NATIONAL ENERGY TECHNOLOGY LABORATORY

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CFD simulation of entrained-flow gasification with improved physical and chemical sub-models

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General Approach and Sub-models

- ANSYS Fluent with UDFs
- Turbulence: k-ε model
- Multiphase coupling: Euler/Lagrange (Fluent DPM)
  - Gas phase: Eulerian PDEs
    - SIMPLE (momentum/continuity coupling)
    - Energy
    - Species continuity
    - k and ε
  - Discrete phase: Lagrangian ODEs with stochastic dispersion
    - Moisture vaporization
    - Coal devolatilization
    - Char oxidation and gasification
- Radiation: Discrete Ordinate (gas/particle phases)
- Turbulence/chemistry interaction: Eddy dissipation/finite rate
- Gas phase chemistry: Global kinetic mechanisms (9 reactions)

Moisture Vaporization Sub-Model

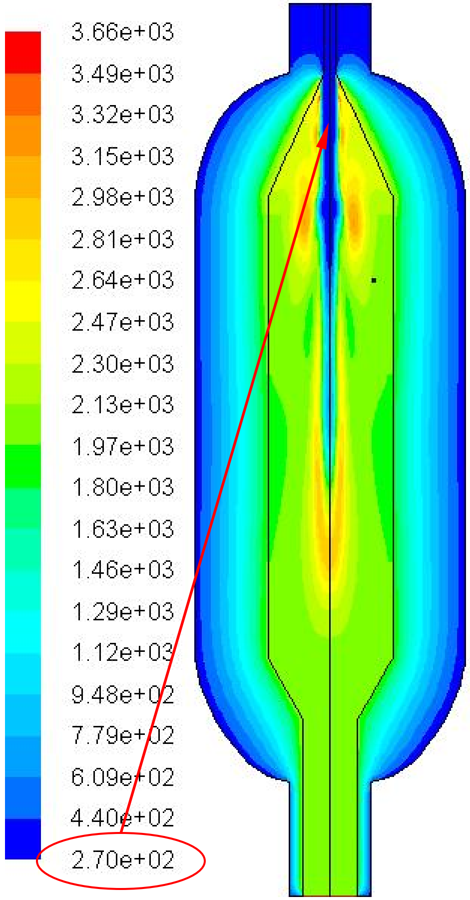
- **Importance**
  - **Ignition delay/flame location**
  - **Gas temperatures near fuel injector**
- **Previous model**
  - **Arrhenius Expression** $r_v = m_{moist} A_v \exp\left(-\frac{E_v}{RT_p}\right)$
- **Revised model**
  - **Consider convective outward flow (Stefan flow)**
  - **Consider high mass transfer correction**

$$r_v = M_w A_{ext} \frac{\theta_{AB} k_{diff} \left(C_{H_2O,s} - C_{H_2O,g}\right)}{1 - x_{H_2O,s}}$$

$$\theta_{AB} = \frac{\ln\left(1 + R_{AB}\right)}{R_{AB}} \qquad R_{AB} = \frac{x_{H_2O,s} - x_{H_2O,g}}{1 - x_{H_2O,s}}$$

  - **Consider boiling (heat transfer limiting)**

$$r_v = A_{ext} \frac{\theta_T h\left(T_g - T_p\right) + \frac{1}{4}\varepsilon_p\left(G - \sigma T_p^4\right)}{H_{vap,H_2O}} \qquad R_T = \frac{C_{p,H_2O}\left(T_g - T_p\right)}{H_{vap,H_2O}}$$



Gas Temperature (K)

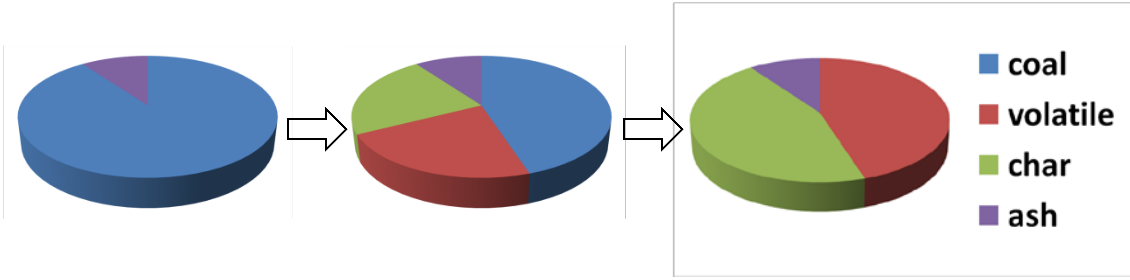
Coal Devolatilization Sub-Model

Reaction Rate and Volatile Yield

- **Yield different from ASTM proximate analysis**
  - **Up to 60% on dry-ash-free basis**
  - **Heating rate effect**
- **Final yield related to particle temperature history**
  - **Cannot be determined *a priori***
- **Two-reaction model (Kobayashi, Ubhavakar)**
  - **1st Rxn: lower E_a, lower yield**
  - **2nd Rxn: higher E_a, higher yield**
  - **Reactant: Coal**
  - **Products: Volatile/Char**
  - **Reaction process:**

$$\text{Coal} \xrightarrow{heat} y_1 \text{Volatile} + (1 - y_1)\text{Char}$$

$$\text{Coal} \xrightarrow{heat} y_2 \text{Volatile} + (1 - y_2)\text{Char}$$

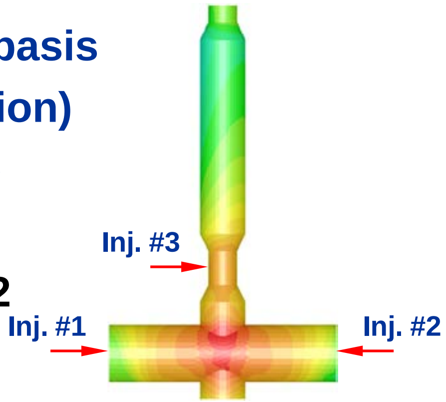


- **Previous Model**
  - **Reaction stops when specified volatile yield is reached**
- **Revised Model**
  - **Reaction stops when there is no reactant (coal) left**

Coal Devolatilization Sub-Model

Volatile Composition

- **Related to source terms for species continuity PDEs**
- **11 species considered as coal volatiles**
  - **Previous model:** O_2, H_2, N_2, CO, CO_2, H_2O, CH_4, H_2S, HCl
  - **Revised model:** Added COS, C_6H_6
- **In-situ calculation procedure**
  - **Assume char contains C and ash (H, O, N, S, Cl in volatiles only)**
    - Composition changes when yield changes
  - **Step 1:** Guess a volatile yield
  - **Step 2:** Calculate elemental composition on molar basis
  - **Step 3:** Form species from elements (Next Slide)
  - **Step 4:** Calculate mass fractions of each species on mass basis
  - **Step 5:** Calculate heat of devolatilization (For energy equation)
  - **Step 6:** Do DPM tracking using results from (Steps 4 and 5)
    - Save volatile yield (as Fluent RP variable)
  - **For next DPM iteration, under-relax volatile yield ⇨ Step 2**
- **Apply above procedure for each injection**



