Oxidation**

- Murphy & Shaddix model C&F 144 (2006)

- **Radiation**

- Discrete Ordinates
- $S_8$  model (80 rays)
- Coal scattering, Grey Gases

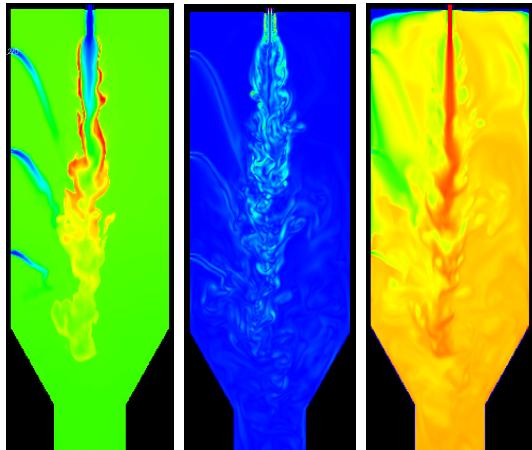
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Soot formation



- **Particle Transport**
- Pedel et al. C&F160 (2013)
- DQMOM
- 3 quadrature nodes
- 7 internal coordinates
  - Raw coal mass
  - Char mass
  - Particle enthalpy
  - 3 velocity components
- Transport equations for node weights and weighted abscissas.

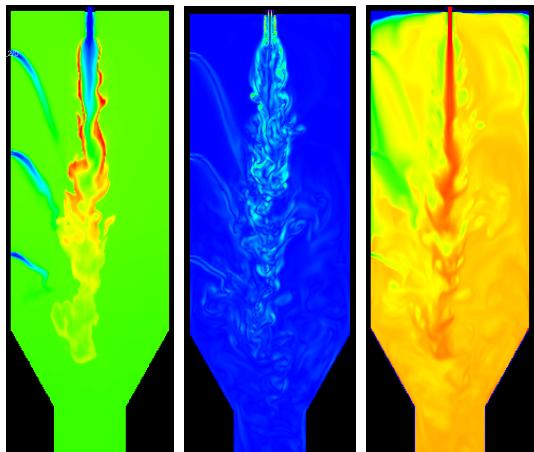
# Simulation: Models

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Particle Combustion

Soot formation



- Semi-empirical model
- Brown and Fletcher
  - *Energy and Fuels*, 12, 745-757, 1998
- Soot formation in coal systems from tar formation
  - $M_{tar} \sim 350$  g/mol

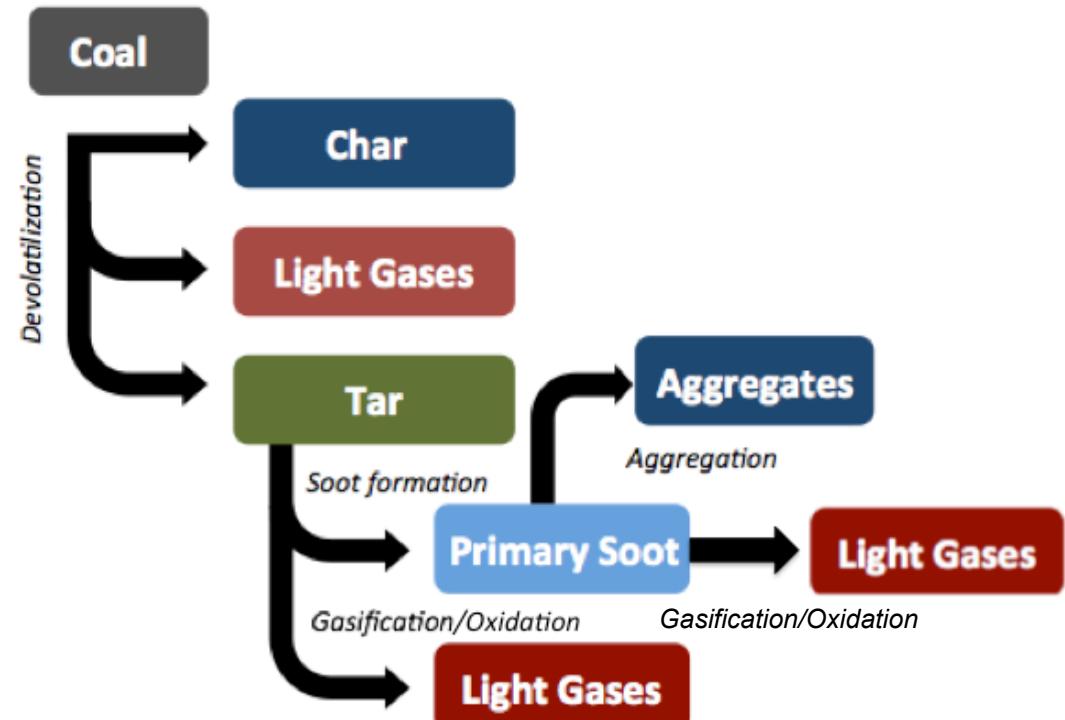
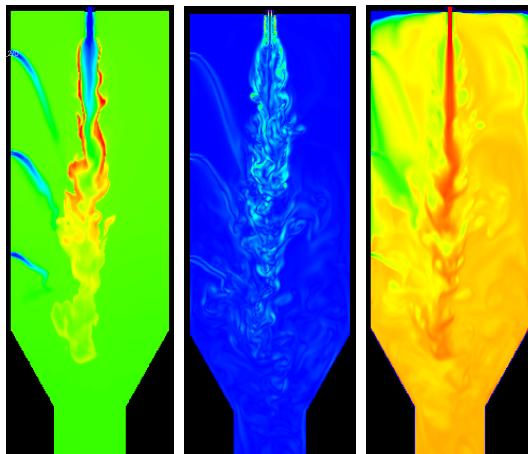
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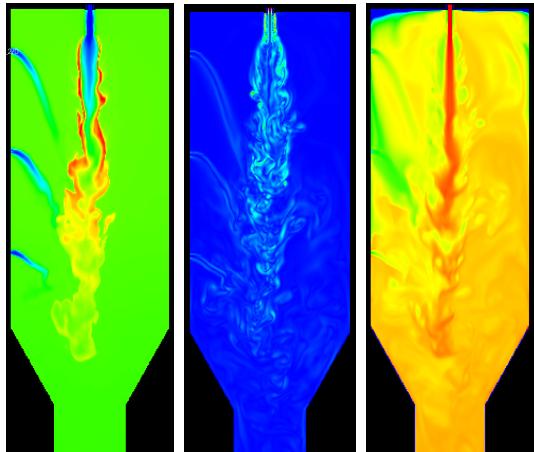
# Simulation: Models

Radiation

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Soot formation



- Transport tar and two soot moments

**Tar mass**

$$\frac{\partial \bar{\rho} \tilde{Y}_T}{\partial t} + \nabla \cdot (\bar{\rho} \tilde{\mathbf{v}} \tilde{Y}_T) + \nabla \cdot (\bar{\rho} \widetilde{\mathbf{v}'' Y_T''}) = \overline{S_{Y_T}}$$

$$S_{Y_{tar}} = form_{tar} - form_{soot} - gasif_{tar} - oxid_{tar}$$

**Soot mass**

$$\frac{\partial \bar{\rho} \tilde{Y}_s}{\partial t} + \nabla \cdot (\bar{\rho} \tilde{\mathbf{v}} \tilde{Y}_s) + \nabla \cdot (\bar{\rho} \widetilde{\mathbf{v}'' Y_s''}) = \overline{S_{Y_s}}$$

$$S_{Y_s} = form_{soot} - oxid_{soot} - gasif_{soot}$$

**Number density**

$$\frac{\partial \bar{\rho} \tilde{N}_s}{\partial t} + \nabla \cdot (\bar{\rho} \tilde{\mathbf{v}} \tilde{N}_s) + \nabla \cdot (\bar{\rho} \widetilde{\mathbf{v}'' N_s''}) = \overline{S_{N_s}}$$

$$S_{N_s} = nucleation - aggregation$$

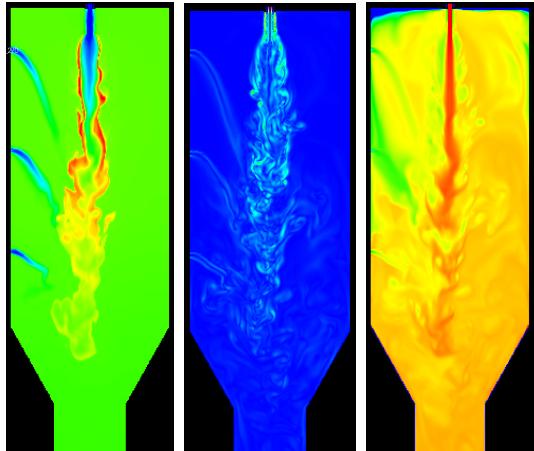
# Simulation: Models

Radiation

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Soot Oxidation

Lee oxidation model

$$oxid_{soot} = \frac{SA_{soot} * P_{O_2}}{T^{1/2}} \cdot A_{O_2} \cdot \exp\left(\frac{-E_{O_2}}{R_{gas} T}\right)$$

