Reduced Chemical Mechanism for Chemical Looping Combustion System

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Barracuda Virtual Reactor Users' Conference 2019

For Energy and Environmental Solutions

REACTION ENGINEERING INTERNATIONAL

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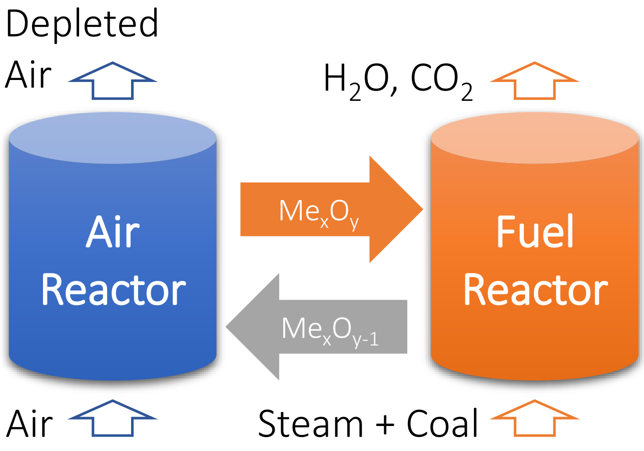
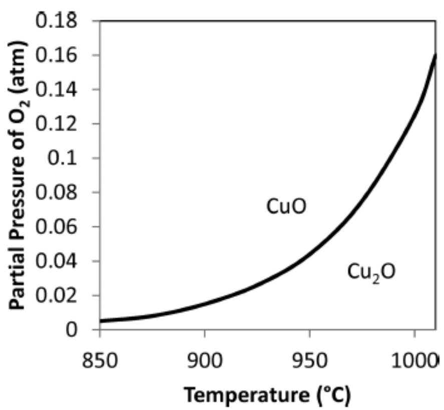
Reaction Engineering International

Privately held consulting firm recognized for independent analysis and evaluations involving a range of industrial reacting flow applications

- Technical focus on multi-phase, chemically reacting flows
- Serving the industries since 1990
- Affiliates in Asia and Europe
- Established capabilities include advanced modeling, process evaluation and testing

Chemical Looping Combustion with Oxygen Uncoupling





- Avoid coal gasification step by introducing metal oxide that spontaneously releases O_2 in fuel reactor
- Cu_2O/CuO equilibrium lies within CLC operating temperature

$$2\ CuO\ (s) \rightleftarrows Cu_2O\ (s) + \tfrac{1}{2}\ O_2\ (g)$$

- REI collaborates with the University of Utah and CPFD to improve chemistry description for CFD simulation under the DOE project

Coal Combustion and…

- Sulfur containing species can interact with the oxygen carrier:
  - **formation of sulfide or sulfate**
    - **deactivation** of the OC reducing combustion efficiency
    - **agglomeration** of the OC due to the low melting points hindering the solids circulation pattern between the interconnected fluidized bed reactors
  - **release of SO_2** in the gas outlet, causing emission and flue gas treatment concerns
- NO_x and N_2O: greenhouse gas, interaction with ozone chemistry

Detailed vs. Reduced Chemistry

Practical Combustion Chemistry:

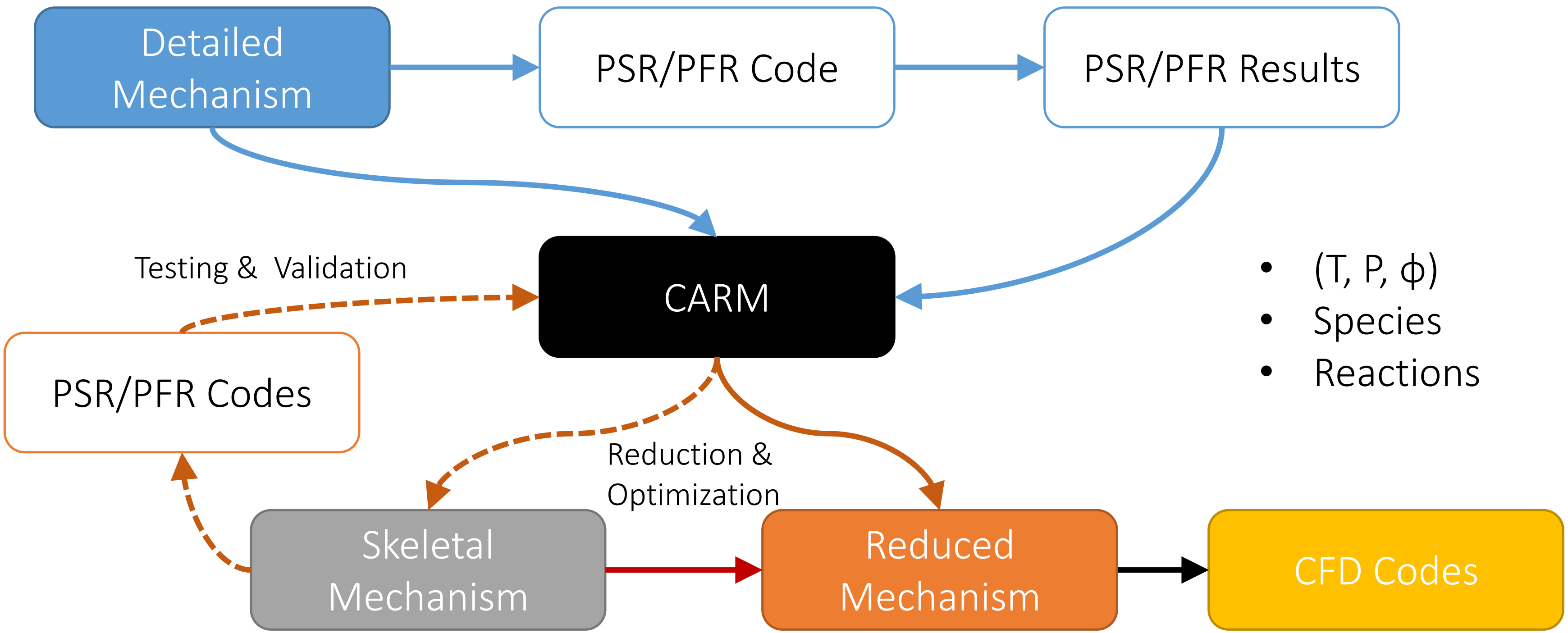
- Dozens to hundreds of species
- Hundreds to thousands of reactions
- Detailed chemistry not feasible for CFD simulation of practical devices
- Present simplified schemes may not work under a sufficiently broad range of conditions

Reduced chemical kinetic mechanism is proposed

CARM (Computer Aided Reduction Method)

- Software developed by Prof. J.-Y. Chen and students at U.C. Berkeley.
- Objectives:
  - reduce the number of species
  - maintain behavior of original system

Reduced Mechanism Development



- (T, P, ϕ)
- Species
- Reactions

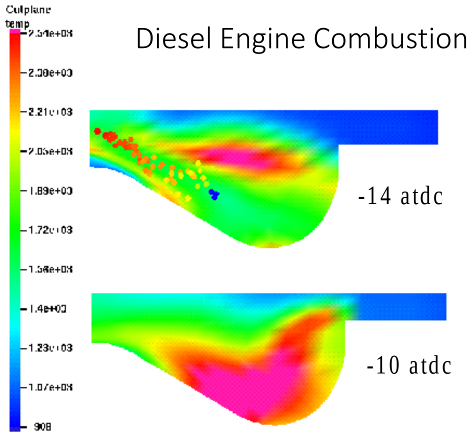
Mechanism Reduction/Optimization

- Assumes some species are in steady state (SS), (net rate of production is negligibly small)
- Minimizes error vs. detailed chemistry over a prescribed parameter space (e.g. T, P, ϕ) of simple reactor models for the fixed number of species
- Objective function: reduced mechanism error for selected outputs (T, species concentrations, ignition delay, etc.)
- Major species can be specified to never be in SS
- Minor species can be specified to always be in SS
- Produces subroutine that solves for SS species and reaction rates

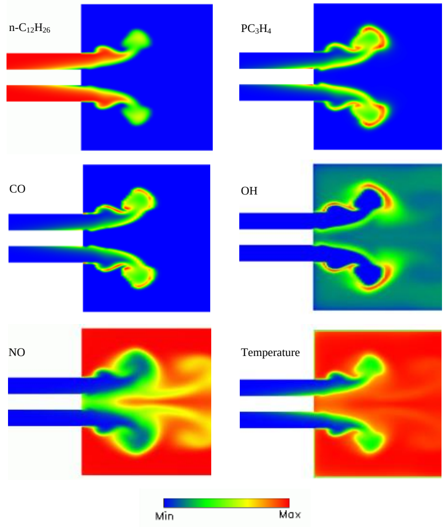
Applications

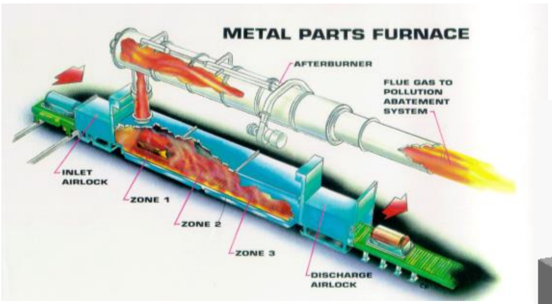
- NOx control
- SOx control
- Hydrocarbon combustion
- Hazardous chemical incineration