Coal Devolatilization Sub-Model

Volatile Composition

C H O S Cl N		$2N \rightarrow N_2$	
C H O S Cl		$Cl + H \rightarrow HCl$	
C H O S	$y_{S \rightarrow COS}$	$S + 2H \rightarrow H_2S$	$S + C + O \rightarrow COS$
C H O	$y_{O \rightarrow O_2}$	$2O \rightarrow O_2$	
C H O	$y_{H \rightarrow H_2}$	$2H \rightarrow H_2$	
C H O	$y_{H,O \rightarrow H_2O}$	$2H + O \rightarrow H_2O$	
C H O	$y_{O \rightarrow CO_2}$	$C + 2O \rightarrow CO_2$	$C + O \rightarrow CO$
C H		$C + 4H \rightarrow CH_4$	$6C + 6H \rightarrow C_6H_6$

Char Combustion/Gasification Sub-Model

- **Shrinking Core Model, Wen and Chuang (1979)**

$$\frac{dm_p}{dt} = \frac{A_{ext}\left(p_i - p_i^*\right)}{\frac{1}{k_{film}} + \frac{1}{k_{rxn}Y^2} + \frac{1}{k_{ash}}\left(\frac{1}{Y} - 1\right)}$$

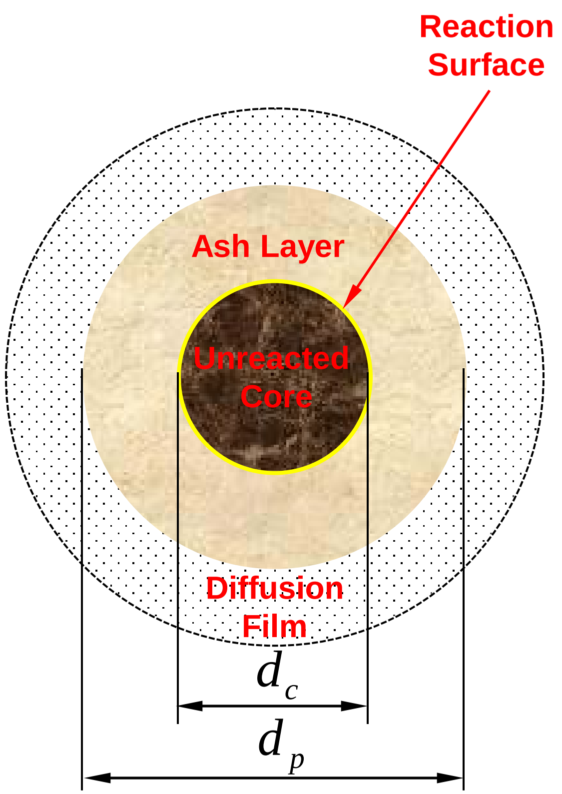
- **Diameter Ratio:** $Y = \frac{d_c}{d_p}$
- **Reactions:**

$C + O_2 \rightarrow CO_2$ $\quad$ $C + 0.5O_2 \rightarrow CO$

$C + H_2O \rightarrow CO + H_2$

$C + CO_2 \rightarrow 2CO$

$C + 2H_2 \rightarrow CH_4$



Gas Phase Chemistry

- **Fuel oxidation**

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
$$CO + 0.5O_2 \rightarrow CO_2$$
$$H_2 + 0.5O_2 \rightarrow H_2O$$

- **Water gas shift**

$$CO + H_2O \rightarrow CO_2 + H_2$$
$$CO_2 + H_2 \rightarrow CO + H_2O$$

- **Reforming reaction**

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

- **Tar reactions**

$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$$
$$C_6H_6 + 6H_2O \rightarrow 9H_2 + 6CO$$

- **Reverse reaction of H_2 oxidation**

$$H_2O \rightarrow H_2 + 0.5O_2$$

Gas Phase Kinetics

Water Gas Shift Reaction

$$R_{rxn} = AT^m \exp\left(-\frac{E}{RT}\right) C_{r_1}^{n_1} C_{r_2}^{n_2}$$

Units in kmol, K, m, s

Reaction	m	n_1	n_2	A	E	Reference
$CO + H_2O \rightarrow CO_2 + H_2$	0	0.5	1	2.34×10^{10}	2.88×10^{8}	Bustamante et al. (2005)
$CO_2 + H_2 \rightarrow CO + H_2O$	0	1	0.5	2.2×10^{7}	1.9×10^{8}	Bustamante et al. (2004)

Previous Model: 1st order based on Jones and Lindstedt (1988)

Gas Phase Kinetics

Reverse Reaction of H_2 Oxidation

$$R_{rxn} = AT^m \exp\left(-\frac{E}{RT}\right) C_{r_1}^{n_1} C_{p_1}^{n_2} C_{p_2}^{n_3}$$

Units in kmol, K, m, s

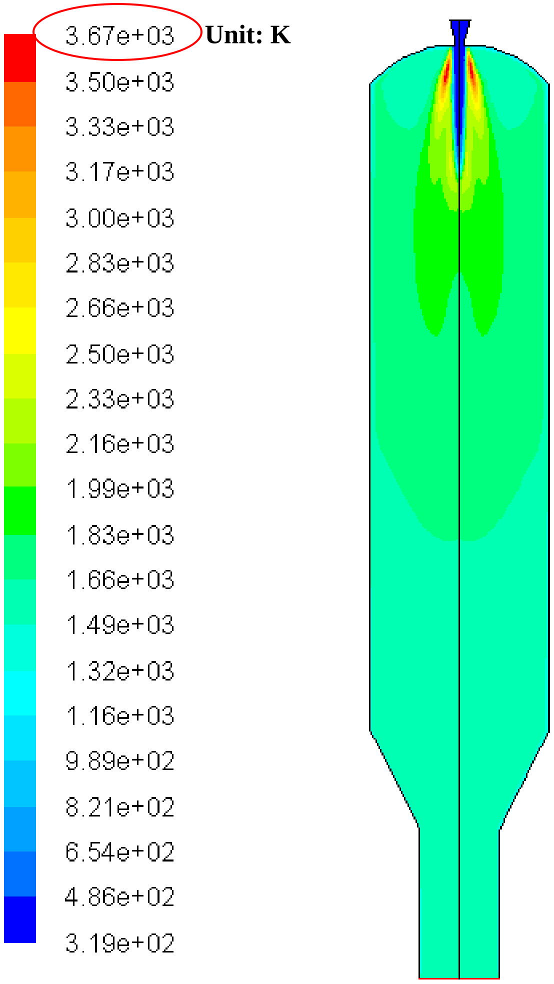
Reaction	m	n_1	n_2	A	E	Reference
$H_2O \rightarrow H_2 + 0.5O_2$	0	1	-	2.5×10^{10}	3.5×10^{8}	Estimated

Note: Also tried kinetic data reported by Andersen et al. (2009)