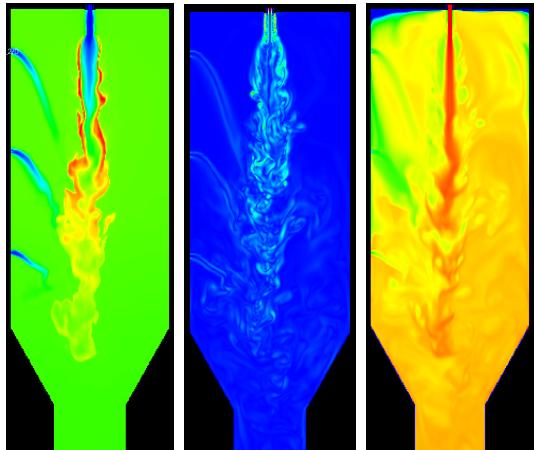
# Simulation: Models

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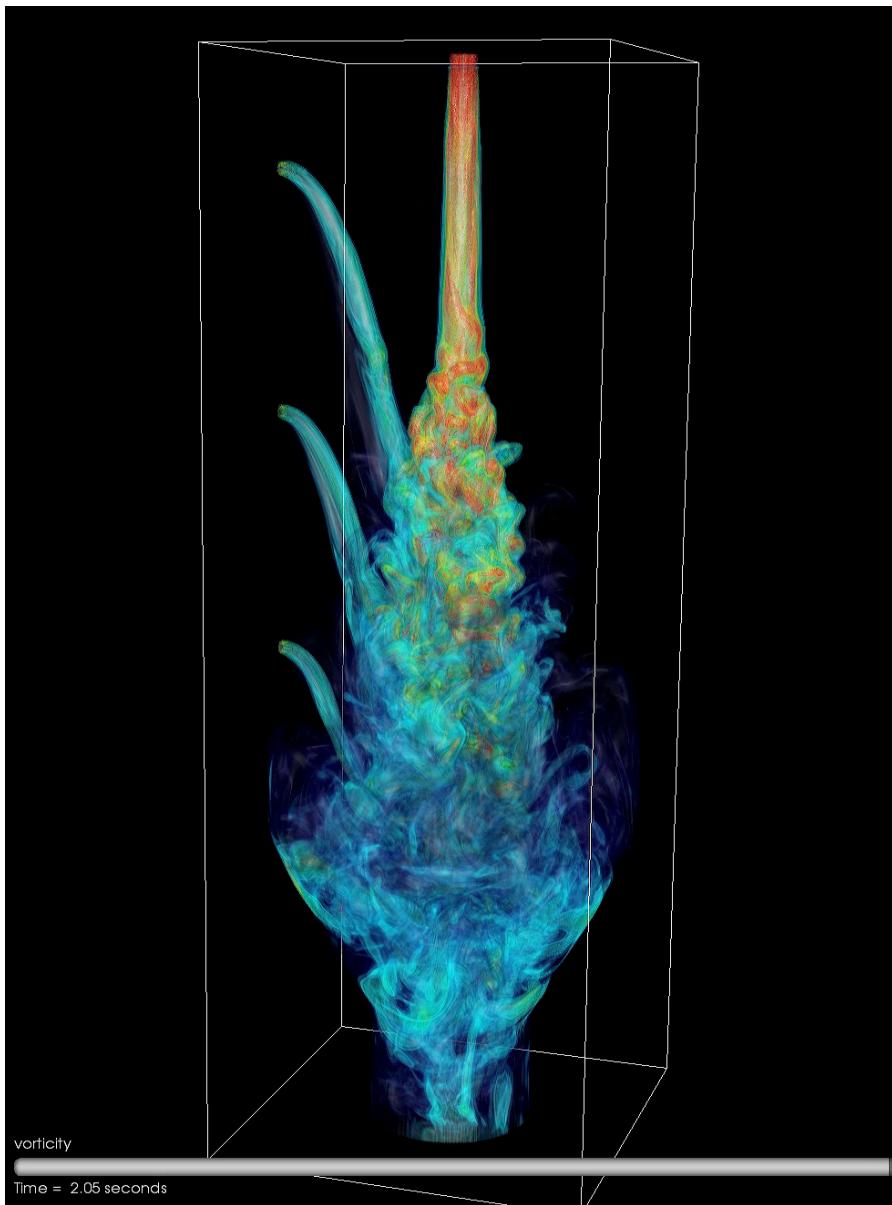
Soot Oxidation

Lee oxidation model

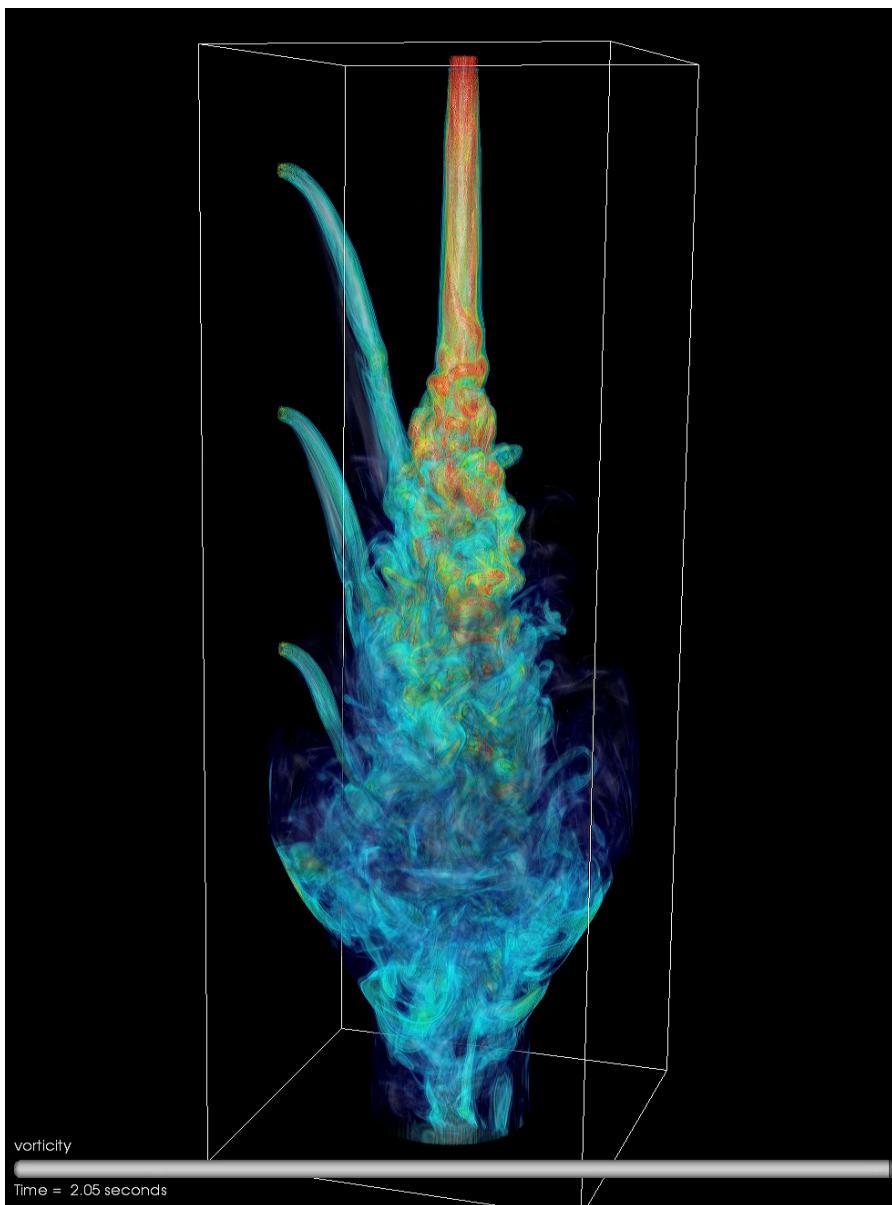
$$oxid_{soot} = \frac{SA_{soot} * P_{O_2}}{T^{1/2}} \cdot A_{O_2} \cdot \exp\left(\frac{-E_{O_2}}{R_{gas}T}\right)$$

- Data limited to temperature range that Lee took his measurements
- Assumes that oxidation happens by O<sub>2</sub> molecule only
- Experiments only took into account input