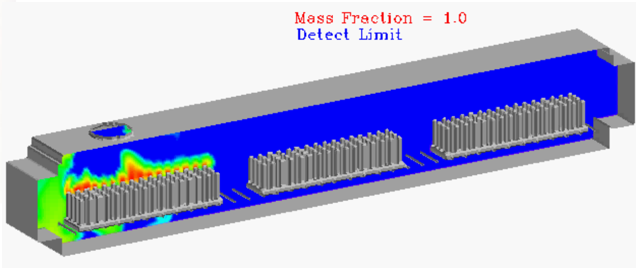
Diesel Engine Combustion



LES of Gas Turbine Combustor Burning JP-8

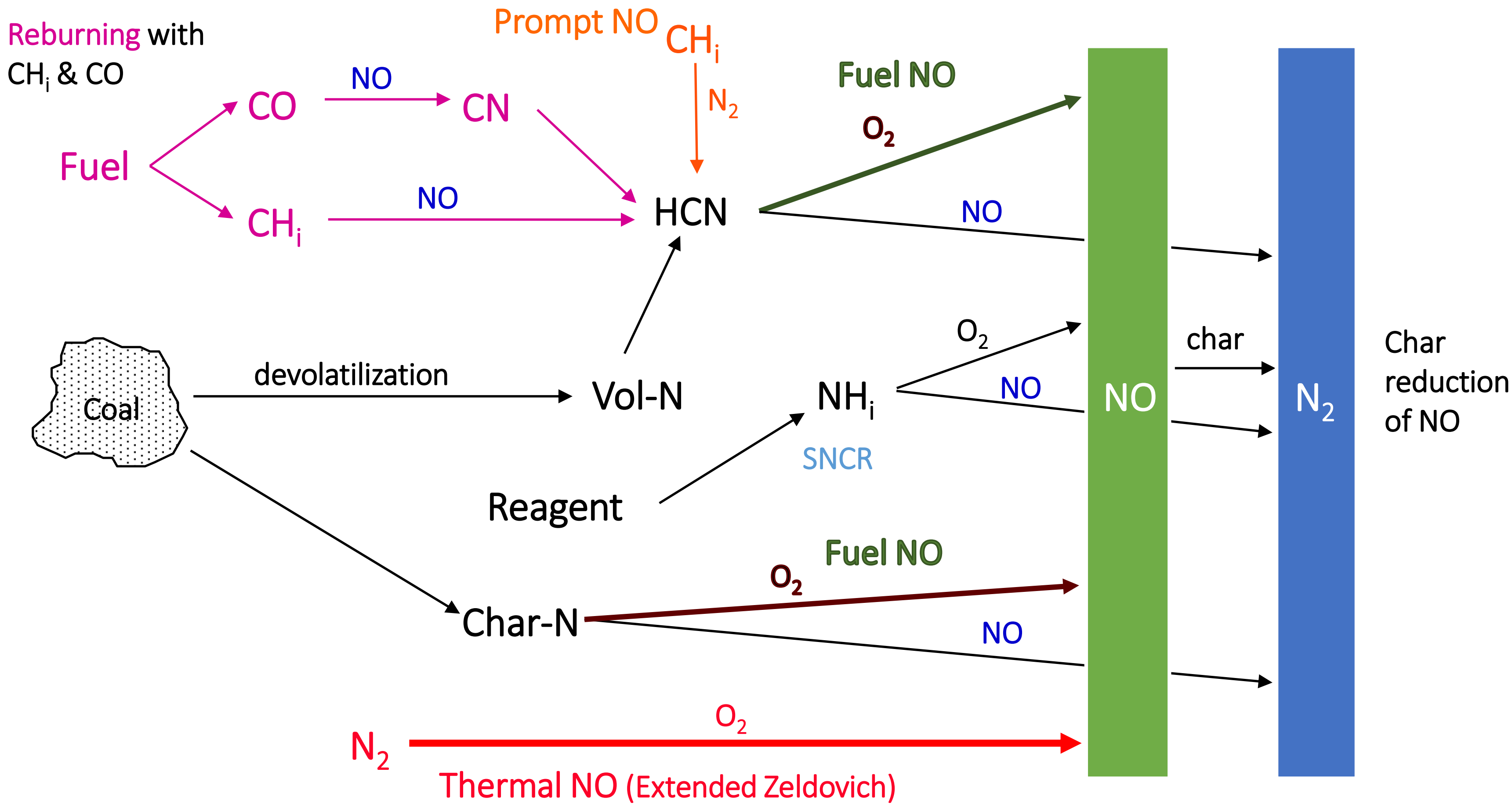






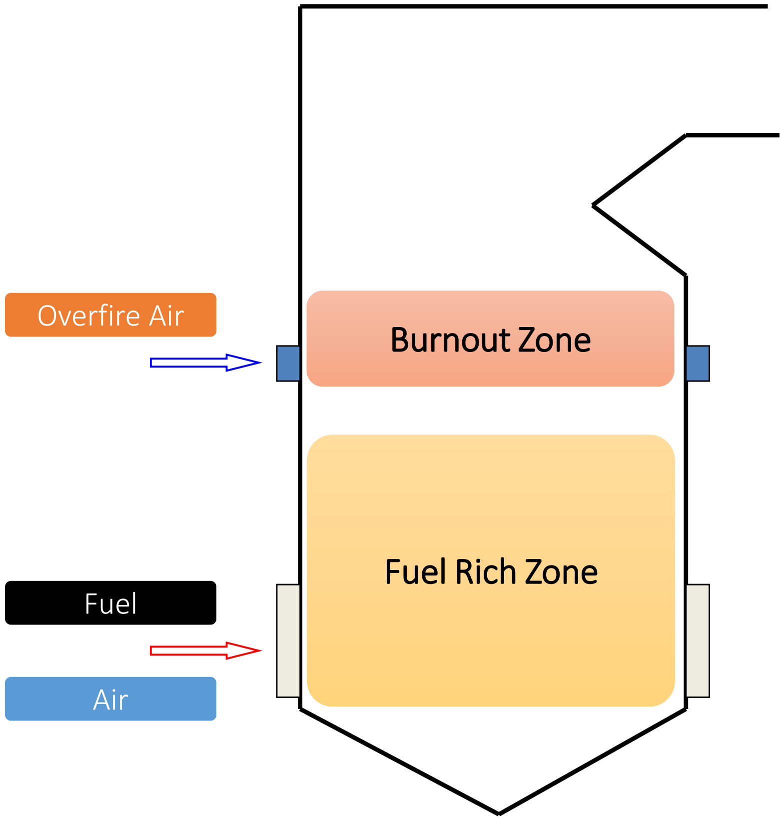
Reduced Chemical Mechanism in NOx Control

NOx Chemistry Pathway

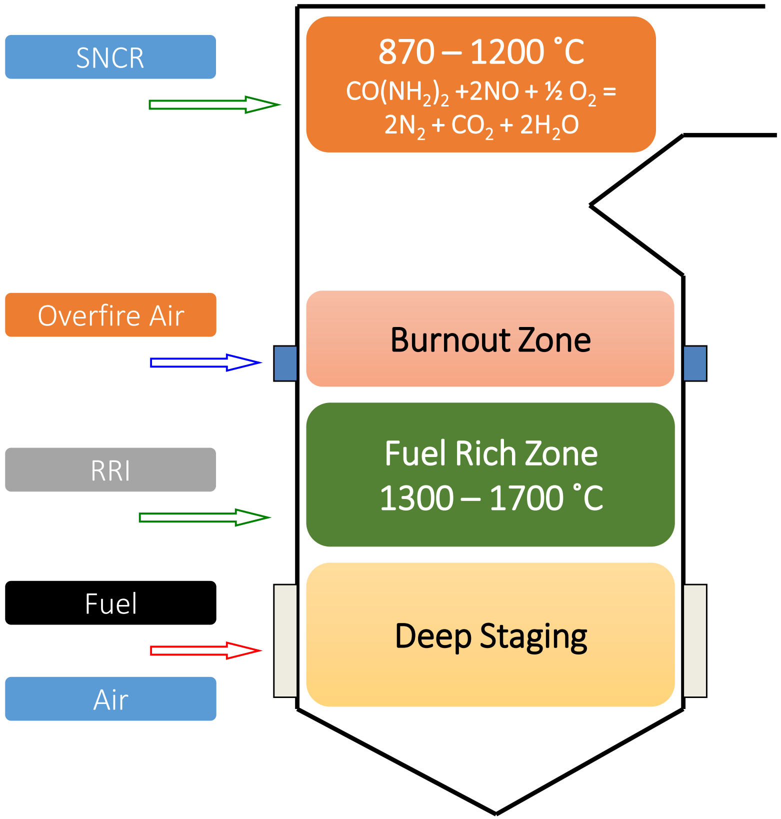


NOx Control Strategies in Boiler

Air Staging (OFA)

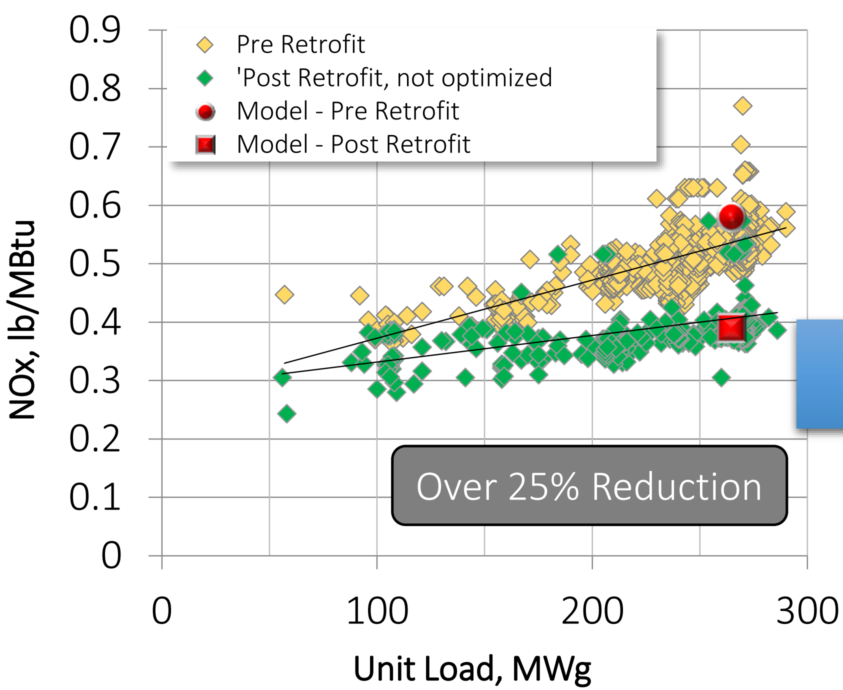


Advanced Layered Technology Approach (ALTA)

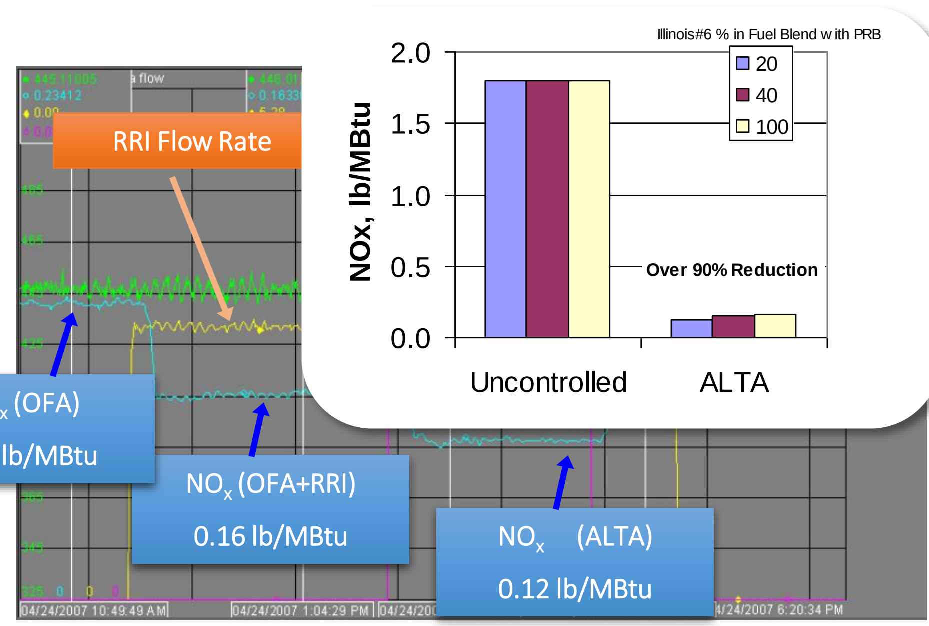


Testing Results

Air Staging (OFA)



Advanced Layered Technology Approach (ALTA)



Chemistry Setup for CLOU Simulation

Chemistry Setup

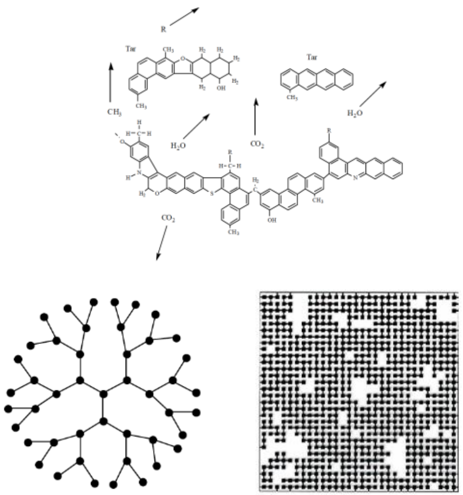
Original Setup is based on M. A. Hamilton, K. J. Whitty and J. S. Lighty, "Incorporating Oxygen Uncoupling Kinetics into Computational Fluid Dynamic Simulations of a Chemical Looping System," *Energy Technol.,* no. 4, pp. 1-11, 2016.