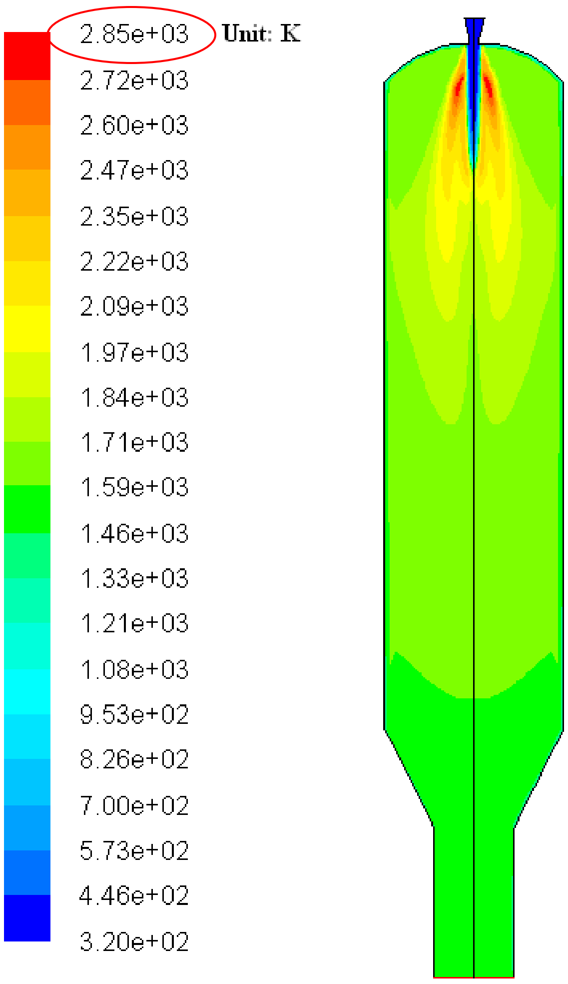
Reaction	m	n_1	n_2	n_3	A	E	Reference
$H_2O \rightarrow H_2 + 0.5O_2$	-0.877	1	-0.75 (H2)	1 (O_2)	1.26×10^{17}	4.1×10^{8}	Andersen et al. (2009)

Gas Phase Kinetics

Effects of $H_2O \rightarrow H_2 + 0.5O_2$

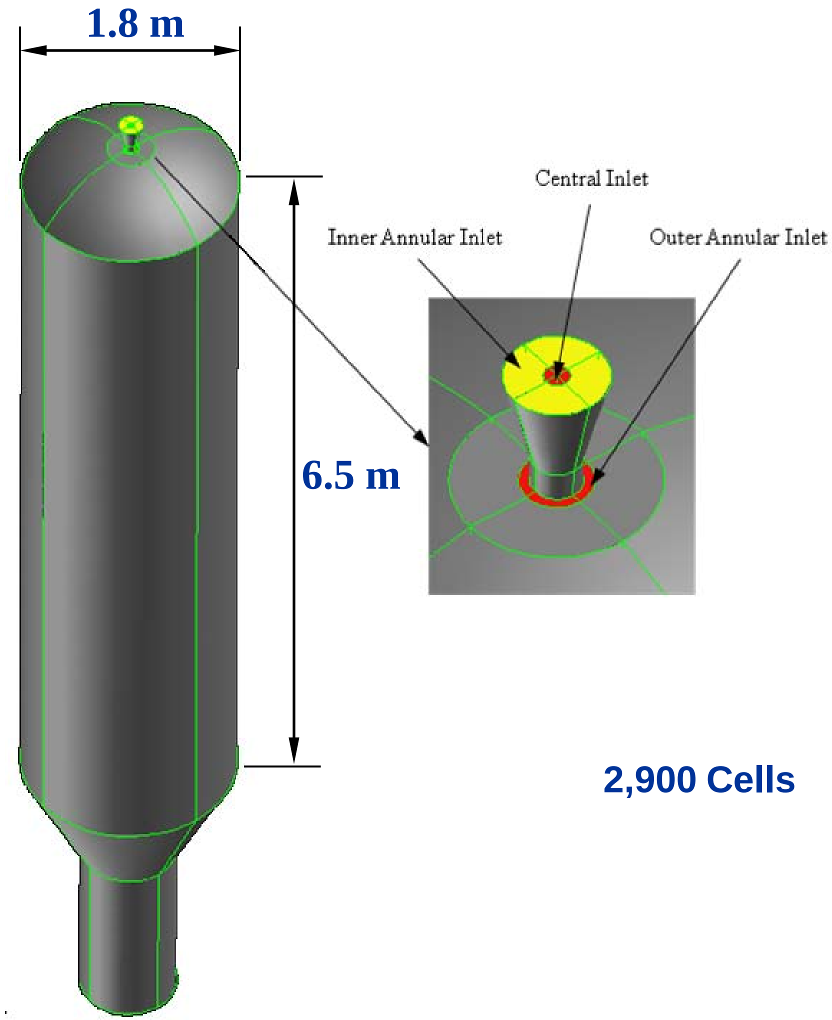


$\Delta T_{peak} = 820K$

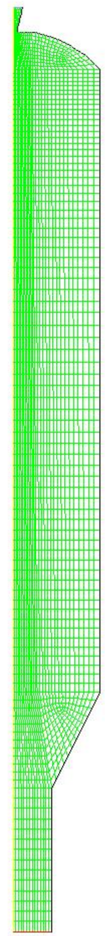


Without Reverse Reaction **With Reverse Reaction**

Single-Stage Gasifier Model



Geometry



2,900 Cells

Mesh

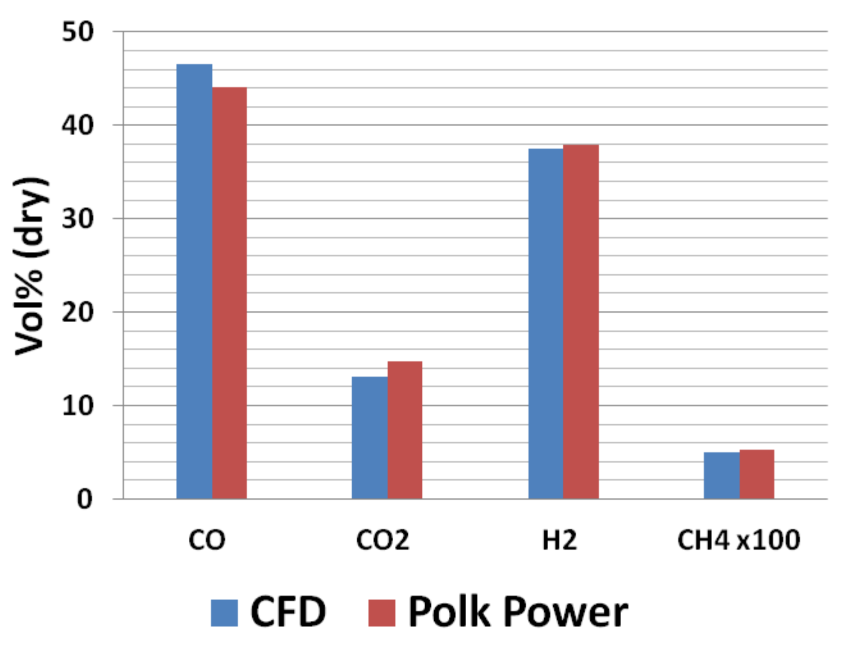
Operating Conditions

Coal Type	Illinois #6
Operating Pressure (MPa)	5.619
Coal Slurry Flow Rate (kg/s)	43.32
Mass Fraction of Water in Slurry	0.29
Coal Particle Mean Diameter (μm)	100
Coal Particle Spread Parameter	1.0
Coal Slurry Inlet Temperature (K)	300
Oxidizer Mass Flow (kg/s)	24.73
Wt% of O_2 in Oxidizer	95%
Wt% of N_2 in Oxidizer	1%
Wt% of Ar in Oxidizer	4%
Oxidizer Inlet Temperature (K)	390
Stoichiometric Ratio	0.380

Single-Stage Gasifier Results

Overall Predictions

Carbon Conversion	98.2%
Syngas Temperature at Exit (K)	1565
Volatile Yield (daf)	59.4%