# Global Jet Structure—Vorticity

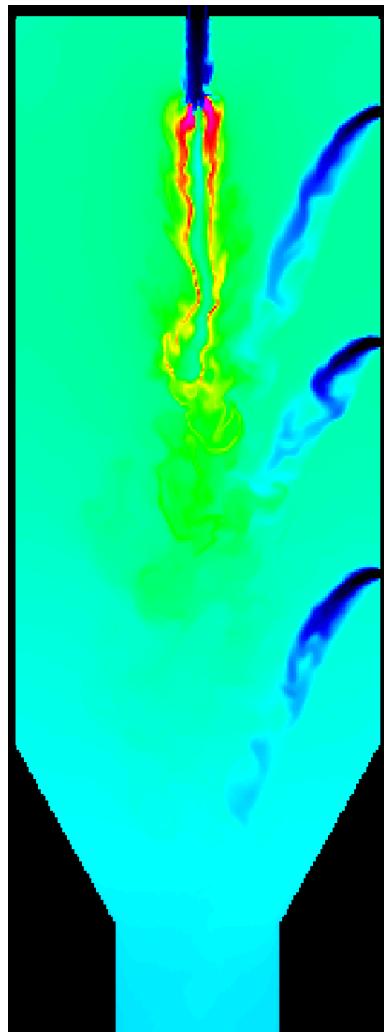
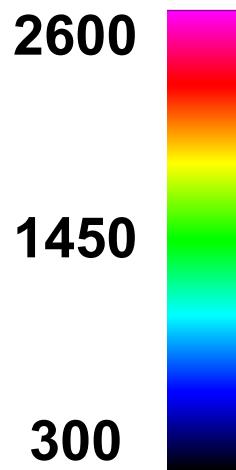


# Global Jet Structure—Vorticity



# Sufco Results

Temperature

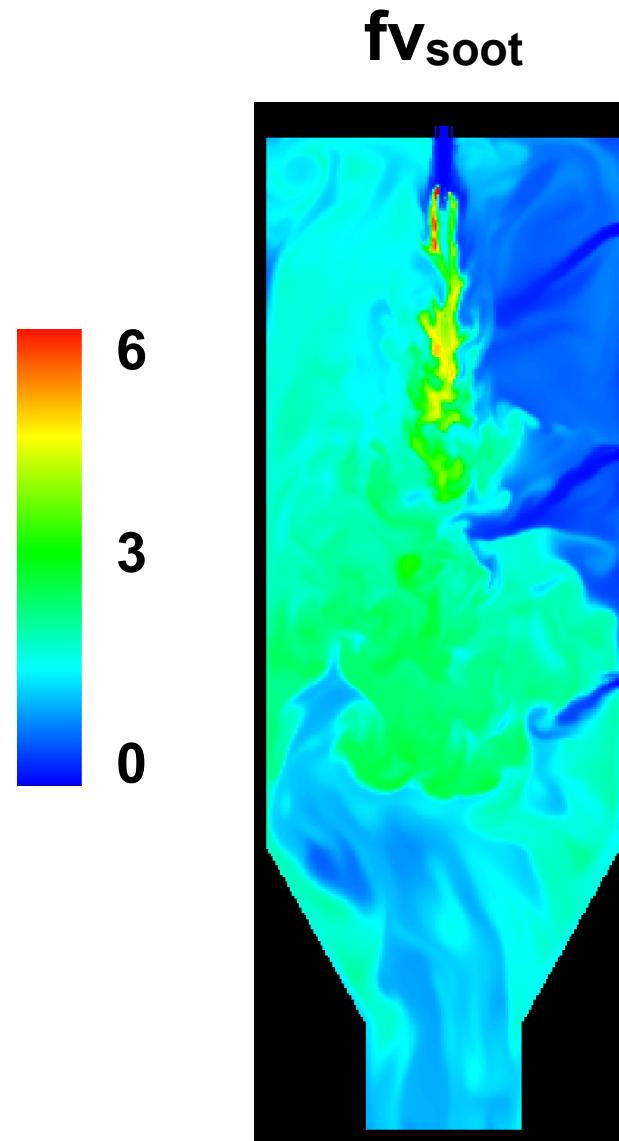


$Y_{O_2}$



# Gasification of Soot

- High soot concentration
- Soot is dispersed throughout the domain
- This was not observed in the experiments
- Neglecting soot gasification
- Not a good assumption for oxy-fired conditions with high CO<sub>2</sub> concentrations.

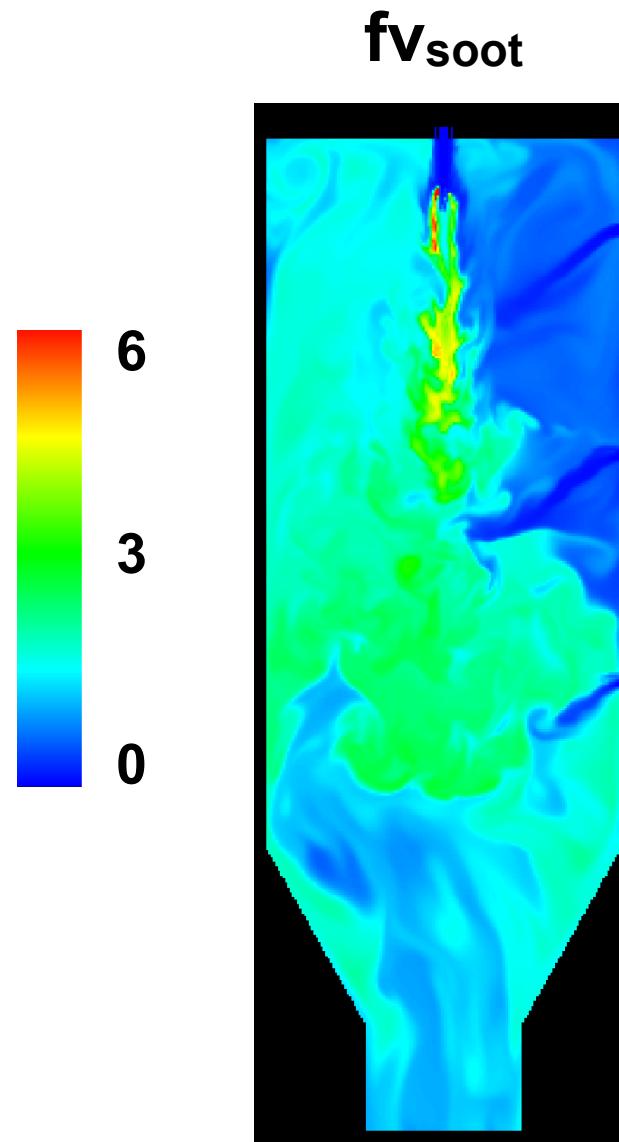


# Gasification of Soot

- Preliminary soot gasification model added.

$$S_{gasif} = \rho_s X_{CO_2} k_{gs} \exp(-E_{gs}/RT)$$

- Qin K., *Characterization of Residual Particulates from Biomass Entrained Flow Gasification*, Energy and Fuels 27:263-270 (2013)