	Original Setup
Water evaporation	■
Coal devolatilization	■ (CH_4, H_2, CO, CO_2)
CO oxidation	■
Water gas shift reaction	■
H_2 oxidation	■
CH_4 oxidation	■
Cu_2O oxidation	■
CuO decomposition	■
Char oxidation	■
Steam gasification	-
CO_2 gasification	-
C(g) oxidation	-
Char methanation	-
S and N chemistry	-

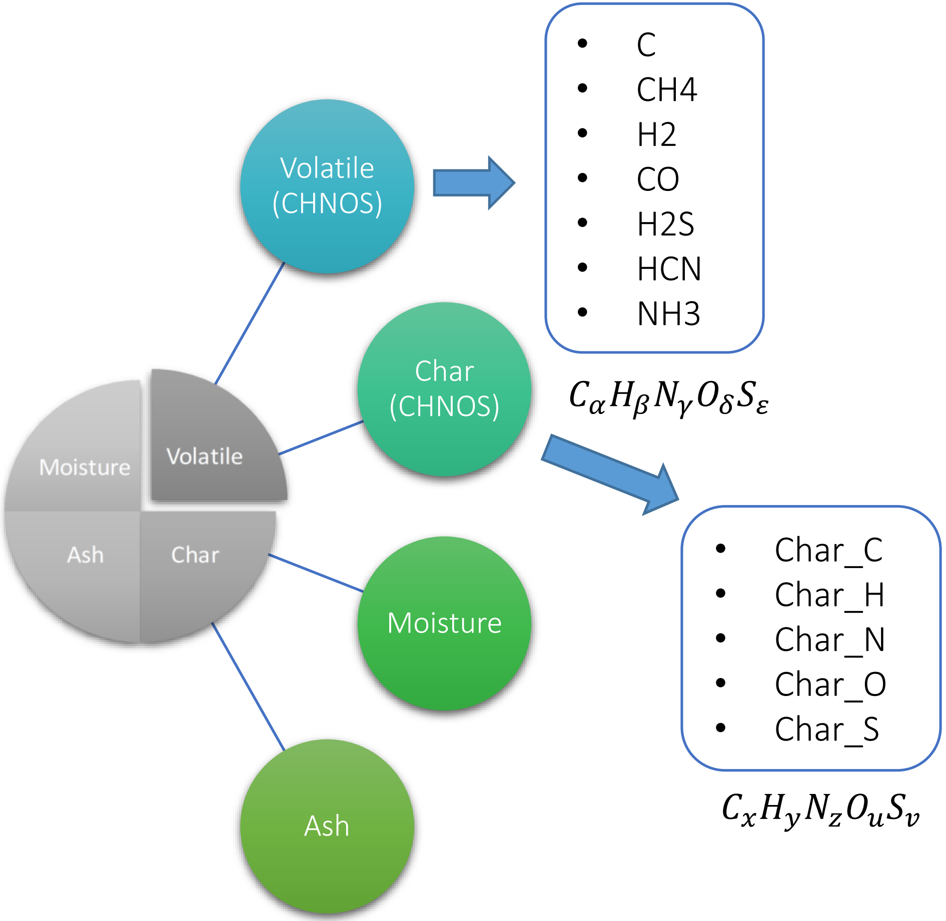
More detailed approach is needed to evaluate chemistry behavior

Mass Balance in Model Setup

Pre-defined yields calculated by CPD* under relevant thermal conditions



*Grant, D. M., R. J. Pugmire, T. H. Fletcher, and A. R. Kerstein, "A Chemical Model of Coal Devolatilization Using Percolation Lattice Statistics," Energy and Fuels, 3, 175 (1989).



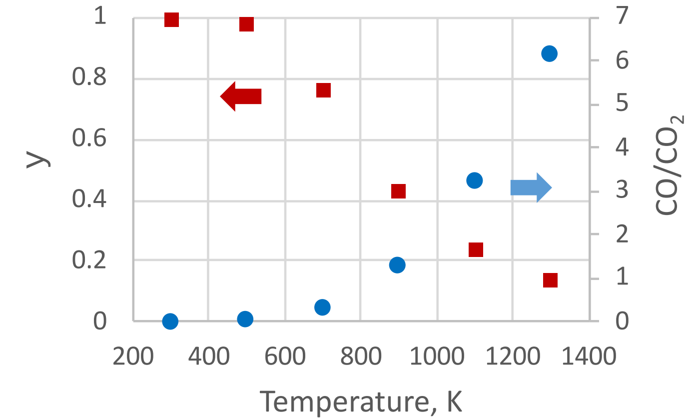
Devolatilization & Oxidation

Coal Devolatilization

$$C_\alpha H_\beta N_\gamma O_\delta S_\varepsilon \xrightarrow{devolatilization} \left[\alpha - \frac{2}{3}(\beta - 2\varepsilon) - \delta - \frac{\gamma}{2}\right] C(g) + \frac{2}{3}(\beta - 2\varepsilon)\ CH_4 + \frac{1}{3}(\beta - 2\varepsilon)\ H_2$$

$$+ \delta\ CO + \varepsilon\ H_2S + \frac{\gamma}{2}\ HCN + \frac{\gamma}{2}\ NH_3$$

$$\Delta H_{devolatilization} = \Delta H_{f,products} - \Delta H_{f,reactants}$$



Char Oxidation

$$C_x H_y N_z O_u S_v + \left(\frac{1+\psi}{2}x + \frac{1}{4}y + v\right) O_2 \xrightarrow{oxidation}$$

$$x\psi\ CO_2 + x(1-\psi)\ CO + \frac{1}{2}y\ H_2O + \frac{1}{2}z\ N_2 + \frac{1}{2}u\ O_2 + v\ SO_2$$

$$\Delta H_{oxidation} = \Delta H_{f,products} - \Delta H_{f,reactants}$$

ψ : The fraction of the carbon content of the particle converted to CO_2, calculated by CO/CO_2 ratio

Other Coal-related Reactions

Steam gasification	$\text{Char\_C} + H_2O \rightarrow CO + H_2$
CO2 gasification	$\text{Char\_C} + CO_2 \rightarrow 2CO$
CO oxidation	$CO + H_2O + \frac{1}{2} O_2 \rightarrow CO_2 + H_2O$
Water-gas shift reaction	$CO + H_2O \leftrightarrow CO_2 + H_2$
Methanation	$\text{Char\_C} + 2H_2 \rightarrow CH_4$
Methane oxidation	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

For reduced mechanism setup, the gas phase reactions will not be specified in the model setup

Chemistry Setup

Original Setup is based on M. A. Hamilton, K. J. Whitty and J. S. Lighty, "Incorporating Oxygen Uncoupling Kinetics into Computational Fluid Dynamic Simulations of a Chemical Looping System," *Energy Technol.*, no. 4, pp. 1-11, 2016.

	Original Setup	Coal Setup (Intermediate)
Water evaporation	■	■
Coal devolatilization	■ (CH_4, H_2, CO, CO_2)	◎ (C, CH_4, H_2, CO, H_2S, HCN, NH_3)
CO oxidation	■	◎
Water gas shift reaction	■	■
H_2 oxidation	■	■
CH_4 oxidation	■	■
Cu_2O oxidation	■	■
CuO decomposition	■	■
Char oxidation	■	◎
Steam gasification	-	◎
CO_2 gasification	-	◎
C(g) oxidation	-	◎
Char methanation	-	◎
S and N chemistry	-	-

Need more advanced approach

Chemistry Setup

Original Setup is based on M. A. Hamilton, K. J. Whitty and J. S. Lighty, "Incorporating Oxygen Uncoupling Kinetics into Computational Fluid Dynamic Simulations of a Chemical Looping System," *Energy Technol.,* no. 4, pp. 1-11, 2016.

	Original Setup	Coal Setup (Intermediate)	+ Reduced Mechanism (RM)
Water evaporation	■	■	■
Coal devolatilization	■ (CH_4, H_2, CO, CO_2)	◎ (C, CH_4, H_2, CO, H_2S, HCN, NH_3)	◎ (C, CH_4, H_2, CO, H_2S, HCN, NH_3)
CO oxidation	■	◎	RM
Water gas shift reaction	■	■	RM
H_2 oxidation	■	■	RM
CH_4 oxidation	■	■	RM
Cu_2O oxidation	■	■	■
CuO decomposition	■	■	■
Char oxidation	■	◎	◎
Steam gasification	-	◎	◎
CO_2 gasification	-	◎	◎
C(g) oxidation	-	◎	RM
Char methanation	-	◎	◎
S and N chemistry	-	-	RM

Detailed Chemistry

- REI97 mechanism for coal/natural gas combustion and NOx chemistry based on:
  - Miller & Bowman, 1989
  - Dean et al., 1991
- Sulfur chemistry based on Haynes et al., 2012 that describes low temperature behavior of the H_2S reactions
- Nitrogen and sulfur interactions based on Gargurevichm 2005
- 101 chemical species and 557 reversible elementary reactions

Reduced Mechanism

- 25 species mechanism has been developed

CH_4, CO_2, CO, H_2, O_2, OH, H_2O, C_2H_2, C_2H_4, C_2H_6, N_2, NO, HCN, N_2O, HNCO, NH_3, NO_2, HO_2, C, AR, H_2S, S_2, SH, SO, SO_2

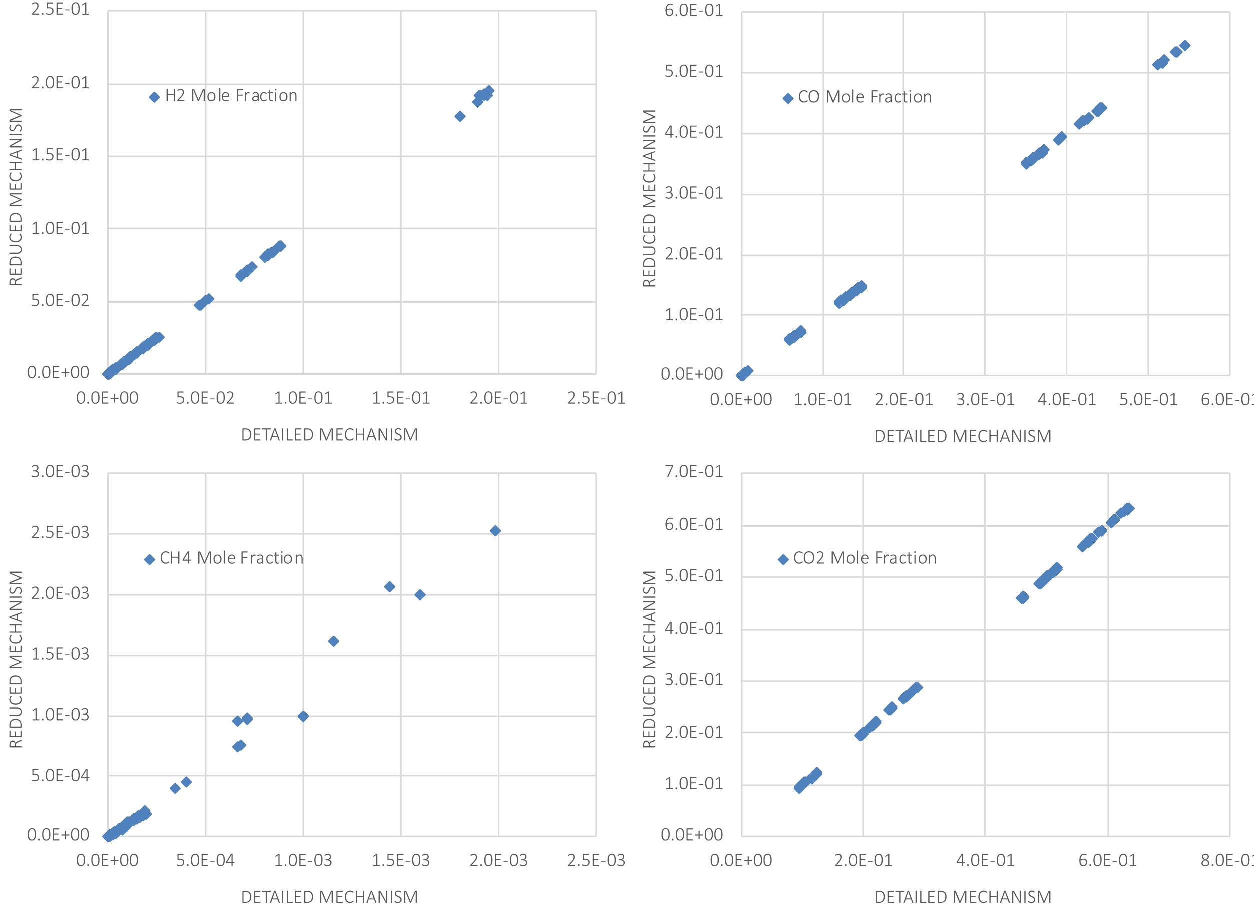
- Comparisons between the detailed and the reduced mechanisms are shown in the following slides focusing on
  - Kinetics of H_2, CO, CH_4
  - NO_x chemistry
  - Sulfur chemistry