Comparison With Polk Power Data

Syngas Composition

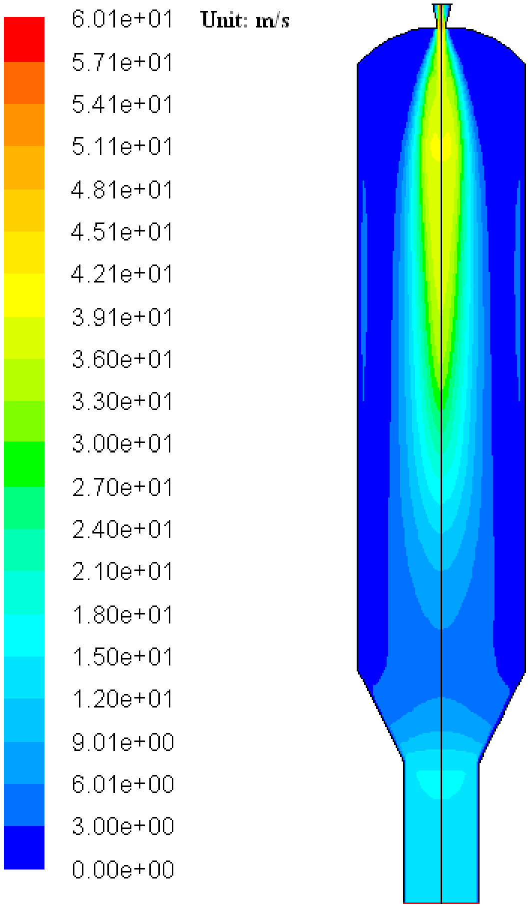
	Vol%, Wet (CFD)	Vol%, Dry (CFD)	Vol%, Wet (Equil.)
H_2O	17.13		18.86
CO	38.57	46.55	40.34
CO_2	10.83	13.07	9.09
H_2	31.12	37.56	29.37
CH_4	0.04	0.05	0.04
H_2S	0.67	0.81	0.70
COS	0.07	0.08	0.04
HCl	0.08	0.10	0.08
Ar	0.77	0.93	0.77
N_2	0.71	0.86	0.71