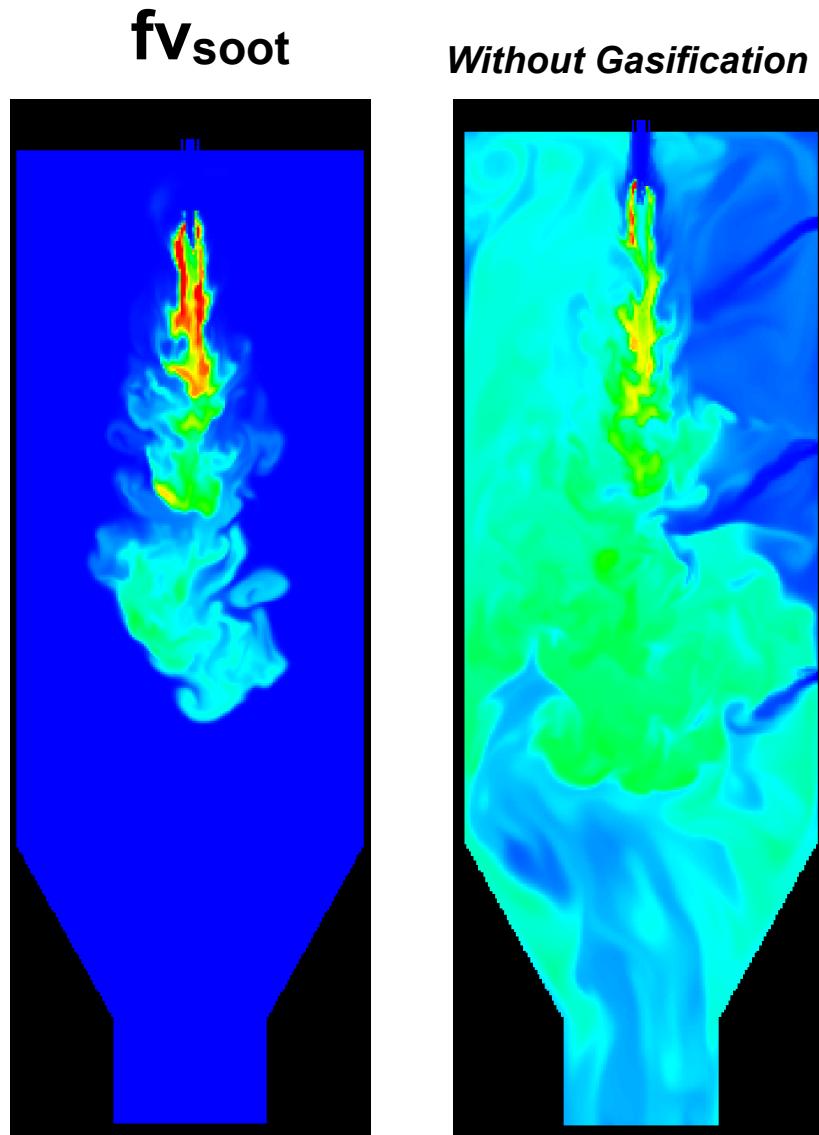


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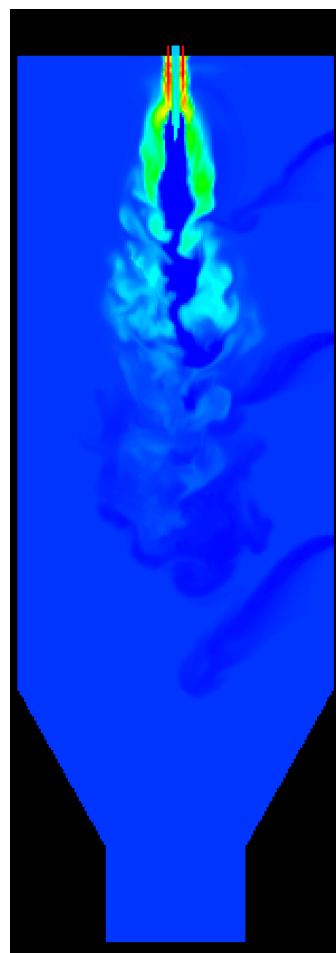
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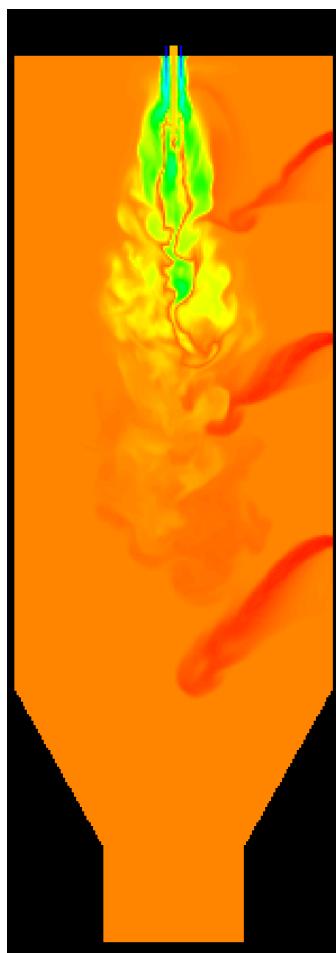
$Y_{O_2}$

1.0  
0.5  
0

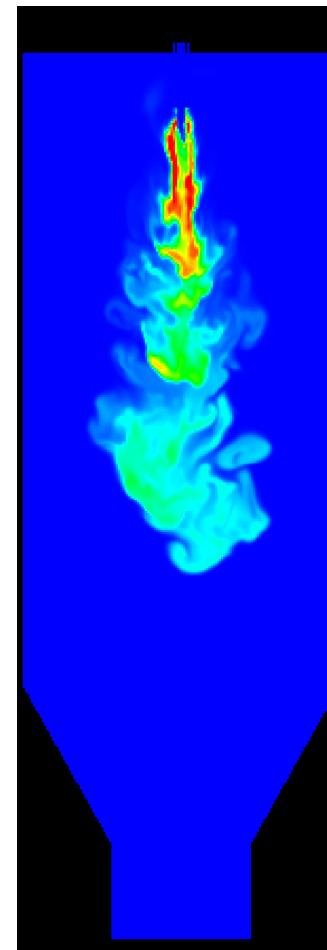


$Y_{CO_2}$

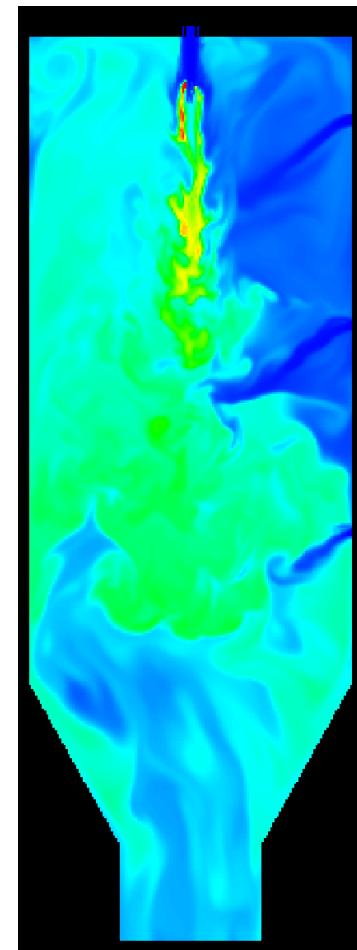
6  
3  
0



$f_{V_{soot}}$



*Without Gasification*



# Soot Gasification and Oxidation Rates

- A detailed Bayesian analysis was used to find optimal soot gasification and oxidation rates.
- **Oxidation**
  - O<sub>2</sub>, OH
  - 13 studies included
  - Premixed, nonpremixed, TGA
  - Parameters: A<sub>O<sub>2</sub></sub>, E<sub>O<sub>2</sub></sub>, A<sub>OH</sub>

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

study	data points	oxidizing agent	experiment	temp (K)
Fenimore and Jones, 1967 <sup>29</sup>	3	O <sub>2</sub> and OH	premixed ethylene flame	1530–1710
Neoh et al., 1981 <sup>30</sup>	14	O <sub>2</sub> and OH	laminar methane diffusion flame	1768–1850
Ghiassi et al., 2016 <sup>17</sup>	54	O <sub>2</sub> and OH	premixed varied-fuel flame	1265–1570
Kim et al., 2004 <sup>31</sup>	2	O <sub>2</sub> and OH	laminar ethylene diffusion flame	1735–1740
Kim et al., 2008 <sup>32</sup>	3	O <sub>2</sub> and OH	laminar ethylene diffusion flame	1892–1916
Garo et al., 1990 <sup>22</sup>	6	O <sub>2</sub> and OH	laminar methane diffusion flame	1809–1851
Puri et al., 1994 <sup>33</sup>	15	O <sub>2</sub> and OH	laminar methane diffusion flame	1236–1774
Xu et al., 2003 <sup>34</sup>	15	O <sub>2</sub> and OH	laminar mixed hydrocarbon diffusion flames	1775–1900
Lee et al., 1962 <sup>9</sup>	29	O <sub>2</sub> and OH	laminar mixed hydrocarbon diffusion flame	1315–1660
Chan et al., 1987 <sup>35</sup>	14	O <sub>2</sub>	TGA	780–1210
Higgins et al., 2002 <sup>36</sup>	28	O <sub>2</sub>	tandem differential mobility analyzer	773–1348
Kalogirou and Samaras, 2010 <sup>28</sup>	6	O <sub>2</sub>	TGA	823–973
Sharma et al., 2012 <sup>37</sup>	18	O <sub>2</sub>	TGA	823–923

# Soot Gasification and Oxidation Rates

- A detailed Bayesian analysis was used to find optimal soot gasification and oxidation rates.
- **Gasification**
  - CO<sub>2</sub>, H<sub>2</sub>O
  - 8 studies included
  - Parameters: A<sub>CO<sub>2</sub></sub>, E<sub>CO<sub>2</sub></sub>, A<sub>H<sub>2</sub>O</sub>, n, E<sub>H<sub>2</sub>O</sub>