PSR Calculations

Under the relevant conditions:

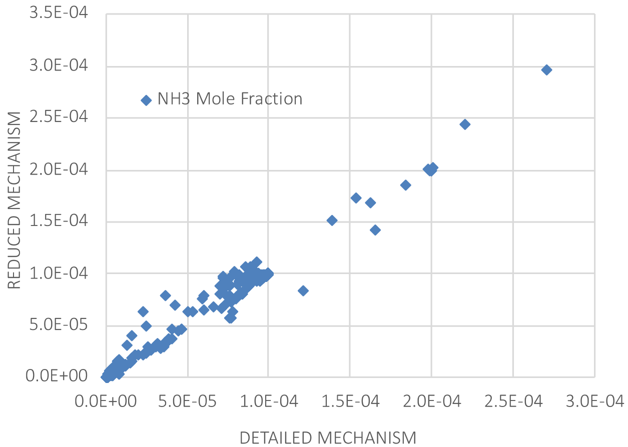
- Stoichiometric Ratio (SR) 0.5 - 1.5
- Temperatures: 800 - 2000 K
- Residence time: 0.02 - 0.2 sec
- Vary initial concentration of H_2, CO, CH_4, NH_3, HCN, NO and H_2S etc

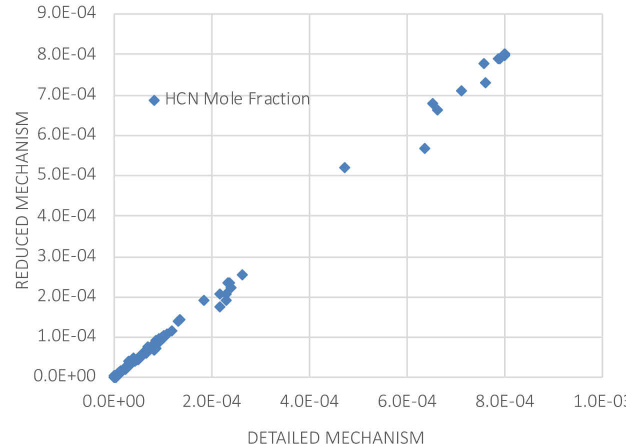
H_2, CO, CH_4, CO_2

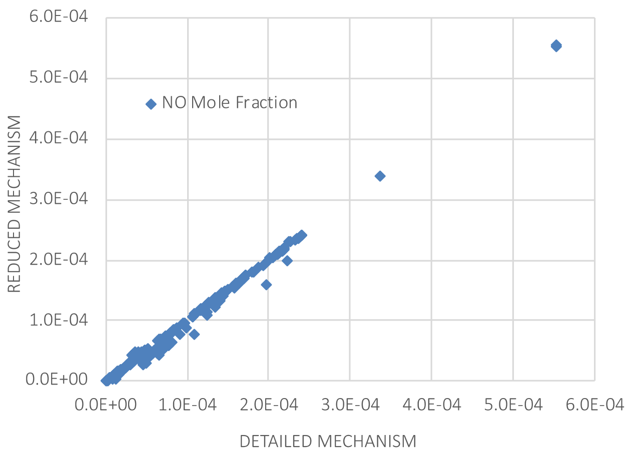


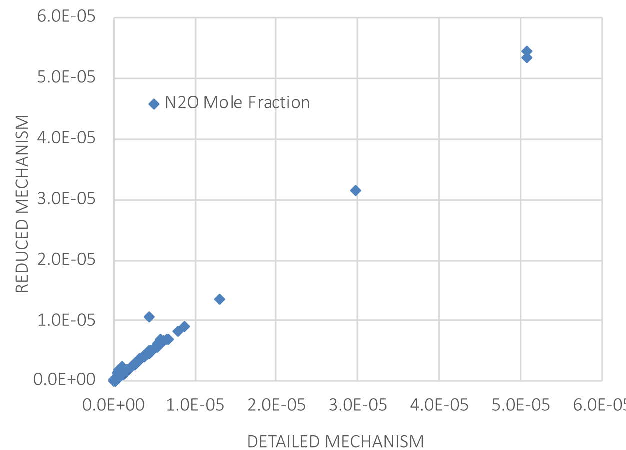
H2 Mole Fraction
REDUCED MECHANISM
DETAILED MECHANISM
2.5E-01
2.0E-01
1.5E-01
1.0E-01
5.0E-02
0.0E+00
CO Mole Fraction
6.0E-01
5.0E-01
4.0E-01
3.0E-01
2.0E-01
1.0E-01
CH4 Mole Fraction
3.0E-03
2.5E-03
2.0E-03
1.5E-03
1.0E-03
5.0E-04
CO2 Mole Fraction
7.0E-01
8.0E-01

Nitrogen Containing Species

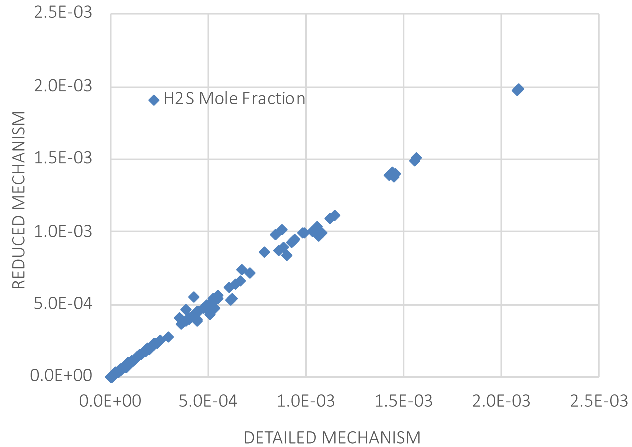


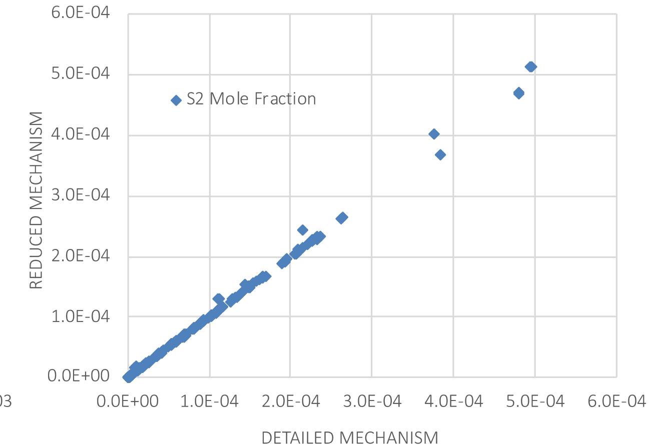


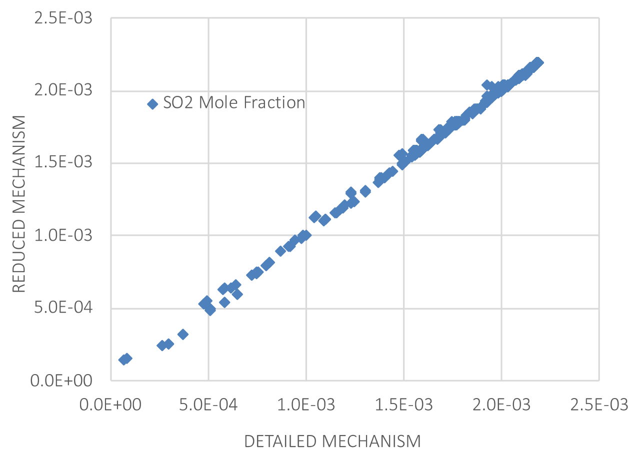


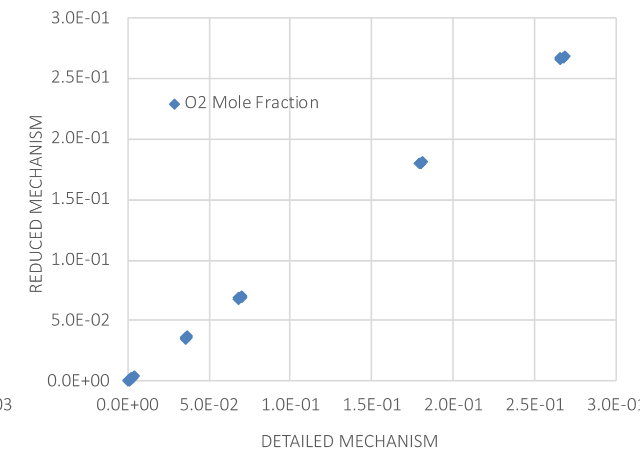


Sulfur Containing Species and O_2



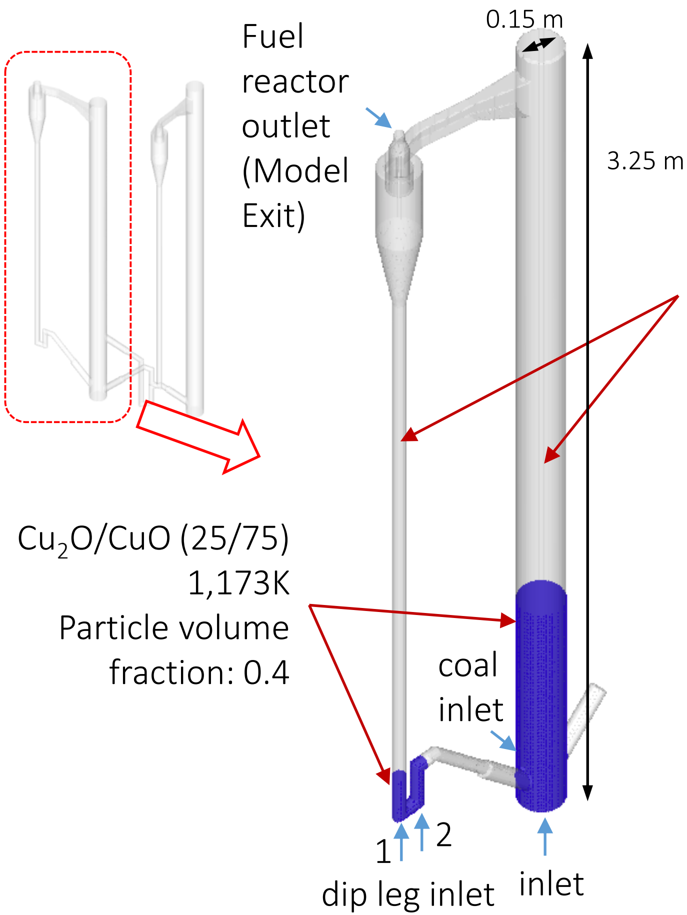






Impacts of Coal Selection

Fuel Reactor Boundary Conditions



- CLC PDU at the University of Utah
- Two interconnected circulating fluidized bed reactors (only the fuel reactor is simulated)
- Operating at 100 kWth
- Simulation with Barracuda VR