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

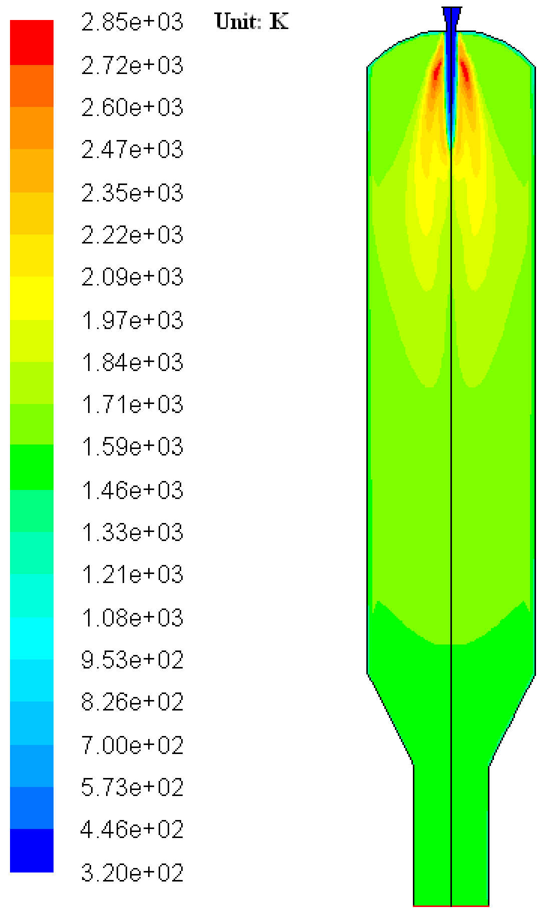
$$K_{eq}(1565\text{K}) = 0.351$$

$$Q_r = \frac{[H_2]\times[CO_2]}{[CO]\times[H_2O]} = 0.510 > K_{eq}$$

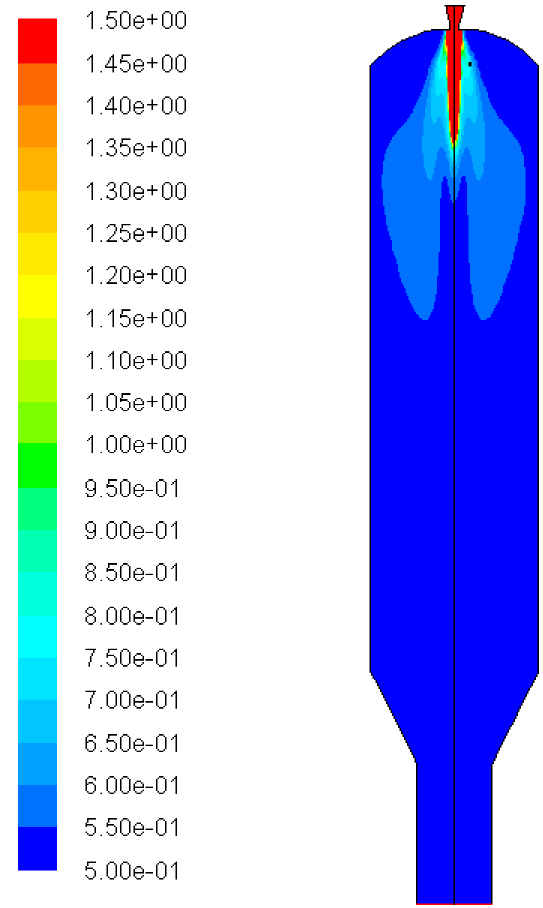
Single-Stage Gasifier Results



Velocity Magnitude

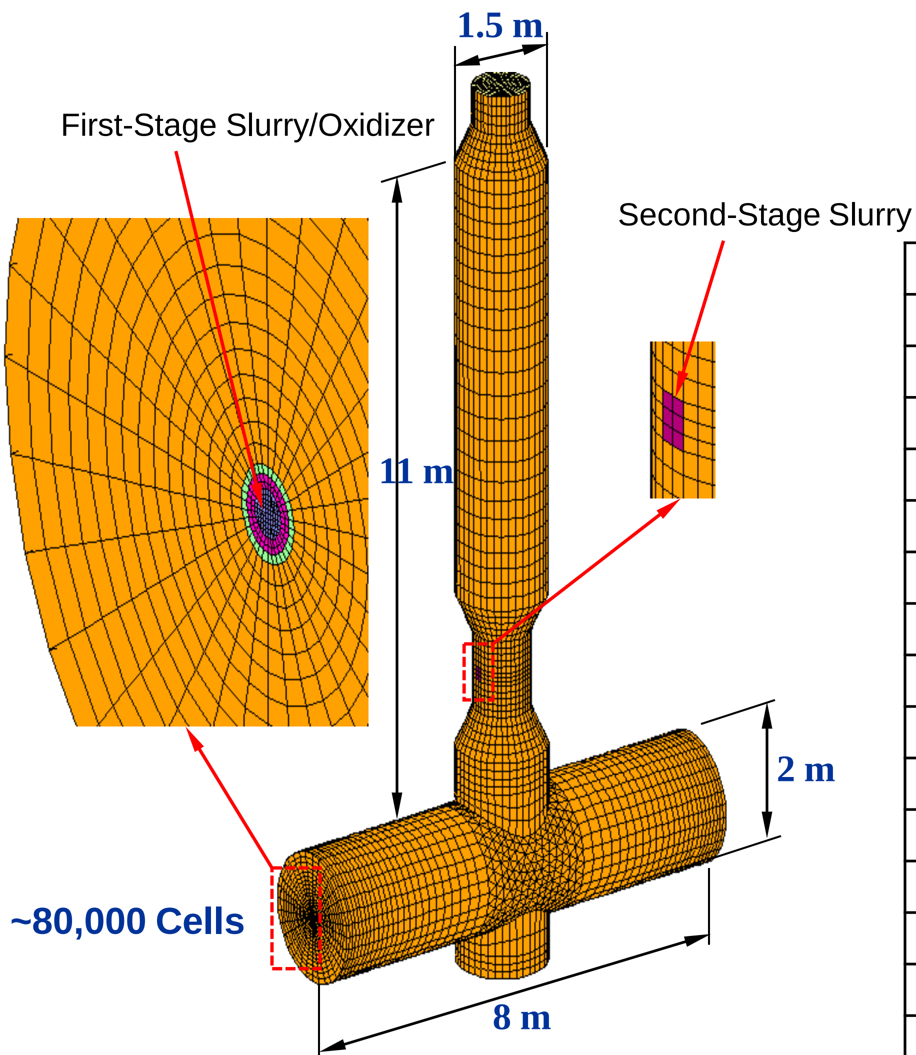


Gas Temperature



Stoichiometric Ratio

Two-Stage Gasifier Model



Geometry and Grid

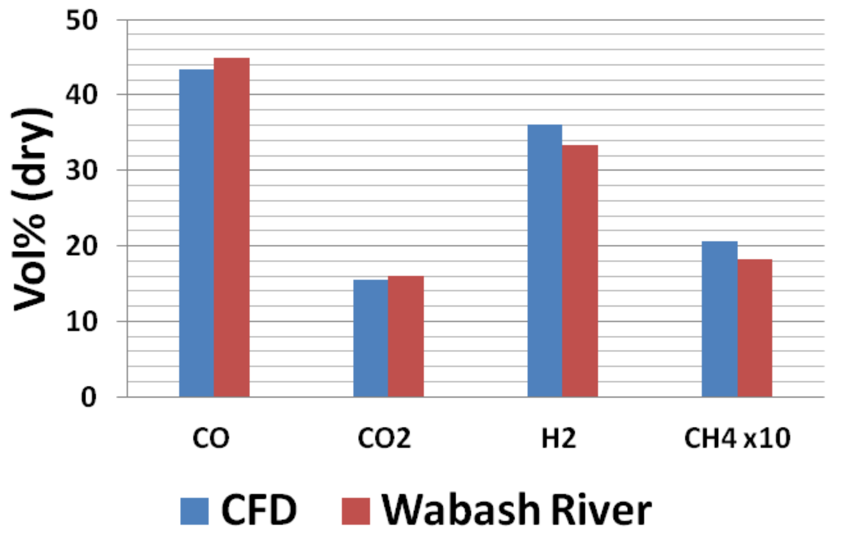
Operating Conditions

Coal Type	Illinois #6
Operating Pressure (MPa)	2.84
1st Stage Coal Slurry Flow Rate (kg/s)	32.84
2nd Stage Coal Slurry Flow Rate (kg/s)	9.26
Mass Fraction of Water in Slurry	0.34
Coal Slurry Fed to the 2nd Stage	22%
Coal Particle Mean Diameter (μm)	100
Coal Particle Spread Parameter	1.0
Coal Slurry Injection Temperature (K)	300
Oxidizer Mass Flow (kg/s)	21.2
Wt% of O_2 in Oxidizer	95.0%
Wt% of N_2 in Oxidizer	1.0%
Wt% of Ar in Oxidizer	4.0%
Oxidizer Inlet Temperature (K)	390
Overall Stoichiometric Ratio	0.360
1st Stage Stoichiometric Ratio	0.462

Two-Stage Gasifier Results

Overall Predictions

Overall Carbon Conversion	95.1%
Carbon Conversion (1st Stage)	99.3%
Carbon Conversion (2nd Stage)	80.3%
Syngas Temperature at Exit (K)	1393
Volatile Yield (1st Stage)	55.2%
Volatile Yield (2nd Stage)	47.6%



Comparison With Wabash River Data

Syngas Composition

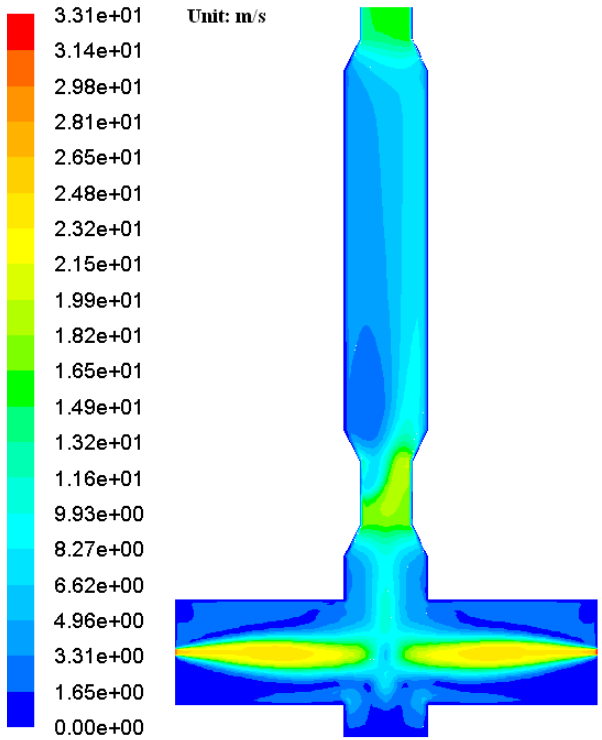
	Vol%, Wet (CFD)	Vol%, Dry (CFD)	Vol%, Wet (Equil.)
H_2O	22.30		20.84
CO	33.71	43.39	34.91
CO_2	12.05	15.51	11.01
H_2	28.03	36.07	30.93
CH_4	1.60	2.06	0.07
H_2S	0.67	0.86	0.68
COS	0.07	0.09	0.03
HCl	0.08	0.10	0.08
Ar	0.73	0.94	0.71
N_2	0.76	0.98	0.74