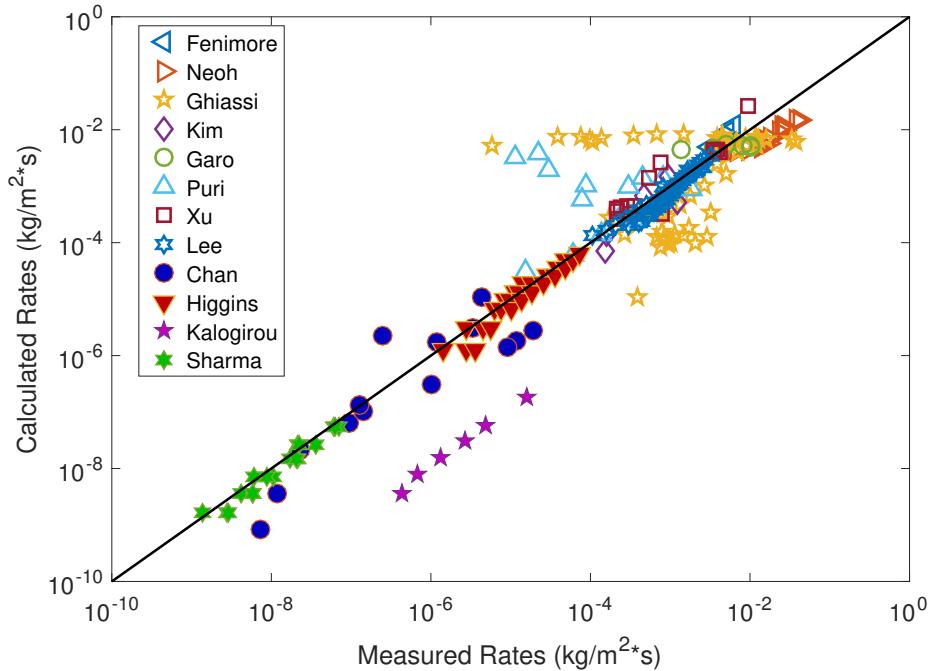
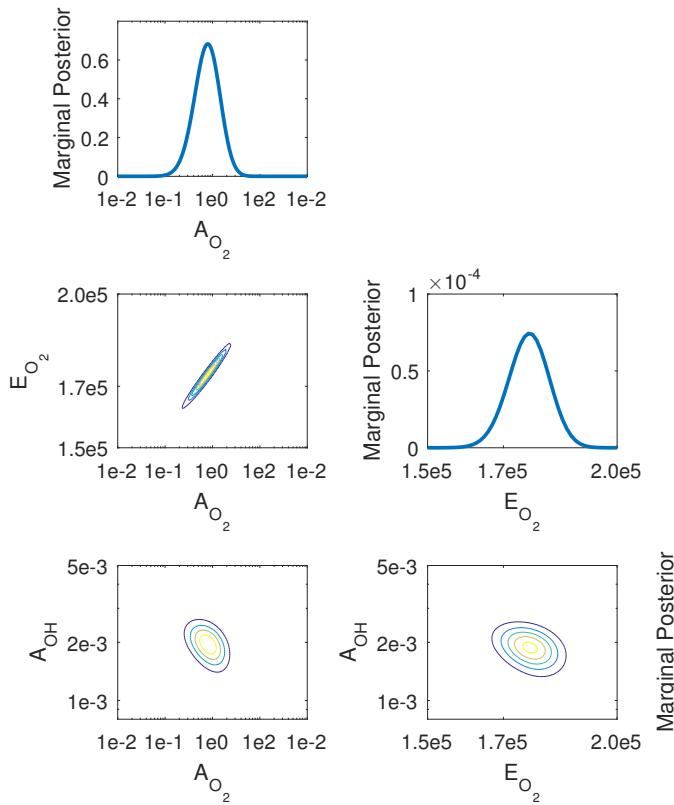
study	no. of data points	gasifying agent	temp (K)
Abian et al., 2012 <sup>16</sup>	14	CO <sub>2</sub>	1132–1650
Kajitani et al., 2010 <sup>26</sup>	6	CO <sub>2</sub>	1123–1223
Qin et al., 2013 <sup>20</sup>	3	CO <sub>2</sub>	305–1261
Otto et al., 1980 <sup>42</sup>	2	H <sub>2</sub> O and CO <sub>2</sub>	1066–1160
Arnal et al., 2012 <sup>43</sup>	6	H <sub>2</sub> O	1273
Chhiti et al., 2013 <sup>44</sup>	28	H <sub>2</sub> O	1373–1673
Neoh et al., 1981 <sup>30</sup>	14	H <sub>2</sub> O	1777–1815
Xu et al., 2003 <sup>34</sup>	15	H <sub>2</sub> O	1770–1840

$$r_{CO_2} = A_{CO_2} P_{CO_2}^{0.5} T^2 \exp\left(\frac{-E_{CO_2}}{RT}\right)$$

$$r_{H_2O} = \frac{A_{H_2O} P_{H_2O}^n}{T^{1/2}} \exp\left(\frac{-E_{H_2O}}{RT}\right)$$

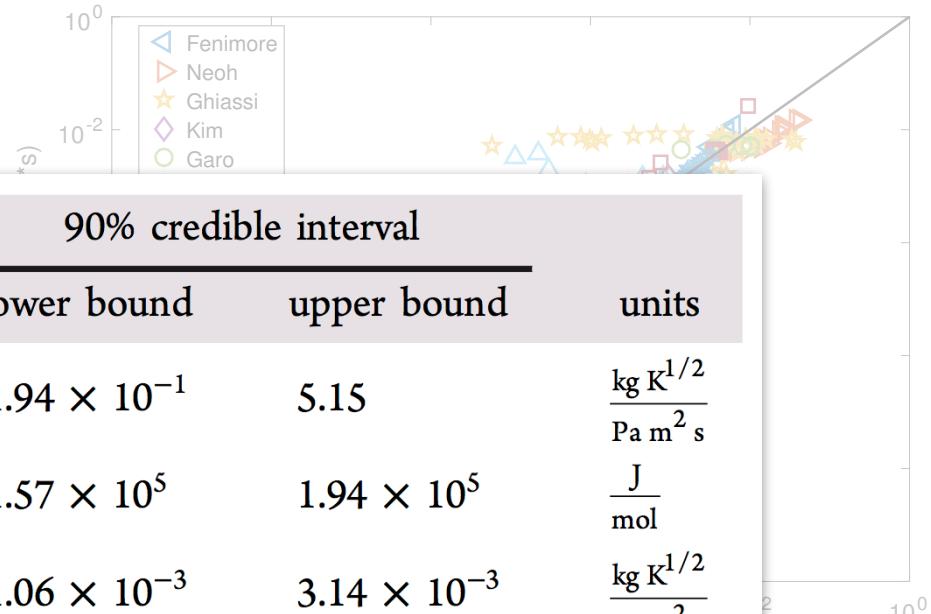
# Oxidation Rates

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

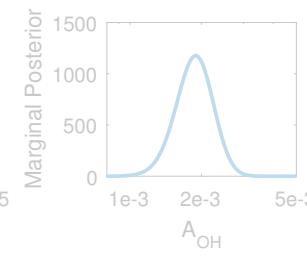
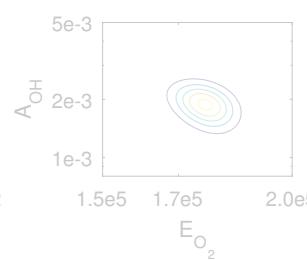
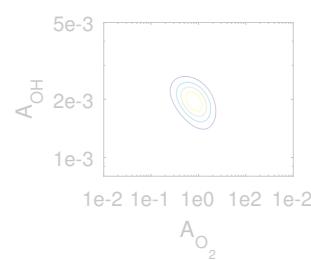
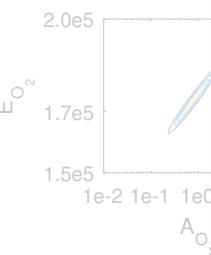
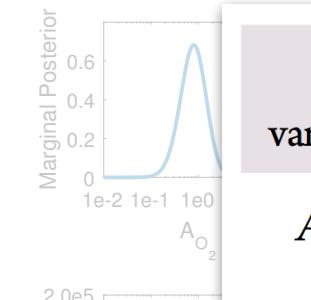