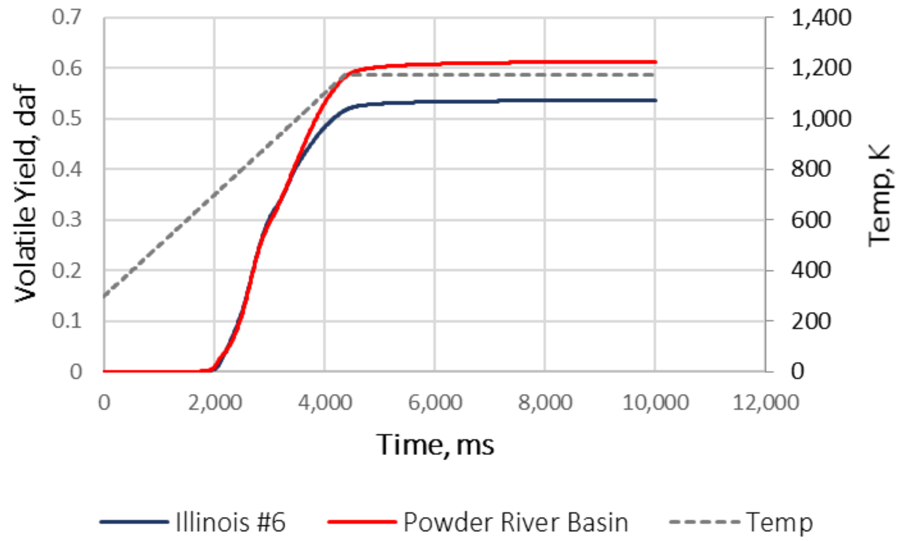
	Material	Temperature [K]	Velocity [m/s]	Mass Flow Rate [kg/s]
coal inlet	coal + steam	673	0.005	0.0036
inlet	steam	973	2.5	--
dipleg inlet 1	steam	1,173	1.5	--
dipleg inlet 2	steam	1,173	1.5	--

Coal Properties

Ultimate, wt%	Illinois #6	PRB
C	61.47	50.40
H	4.10	3.40
N	1.20	0.65
O	7.01	13.02
S	3.00	0.21
Ash	9.21	4.63
H_2O	14.00	27.70
Sum	100.00	100.00
HHV, Btu/lb	10,992	8,694
HHV, kcal/kg	6,111	4,833
Proximate, wt%	**Illinois #6**	**PRB**
Moisture	14.00	27.70
Volatile Matter	36.50	31.37
Fixed Carbon	40.30	36.30
Ash	9.20	4.63
Sum	100.00	100.00

CPD Calculation

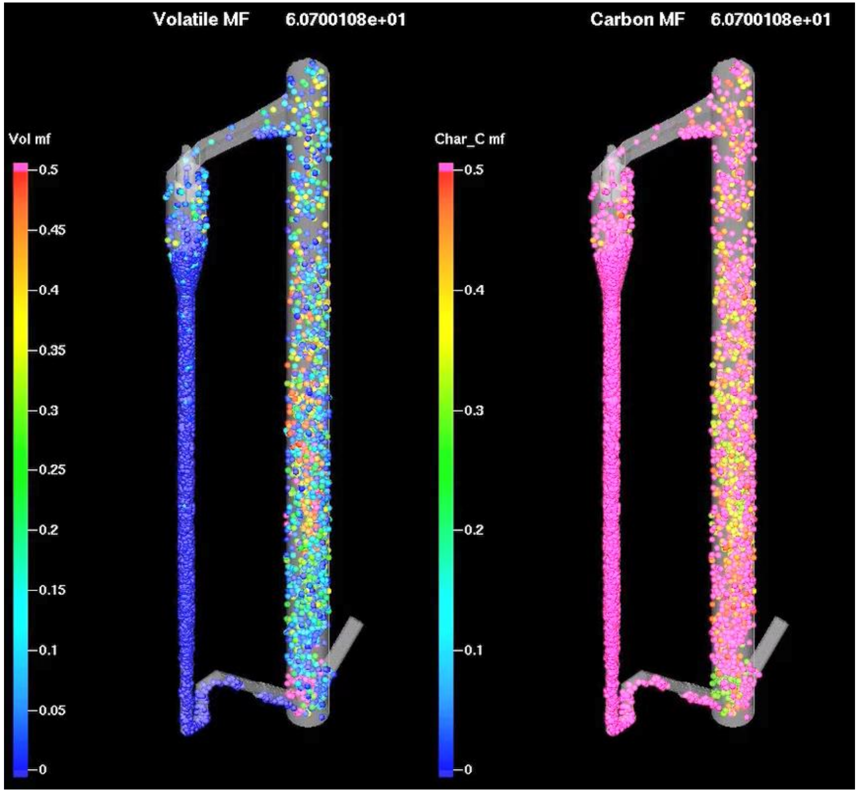
	Volatile Yields, daf
Illinois #6	53.6%
PRB	61.3%