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

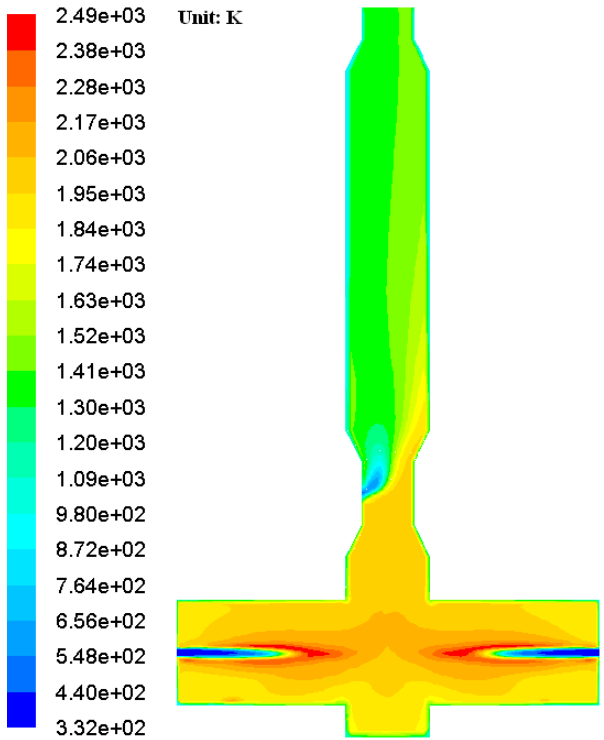
$$K_{eq}(1393\text{K}) = 0.468$$

$$Q_r = \frac{[H_2]\times[CO_2]}{[CO]\times[H_2O]} = 0.449 < K_{eq}$$

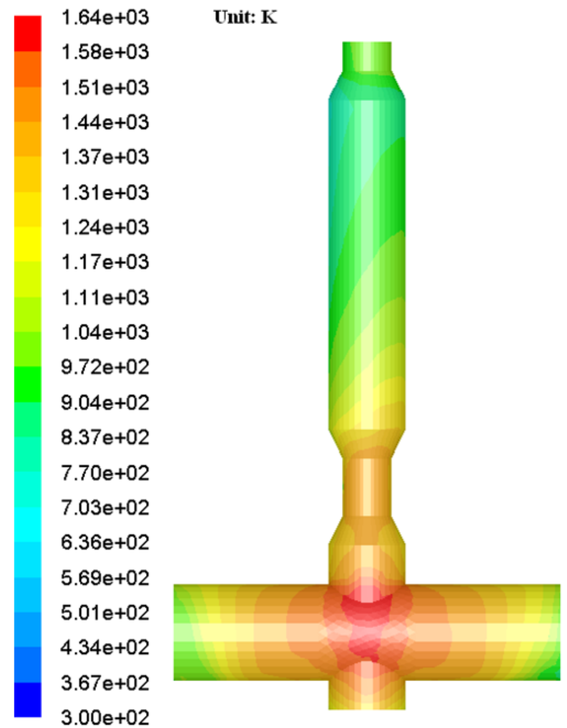
Two-Stage Gasifier Results



Velocity Magnitude



Gas Temperature



Inner Wall Temperature

Conclusions

- **Improved sub-models**
  - Water vaporization
  - Coal Devolatilization
  - Char heterogeneous reaction
  - Gas phase chemistry/kinetics
- **Predictions comparable to plant observations**
  - Consistent model parameters applicable to different design and operating configurations
- **High temperatures predicted near fuel/oxidizer inlets**
  - Diffusion-type flames
  - Have to consider reverse reaction of fuel oxidation
- **Syngas at gasifier exit not in chemical equilibrium**

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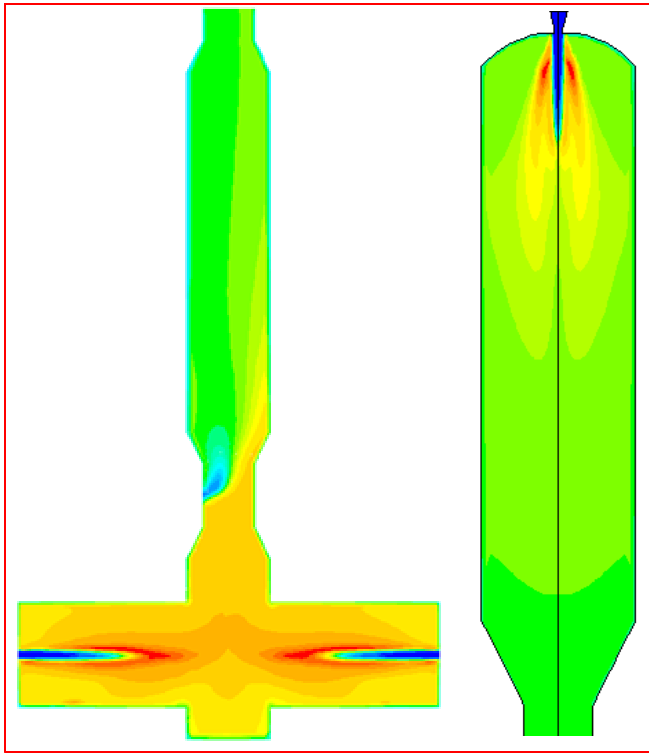
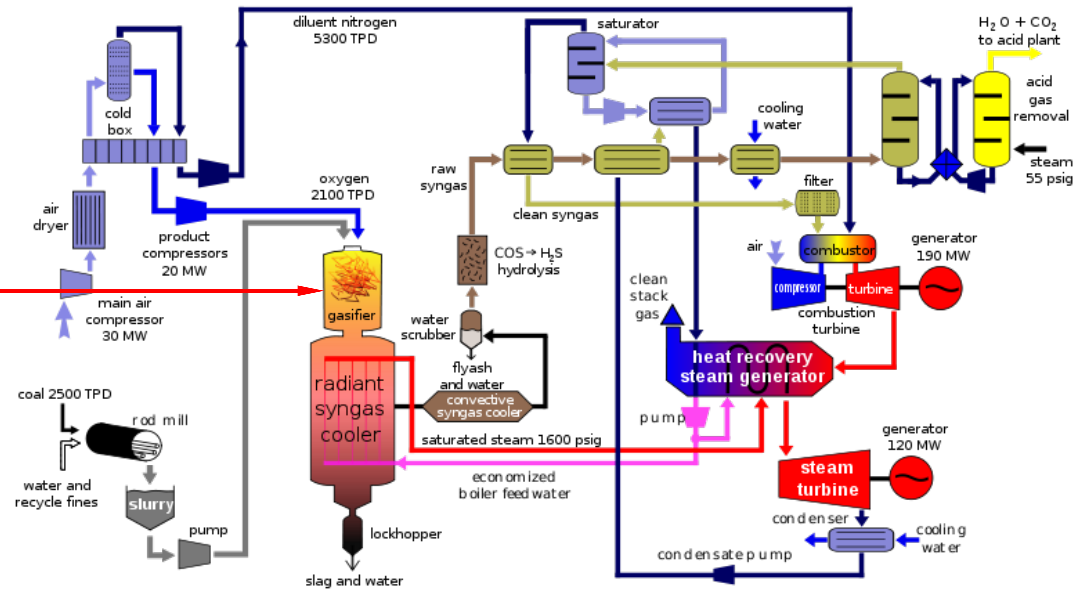
EXTRA SLIDES

Objectives



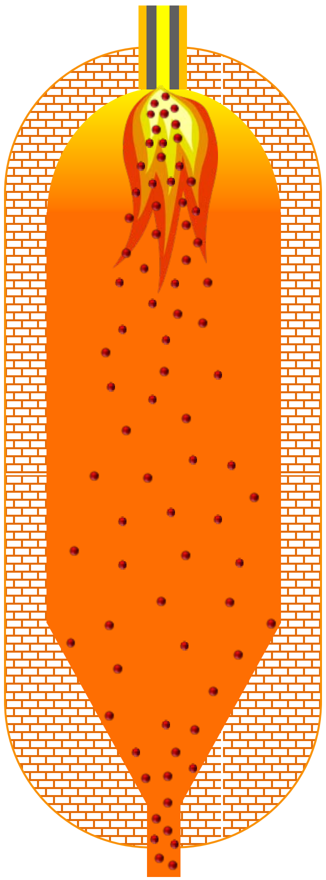
Gasifier CFD Models



IGCC Plant Process Model

- Increase accuracy of CFD model for entrained-flow coal gasification
- Use consistent model parameters for different gasifier configurations
- Embed CFD model for plant wide optimization (Co-Simulation)

Processes Inside an Entrained-Flow Gasifier



- Turbulent particle-laden flow
- Reactions
  - Homogenous
  - Heterogeneous
- Heat transfer
  - Convective
  - Radiative
- Mass transfer
  - Gas phase
  - Particle/droplet boundary
- Phase change
- Ash transformation