# Oxidation Rates

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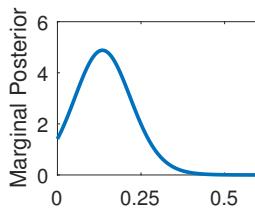
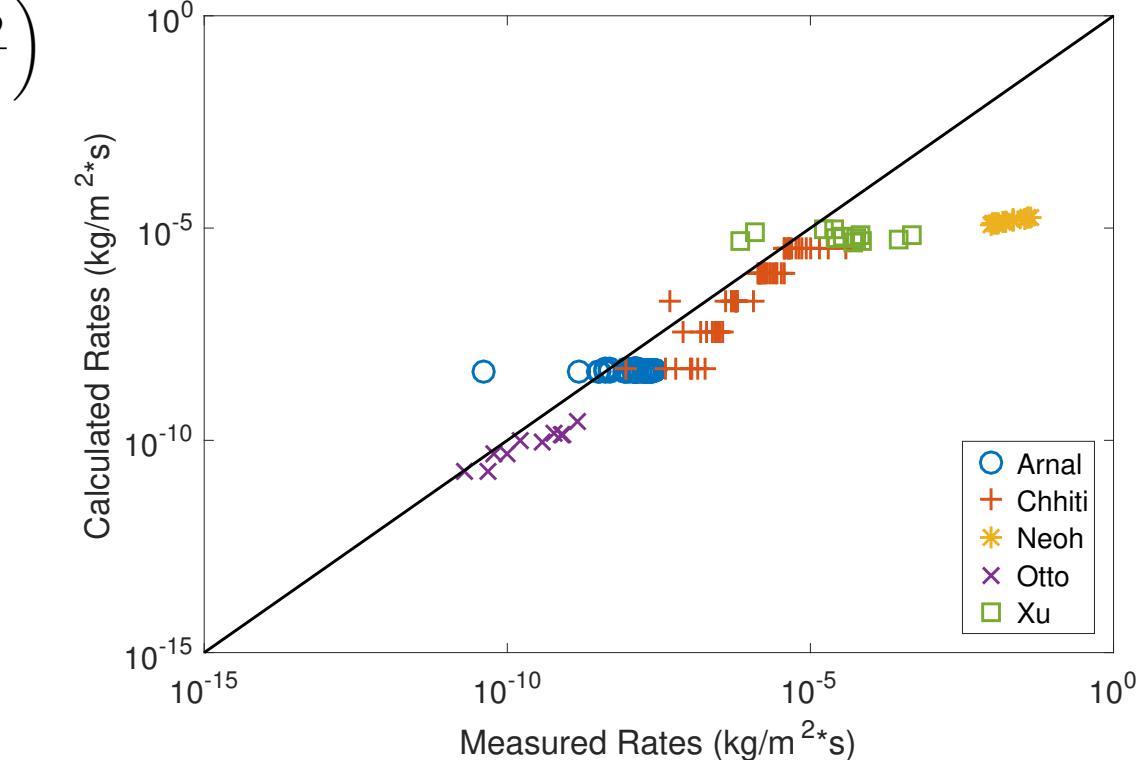
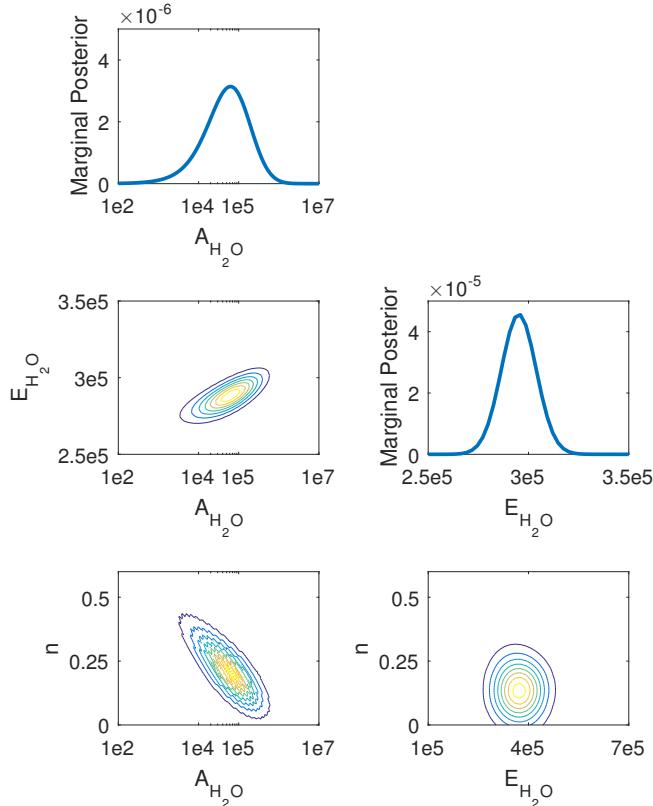


90% credible interval				
variable	value	lower bound	upper bound	units
$A_{O_2}$	$7.98 \times 10^{-1}$	$1.94 \times 10^{-1}$	$5.15$	$\frac{\text{kg K}^{1/2}}{\text{Pa m}^2 \text{s}}$
$E_{O_2}$	$1.77 \times 10^5$	$1.57 \times 10^5$	$1.94 \times 10^5$	$\frac{\text{J}}{\text{mol}}$
$A_{OH}$	$1.89 \times 10^{-3}$	$1.06 \times 10^{-3}$	$3.14 \times 10^{-3}$	$\frac{\text{kg K}^{1/2}}{\text{Pa m}^2 \text{s}}$



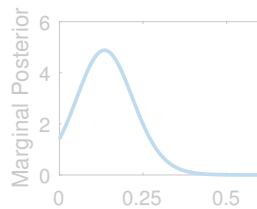
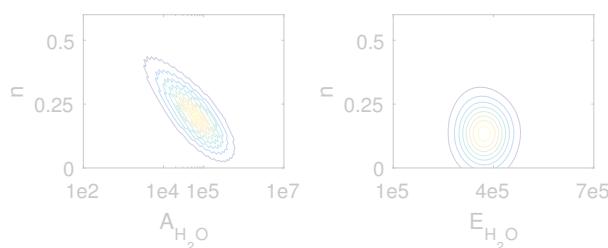
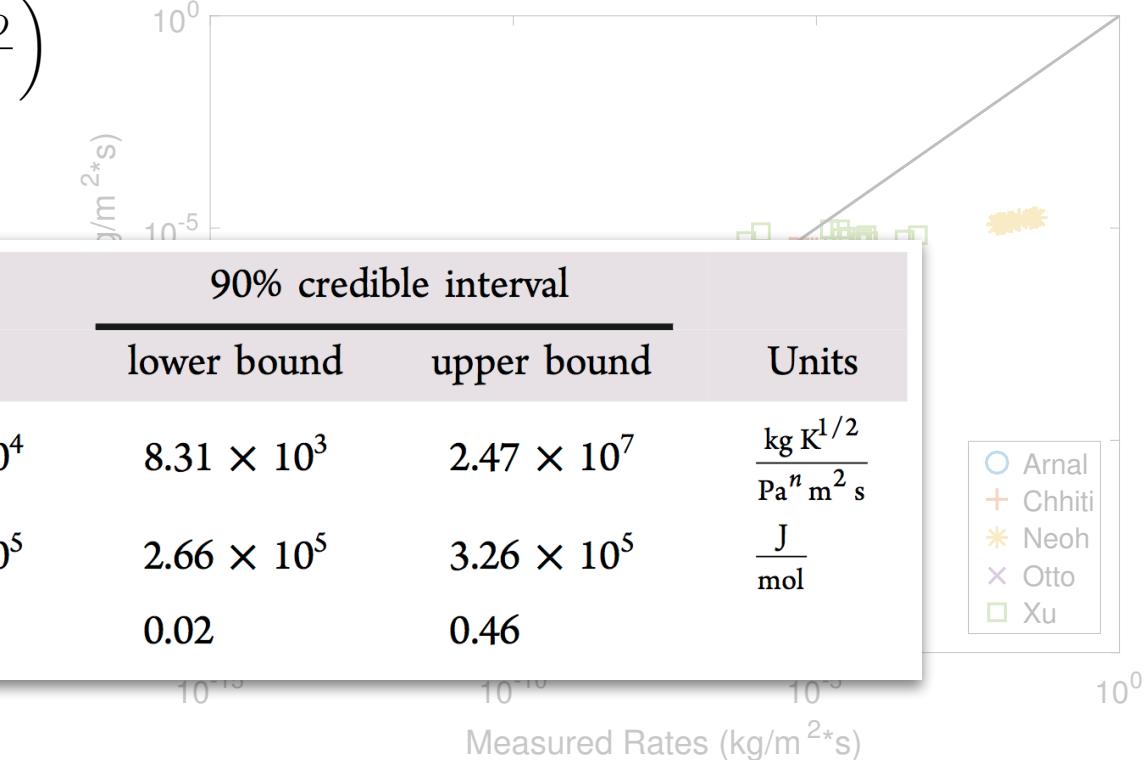
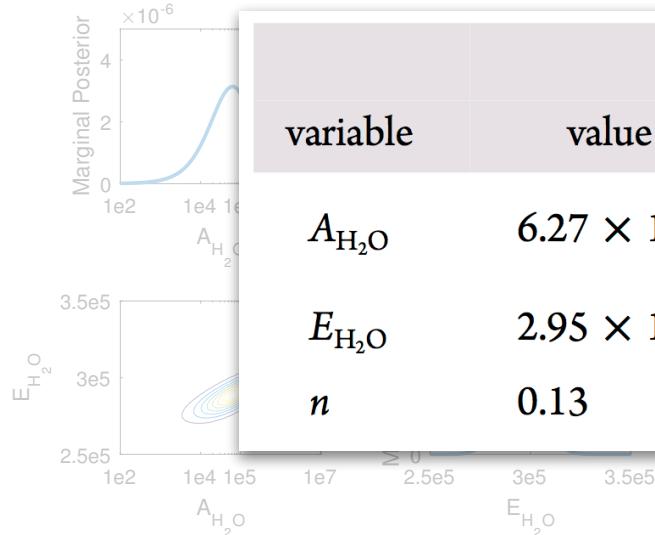
# H<sub>2</sub>O Gasification

$$r_{H_2O} = \frac{A_{H_2O} P_{H_2O}^n}{T^{1/2}} \exp\left(\frac{-E_{H_2O}}{RT}\right)$$