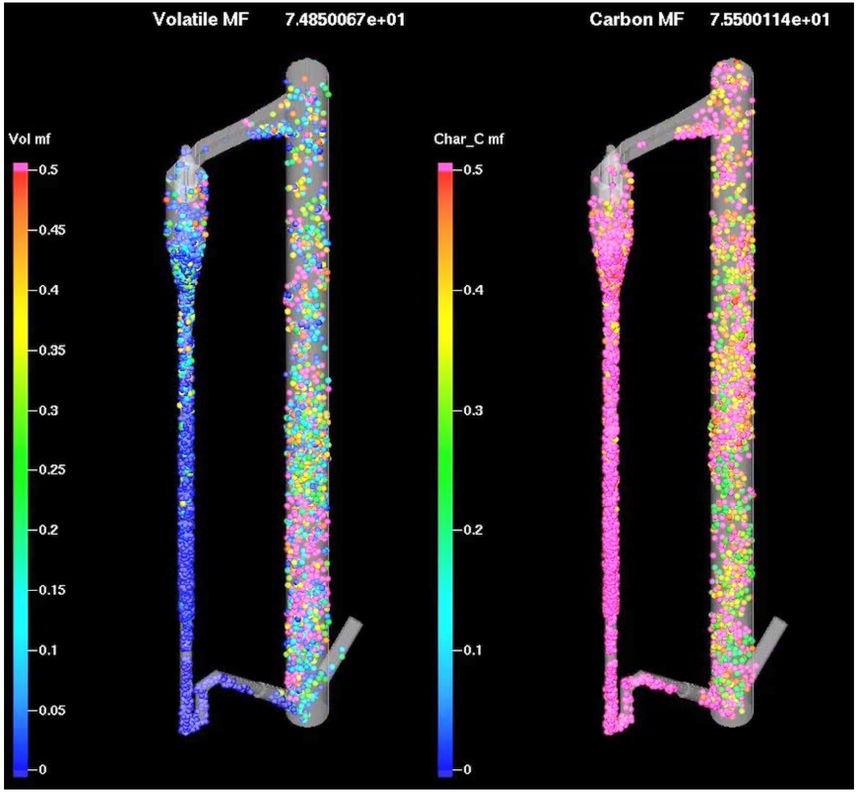
Coal Particles by Volatile and Carbon

Moisture evaporation and devolatilization take slightly longer time in PRB case

Illinois #6



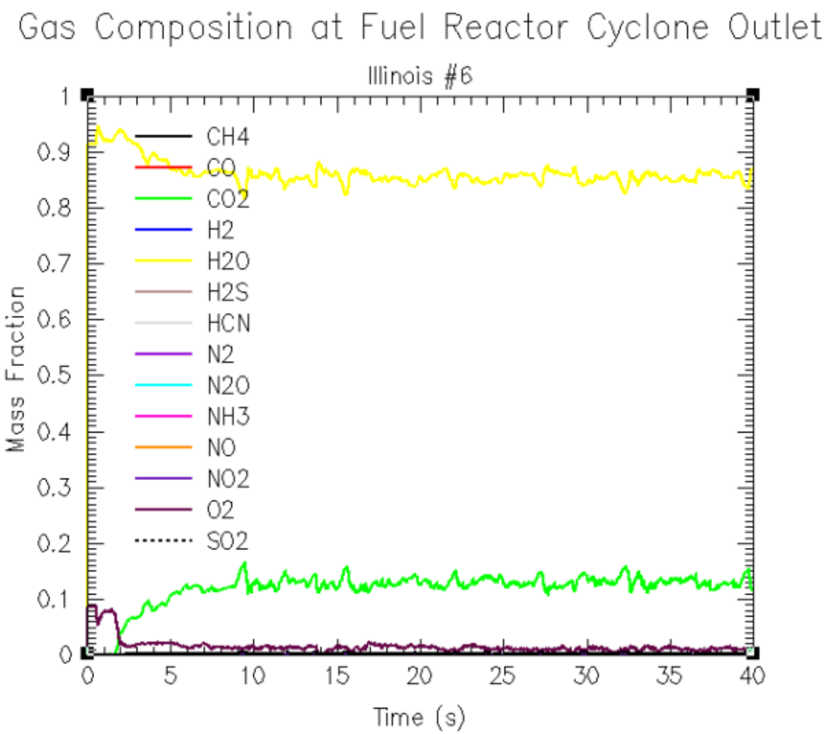
PRB



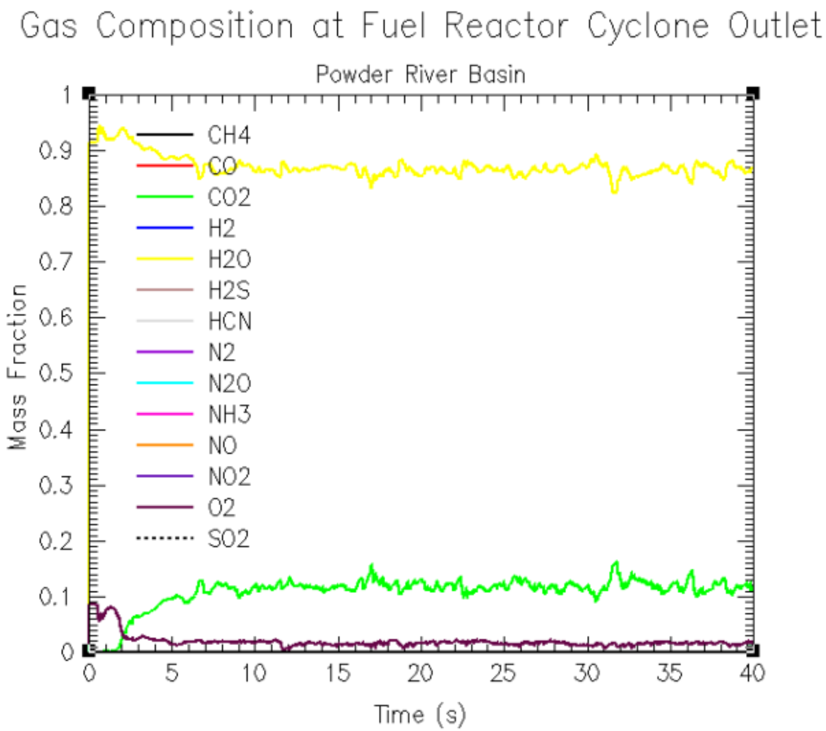
Gas Composition at Model Exit

Major gas species are H_2O, CO_2

Illinois #6



PRB

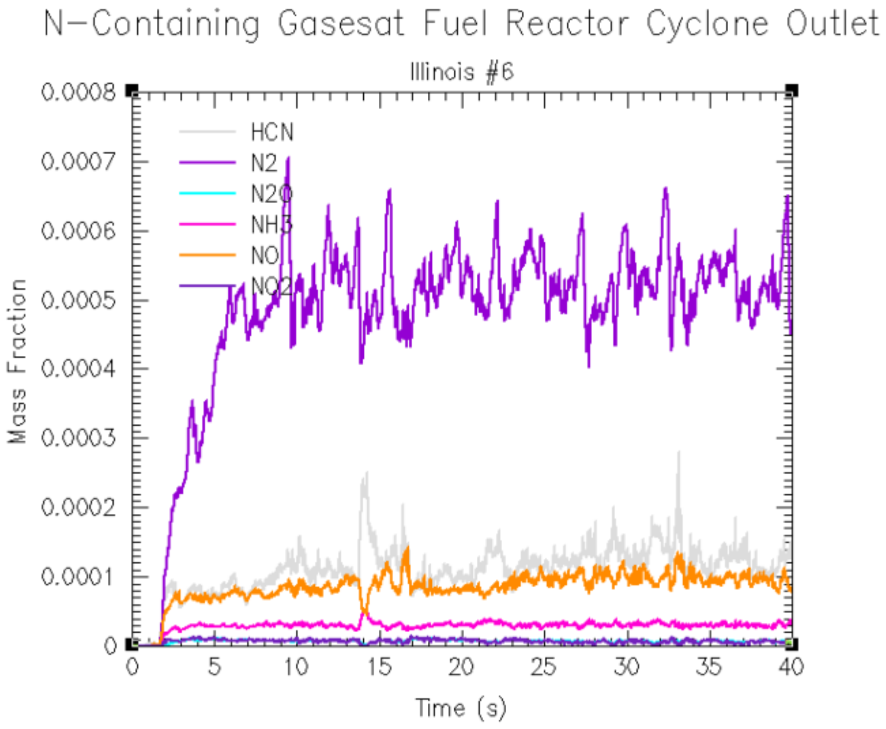


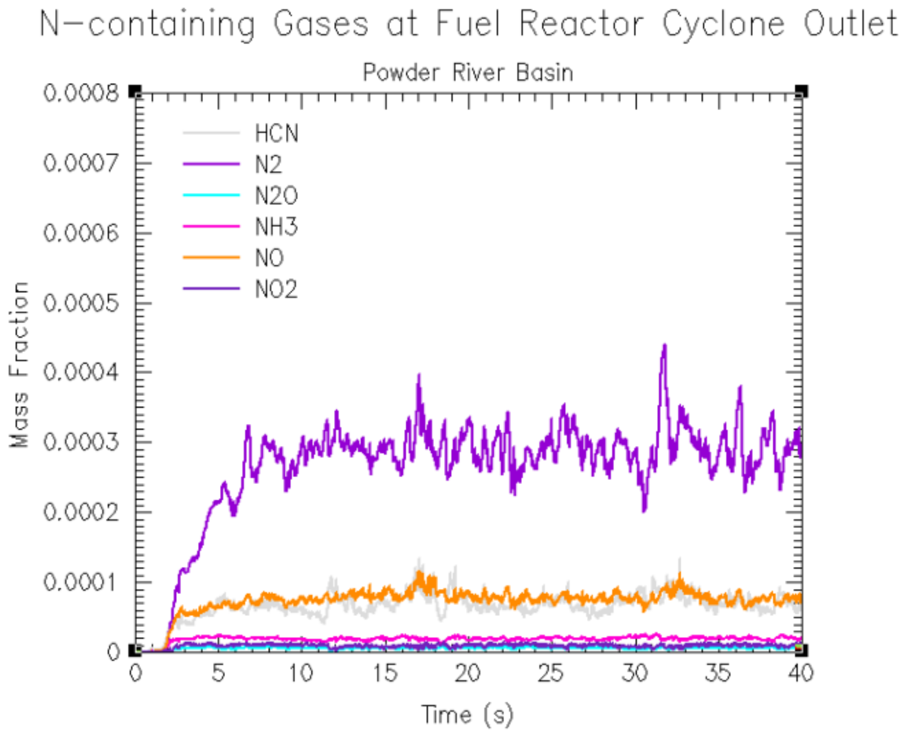
N-containing Species at Model Exit

Illinois #6

Lower N_2, HCN, NH_3 in PRB
Similar NO mass fractions

PRB



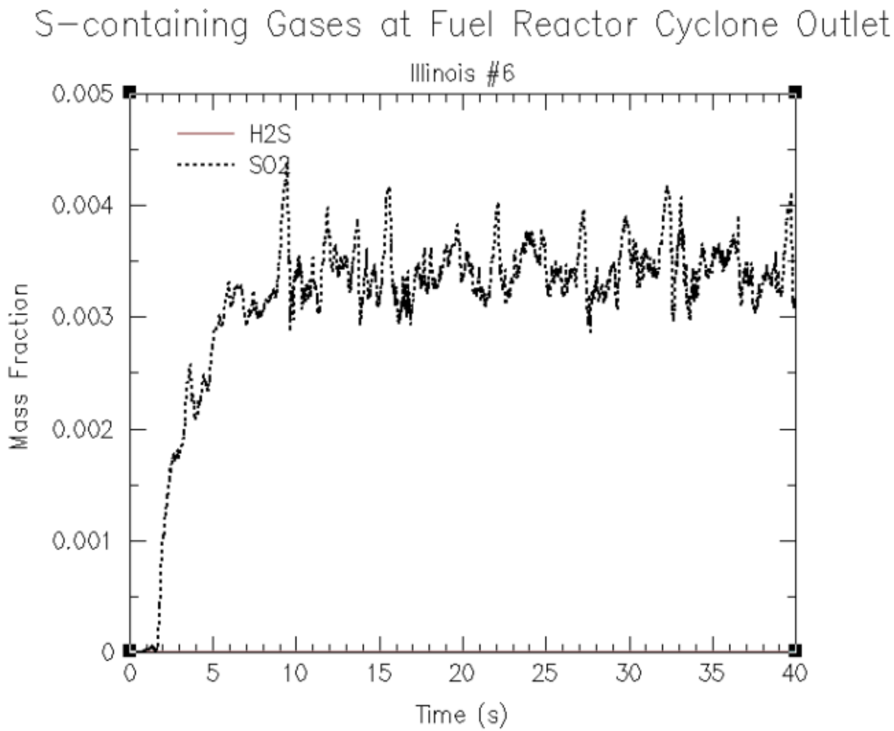


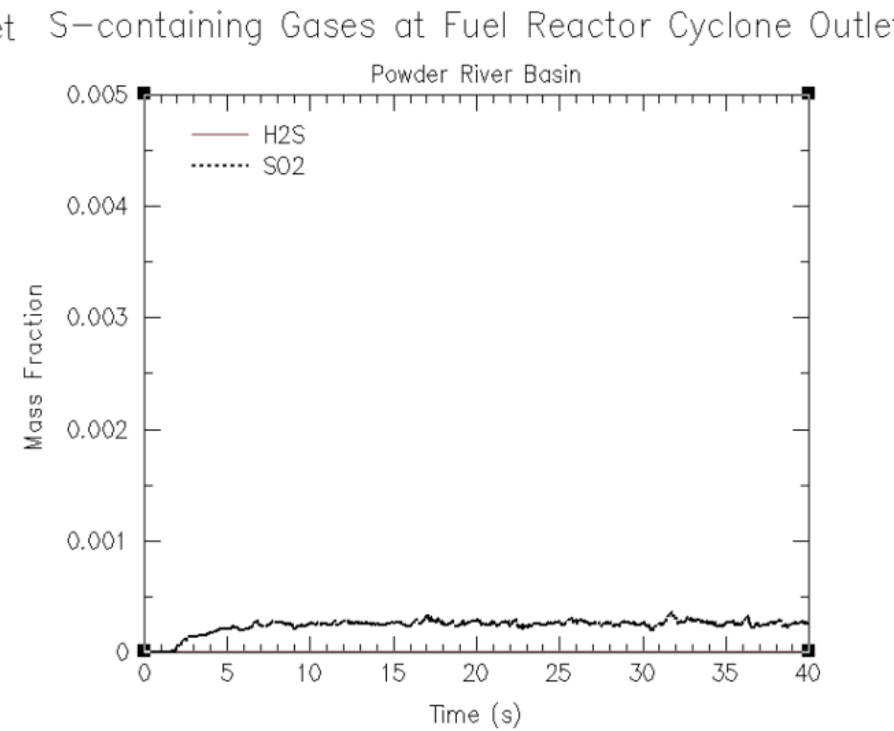
S-containing Species at Model Exit

Illinois #6

Noticeable difference in SO_2

PRB

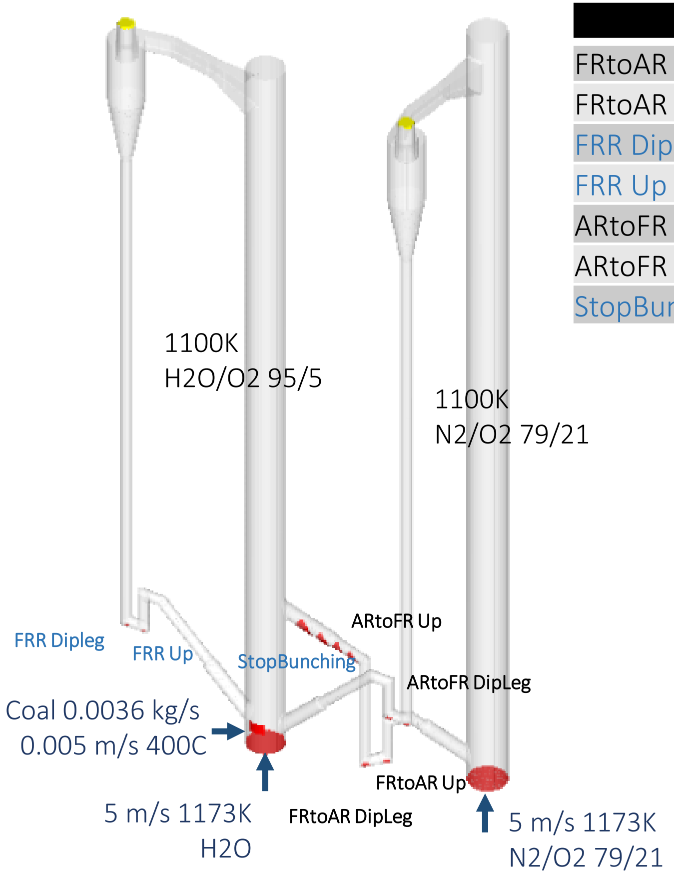




Full PDU Simulation

Full System Simulation

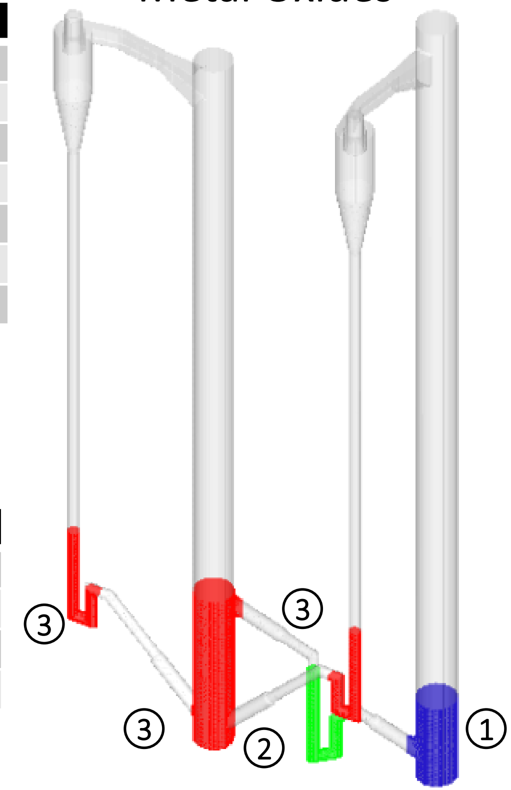
Fuel Reactor   Air Reactor



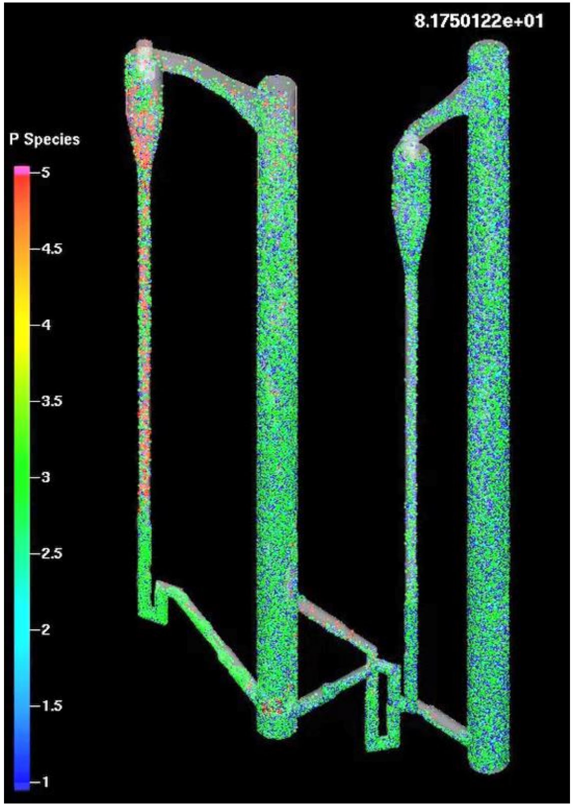
	Vel, m/s	Temp, K	Composition
FRtoAR Up	2	1173	N2/O2 79/21
FRtoAR DipLeg	1.5	1173	N2/O2 79/21