Species In CFD Model

- Major species
  - H_2, O_2, CO, CO_2, H_2O, CH_4, C_6H_6 (Tar)
- Minor species
  - Ar, N_2, H_2S, COS, HCl
- Coal related species (required by APECS)
  - C, S, Cl_2, SiO_2 (Ash)
- Total number of Species: 16
- 11 Coal volatile species
  - H_2, O_2, CO, CO_2, H_2O, CH_4, C_6H_6 , N_2, H_2S, COS, HCl
- Species Added
  - COS, C_6H_6
- Desired output
  - Mass balance for C, H, O, N, S, Cl, Ar, and Ash

Coal Devolatilization Sub-Model

Other Considerations

- **Heat of devolatilization (dry-ash-free basis)**

$$Coal \rightarrow y_{vol} Volatile + (1 - y_{vol}) Char$$

$$Coal \rightarrow y_{vol} \sum_{i=1}^{11} \alpha_i S_i^{vol} + (1 - y_{vol}) Char$$

$$\Delta H_{devol} = (1 - y_{vol}) H_{f,char} + y_{vol} \sum_{i=1}^{11} \alpha_i H_{f,i} - H_{f,coal}$$

- **Pressure effect on volatile yield**
  - **Lower at a higher pressure**
- **Pressure effect on coal particle swelling**
  - **Slightly higher at a higher pressure**
- **Heating rate effect on coal particle swelling**
  - **Lower at a higher heating rate**

Gas Phase Kinetics

Methane/Steam Reforming

$$R_{rxn} = AT^m \exp\left(-\frac{E}{RT}\right) C_{r_1}^{n_1} C_{r_2}^{n_2}$$

Units in kmol, K, m, s

Reaction	m	n_1	n_2	A	E	Reference
$CH_4 + H_2O \rightarrow CO + 3H_2$	0	0.5	1	$8x10^7$	$2.51x10^8$	Estimated

Literature: 1^{st} order based on Jones and Lindstedt (1988), E=$1.255x10^8$

Reverse reaction: Not modeled

Gas Phase Kinetics

Benzene/Steam Reaction

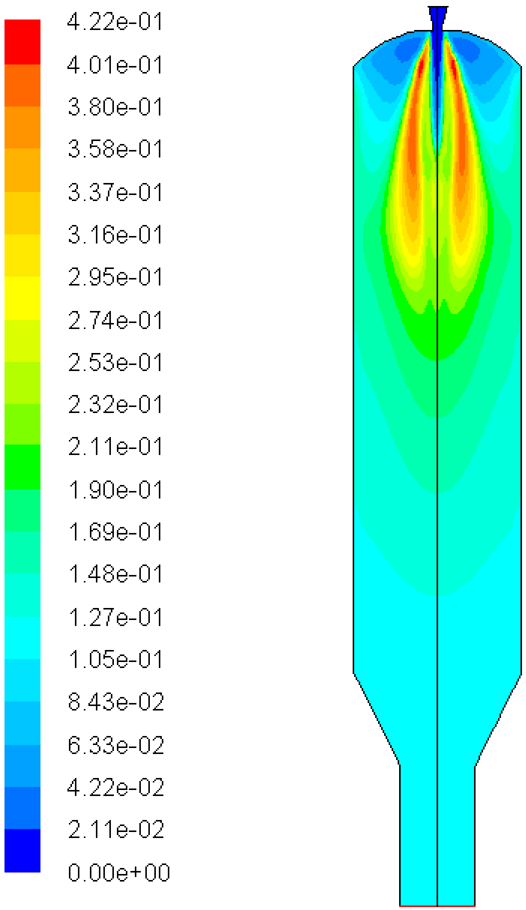
$$R_{rxn} = AT^{m} \exp\left(-\frac{E}{RT}\right) C_{r_1}^{n_1} C_{r_2}^{n_2}$$

Units in kmol, K, m, s

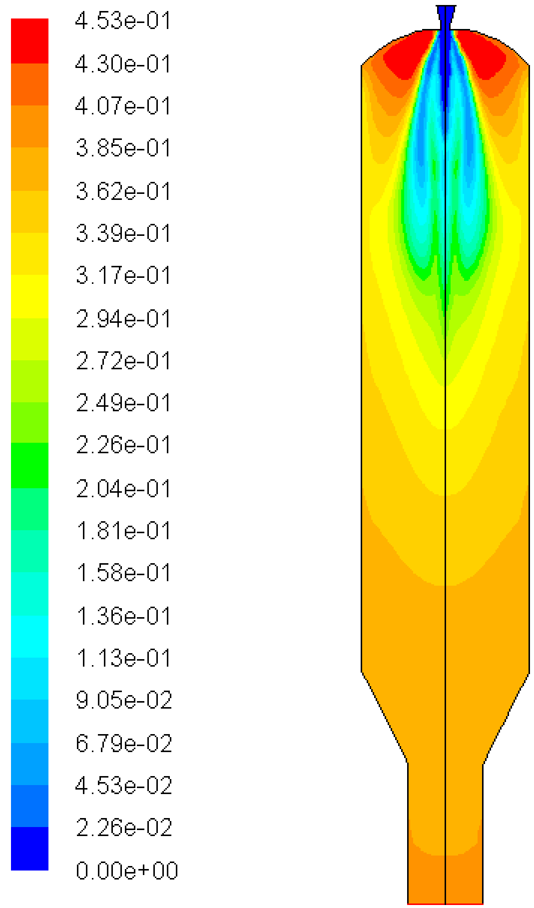
Reaction	m	n_1	n_2	A	E	Reference
$C_6H_6 + 6H_2O \rightarrow 9H_2 + 6CO$	0	0.5	1	8×10^8	2.51×10^8	Estimated