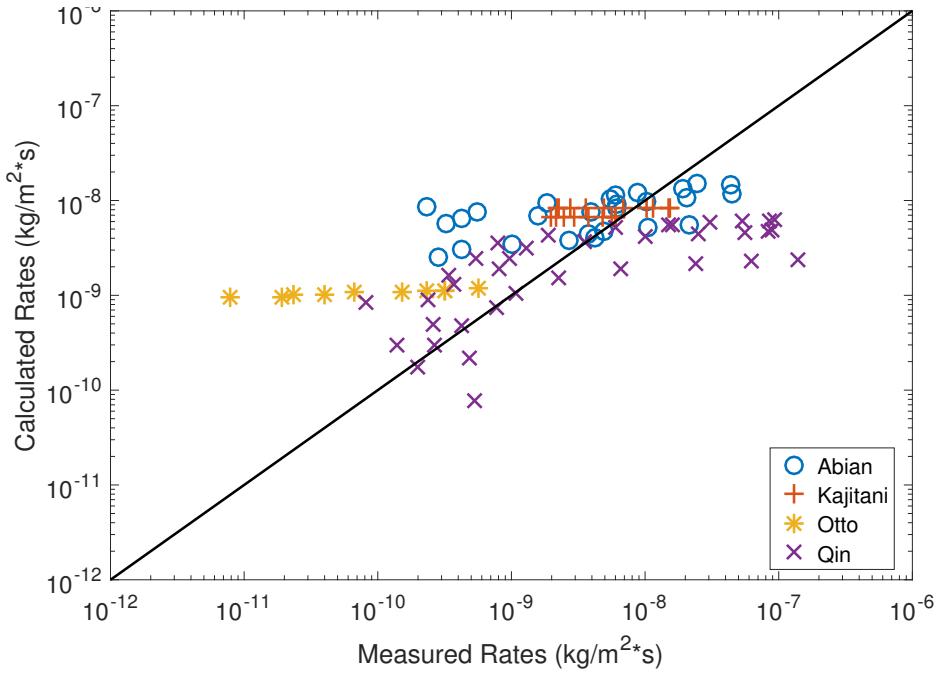
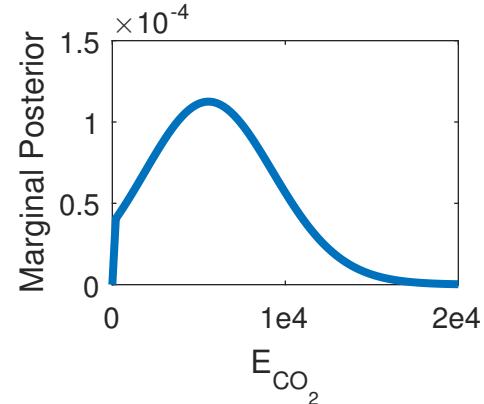
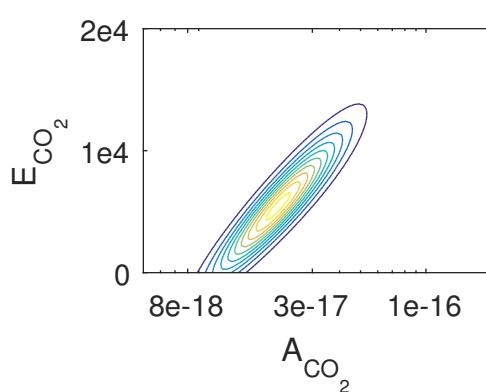
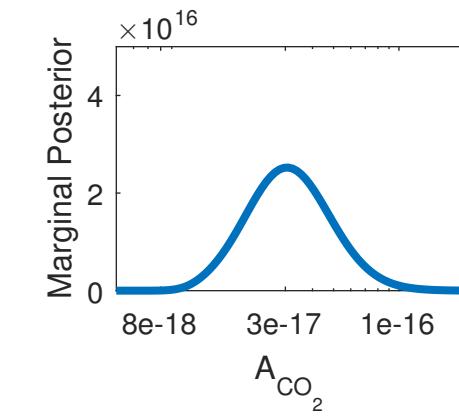
# H<sub>2</sub>O Gasification

$$r_{H_2O} = \frac{A_{H_2O} P_{H_2O}^n}{T^{1/2}} \exp\left(\frac{-E_{H_2O}}{RT}\right)$$



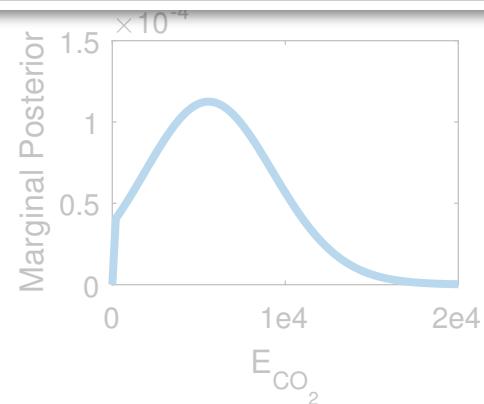
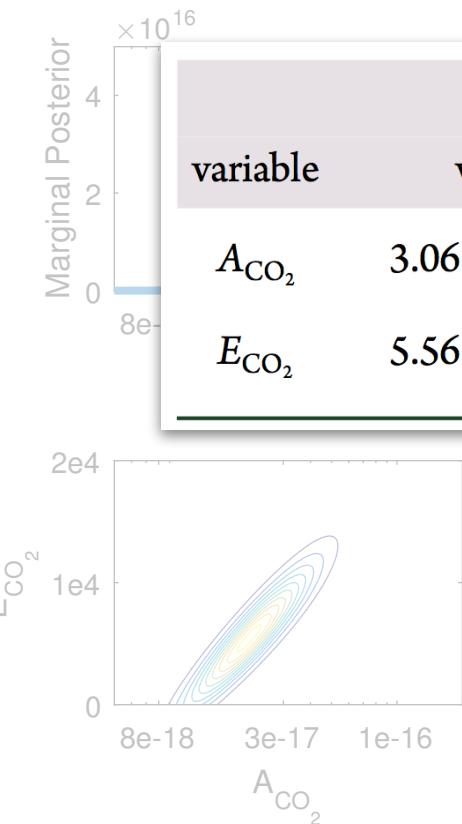
# CO<sub>2</sub> Gasification Rates

$$r_{CO_2} = A_{CO_2} P_{CO_2}^{0.5} T^2 \exp\left(\frac{-E_{CO_2}}{RT}\right)$$

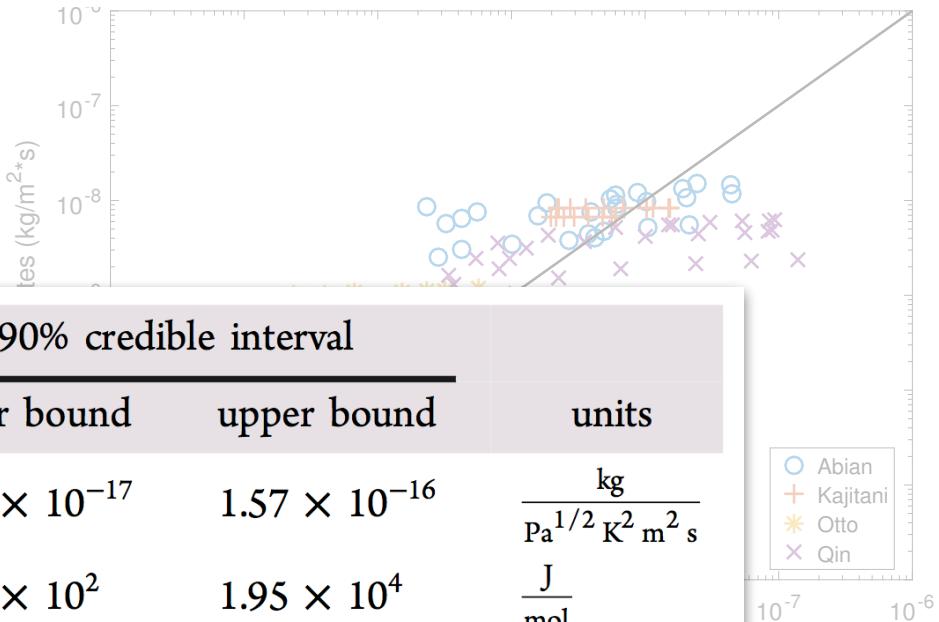


# CO<sub>2</sub> Gasification Rates

$$r_{CO_2} = A_{CO_2} P_{CO_2}^{0.5} T^2 \exp\left(\frac{-E_{CO_2}}{RT}\right)$$



90% credible interval				
variable	value	lower bound	upper bound	units
$A_{CO_2}$	$3.06 \times 10^{-17}$	$1.17 \times 10^{-17}$	$1.57 \times 10^{-16}$	$\frac{kg}{Pa^{1/2} K^2 m^2 s}$
$E_{CO_2}$	$5.56 \times 10^3$	$6.04 \times 10^2$	$1.95 \times 10^4$	$\frac{J}{mol}$