FRR DipLeg	1.5	1173	H_2O
FRR Up	1.5	1173	H_2O
ARtoFR Up	1.5	1173	N2/O2 79/21
ARtoFR DipLeg	1.5	1173	N2/O2 79/21
StopBunching	0.033	1173	H_2O

Species	CuO/Cu2O	CuO	Cu2O	SiO2
1	50/50	0.100	0.093	0.807
2	25/75	0.050	0.140	0.810
3	75/25	0.150	0.047	0.803
4	10/90	0.013	0.175	0.812

Metal Oxides

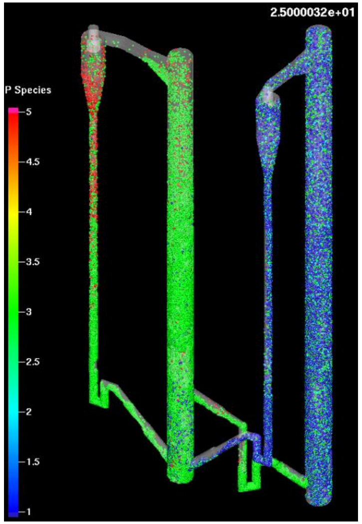


Particle Flow by Species

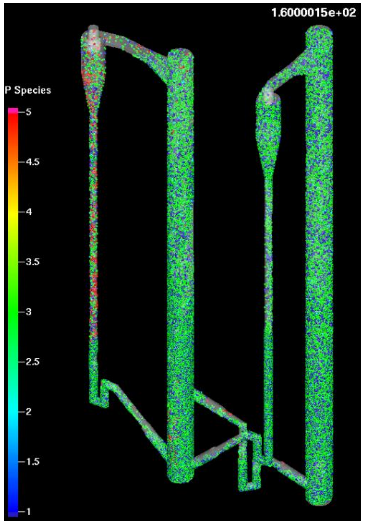


Species	CuO/Cu2O	CuO	Cu2O	SiO2
1	50/50	0.100	0.093	0.807
2	25/75	0.050	0.140	0.810
3	75/25	0.150	0.047	0.803
4	10/90	0.013	0.175	0.812
5	Coal			

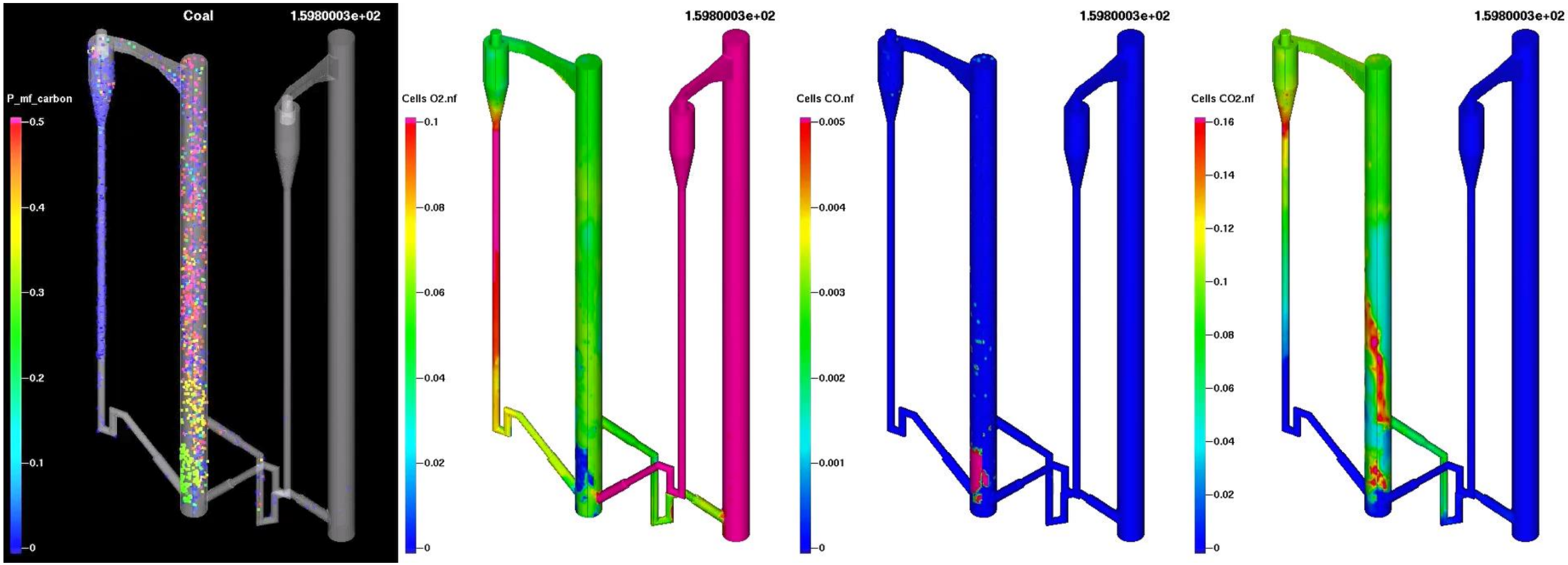
t= 25 sec



t= 160 sec

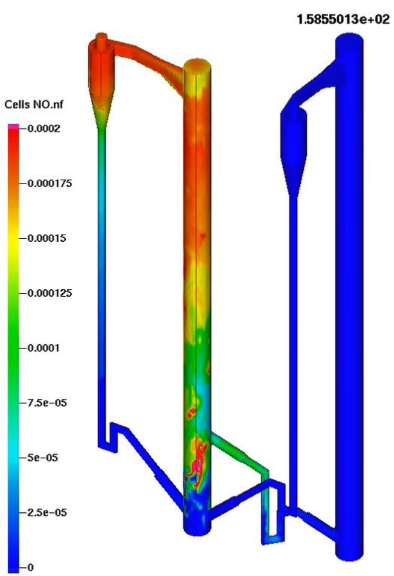


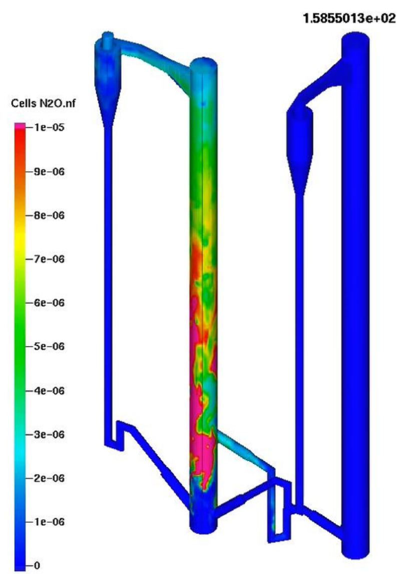
Coal Reactions

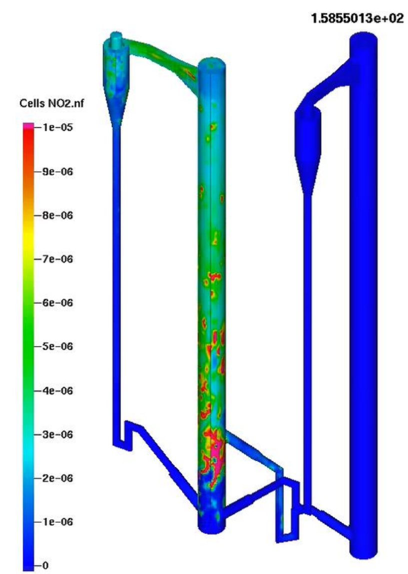


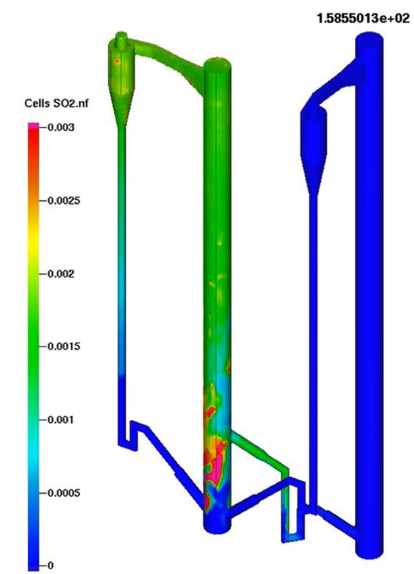
NO, N2O, NO2

SO2





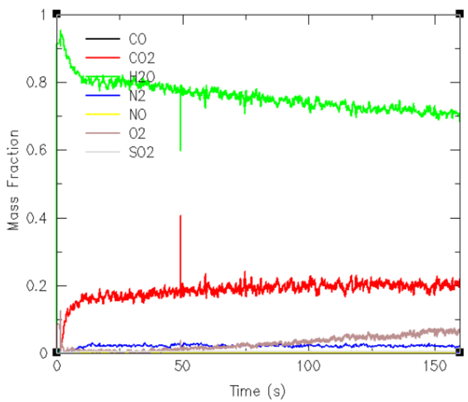




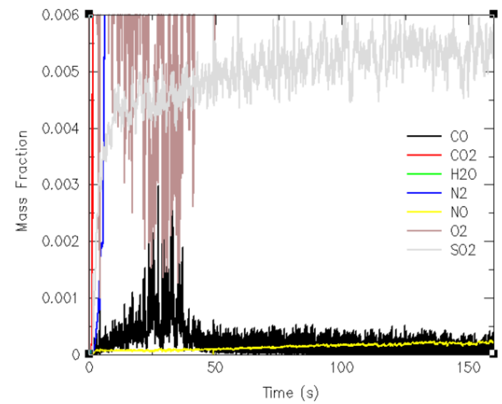
Reactor Cyclone Outlet

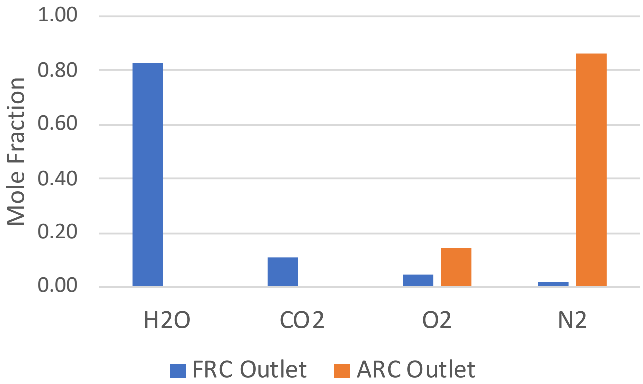
FRC: fuel reactor cyclone
ARC: air reactor cyclone