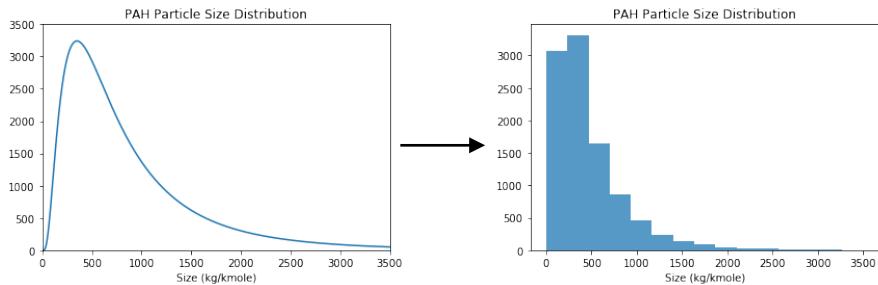


# Detailed Soot Model

- The Brown soot model is highly empirical
- Does not account for tar/PAH dynamics
- No soot growth
- Many existing soot models for gaseous combustion
  - Range from empirical to detailed
  - Nucleation, Growth, Coagulation, Oxidation
  - HACA, PAH condensation
  - Sectional, Method of Moments, monodispersed
- Develop a new physics-based soot model for coal combustion
  - Treat tar precursors with a sectional model.
  - Treat soot with MOMIC

# Detailed Soot Model

## Precursors



- Source terms for

- Formation: CPD model (coal), gas
- Surface growth: HACA
- Oxidation
- Gasification
- Thermal cracking
- Coagulation
- Soot nucleation

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

## Soot

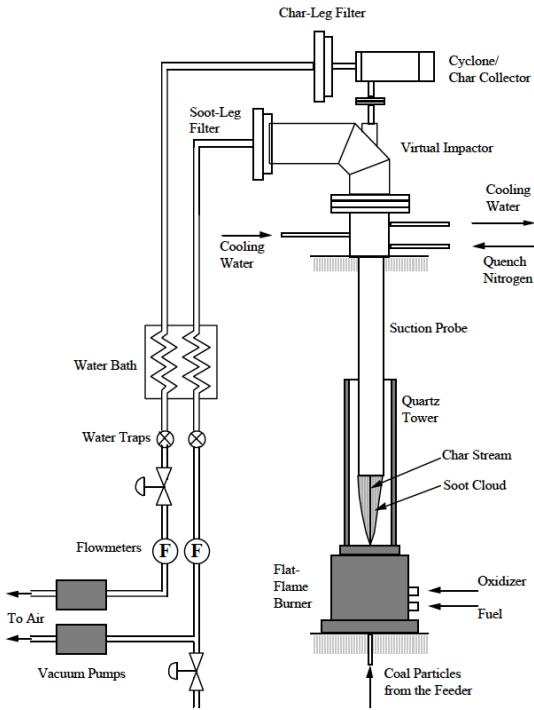
$$M_r = \int_0^{\infty} m_i^r N_i(m) dm$$

- Source terms

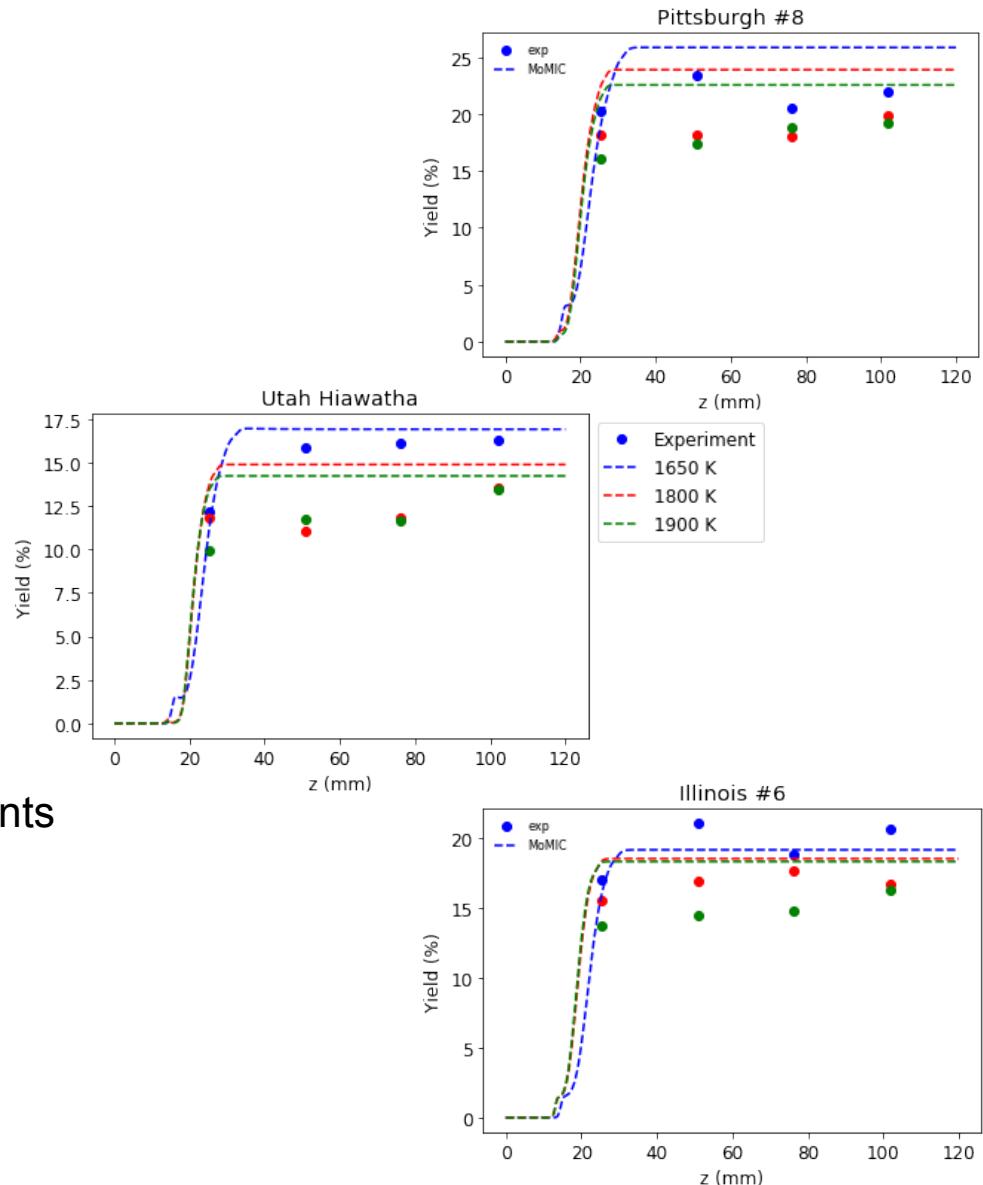
- Nucleation from Precursors
- Surface growth: HACA
- Surface growth: Precursors
- Oxidation
- Gasification
- Coagulation

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

# Model Validation



- BYU laminar flat flame burner experiments
- Jinliang Ma (1998)
- Equilibrium chemistry profile (ABF mechanism)
- CPD model predicts tar



# Conclusions

- LES of an oxy-fuel combustor was performed
- Simulations show need for soot gasification mechanism
- Soot gasification and oxidation study performed using Bayesian Statistics, with optimal rates found using 19 experiments.
- A new detailed soot model has been developed and validated.
- Ongoing LES simulations:
  - Quantify the impact of soot on radiative transfer.
  - Validate soot model against experimental data.
  - Compare detailed and empirical soot models in the pilot scale OFC reactor.