Gas Composition at Fuel Reactor Cyclone Outlet

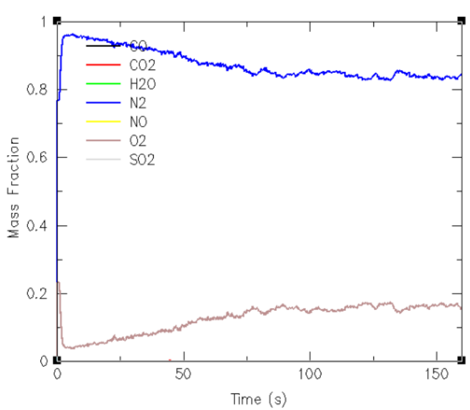


Gas Composition at Fuel Reactor Cyclone Outlet

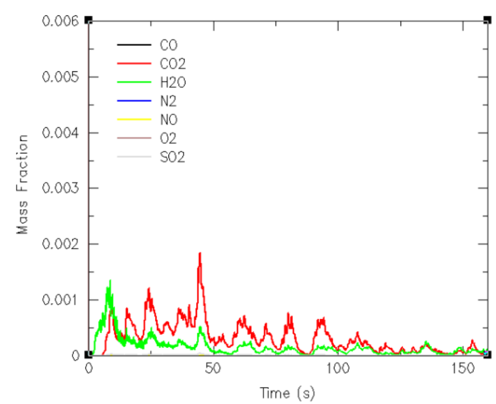


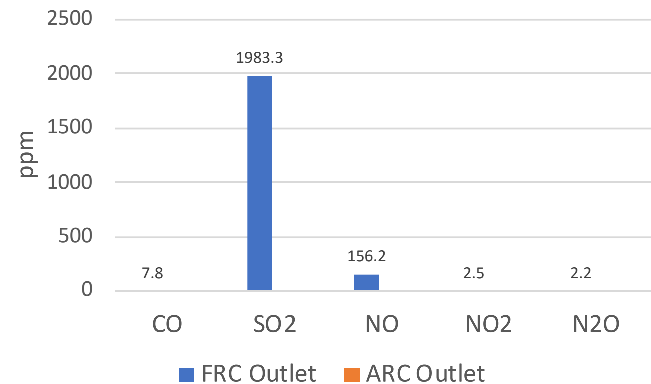


Gas Composition at Air Reactor Cyclone Outlet



Gas Composition at Air Reactor Cyclone Outlet





Conclusions

- A 25-specie reduced chemical kinetics mechanism has been developed and compares well with the detailed mechanism calculations under the conditions relevant to the chemical looping combustion system
- The reduced mechanism show promise when implemented into the Barracuda VR predicting various sulfur and nitrogen containing gas species that can affect operation or design of the system at reasonable computational cost
- The results will be compared with any available measurements and further model refinements will be made

Acknowledgement

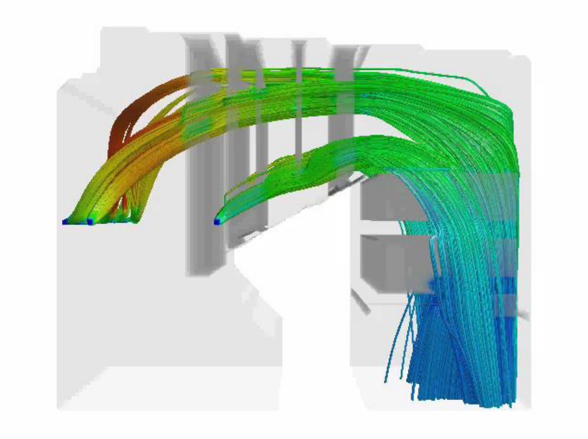
- The authors would like to acknowledge the financial support of the Department of Energy under award number DE-FE0029160
- Thanks are also due to
  - Mr. Zachary Reinking at the University of Utah for providing Barracuda-VR project file of the fuel reactor
  - Dr. James Parker and Mr. Andrew Larson at CPFD Software, LLC. for providing the modified version of Barracuda VR to use with a reduced mechanism

REI Expertise

Combustion, Gasification, Fuel Conversion, and Pollutant Emissions

Modeling

- Unique, Proprietary Modeling Capabilities & Tools
- Ability to develop and apply advanced chemistry to CFD and process modeling tools
- Experienced combustion modelers
- In-house tools tailored as needed



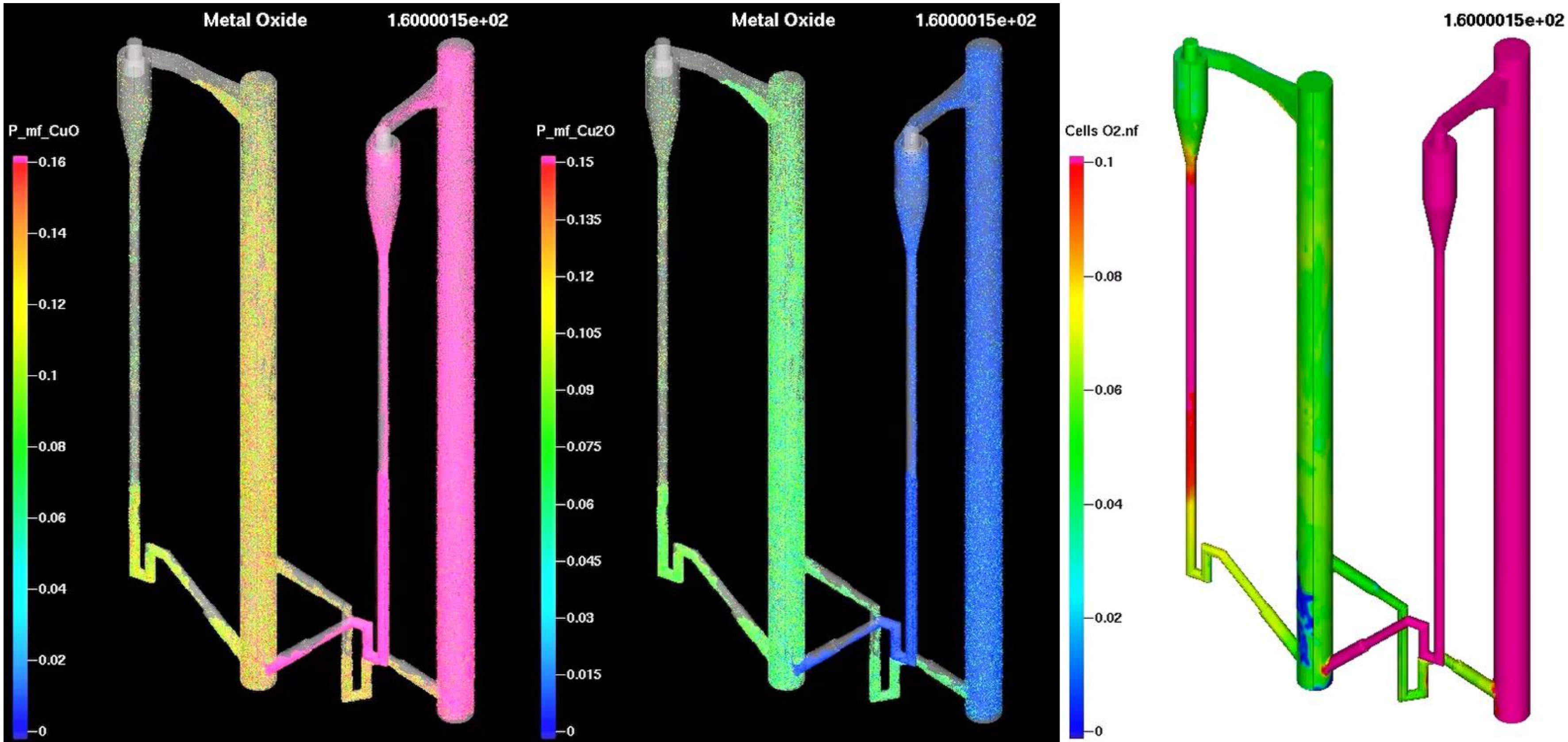
Testing

- R&D Testing Expertise
- Bench-scale & pilot-scale facilities
- Field demonstrations

Specialized Equipment and Control

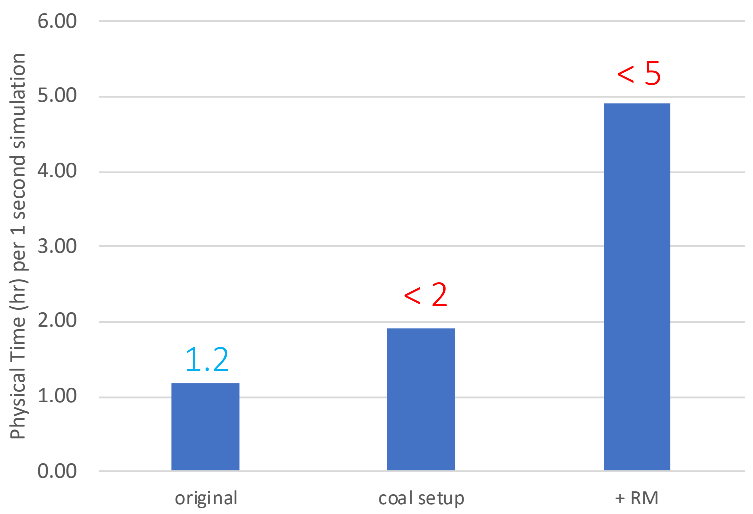
- Customized software development
- Corrosion monitoring

Metal Oxide


Metal Oxide
1.6000015e+02
P_mf_CuO
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
Metal Oxide
1.6000015e+02
P_mf_Cu2O
0.15
0.135
0.12
0.105
0.09
0.075
0.06
0.045
0.03
0.015
0
Cells O2.nf
0.1
0.08
0.06
0.04
0.02
0
1.6000015e+02

Computational Cost

Physical Time (hr) for 1 second simulation time*



* Barracuda 17.3.0 GPU + OMP