Note: Use data for methane/steam reforming with A increased by a factor of 10

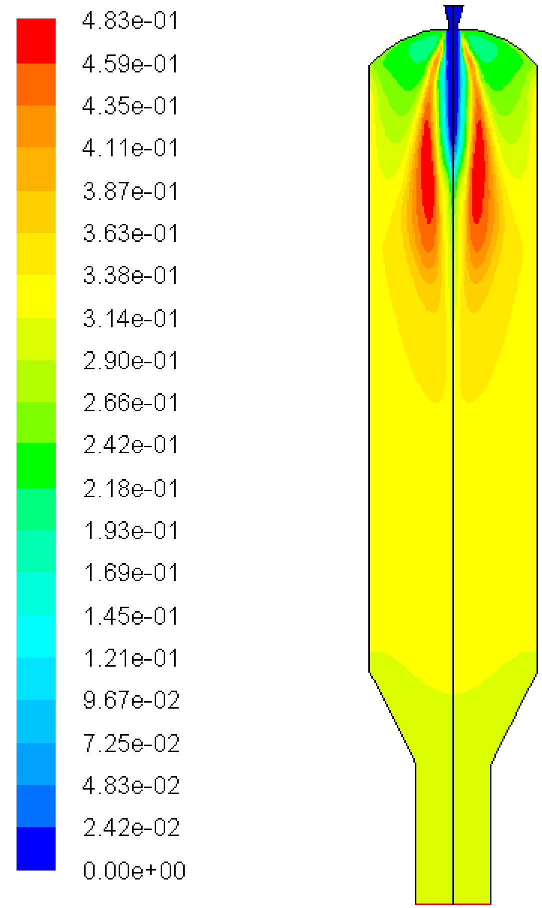
Single-Stage Gasifier Results



CO_2 Mole Fraction

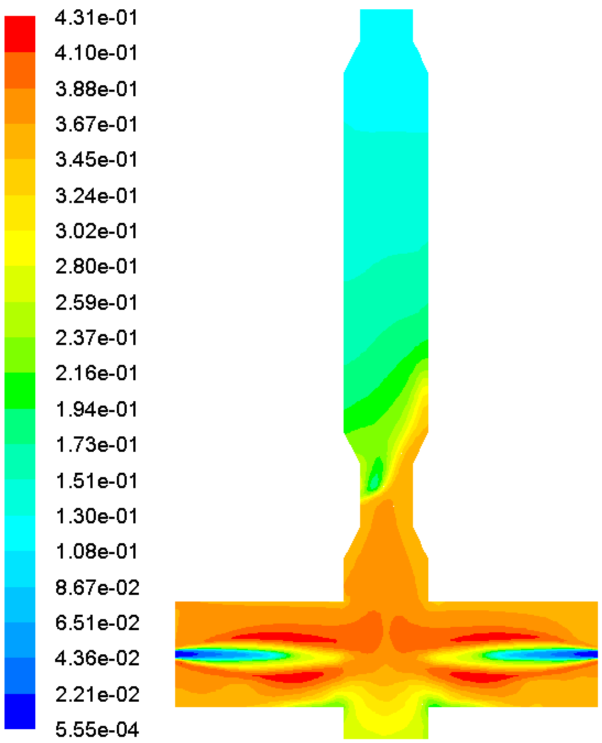


CO Mole Fraction

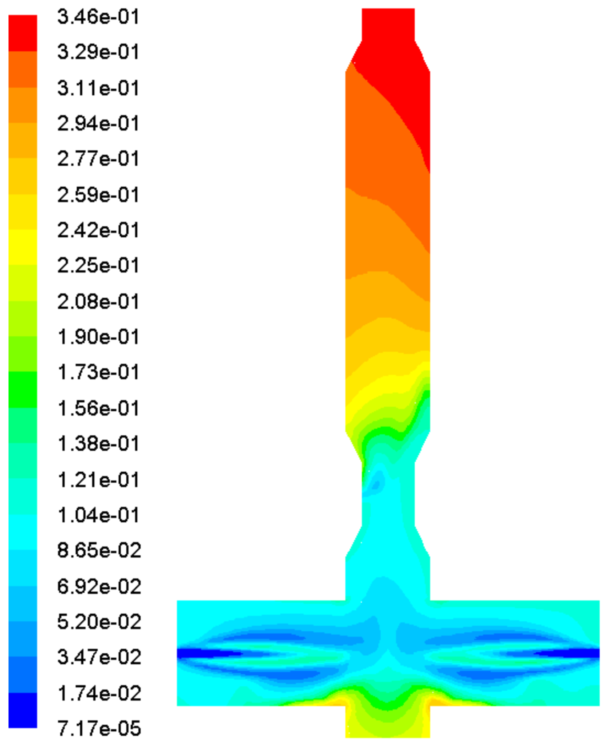


H_2 Mole Fraction

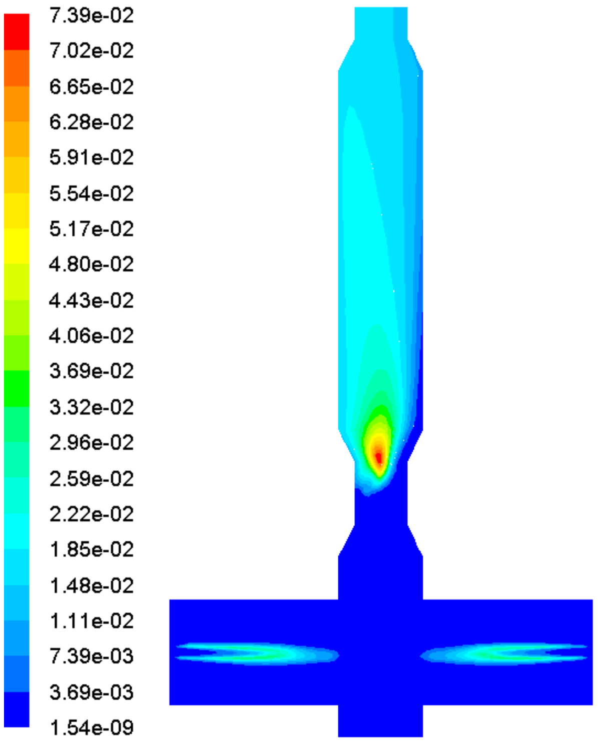
Two-Stage Gasifier Results



CO_2 Mole Fraction

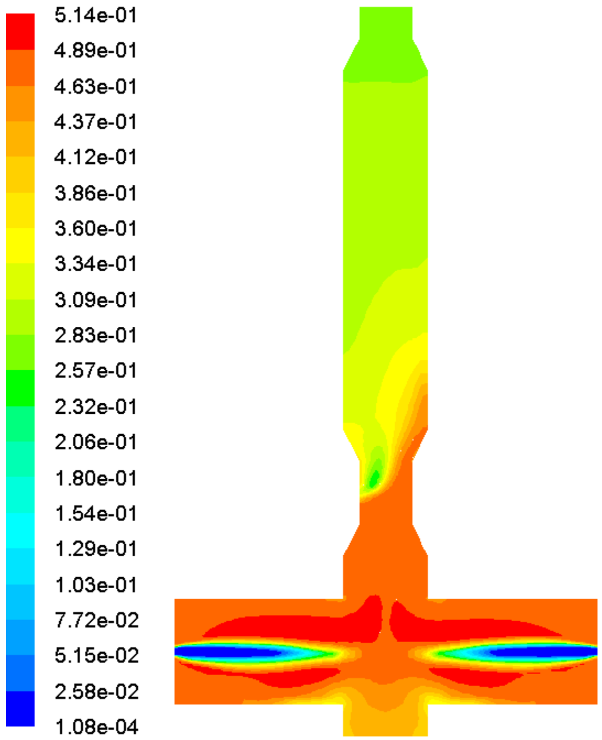


CO Mole Fraction

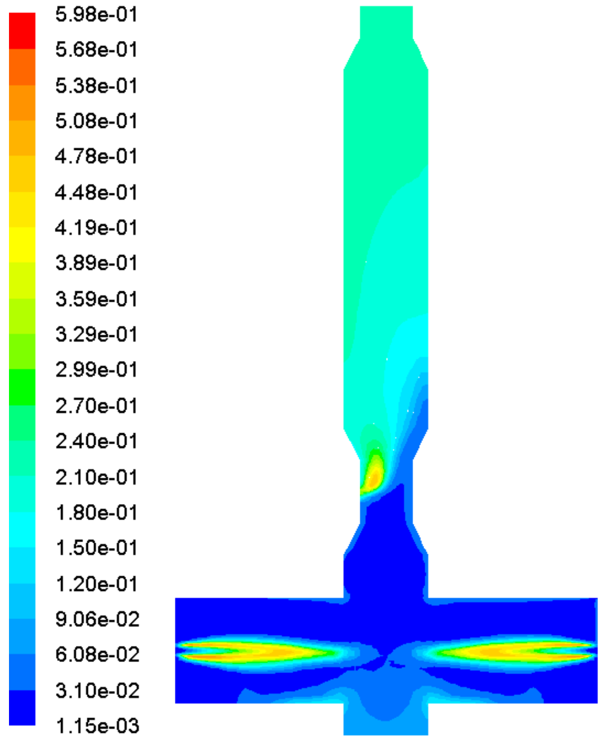


CH_4 Mole Fraction

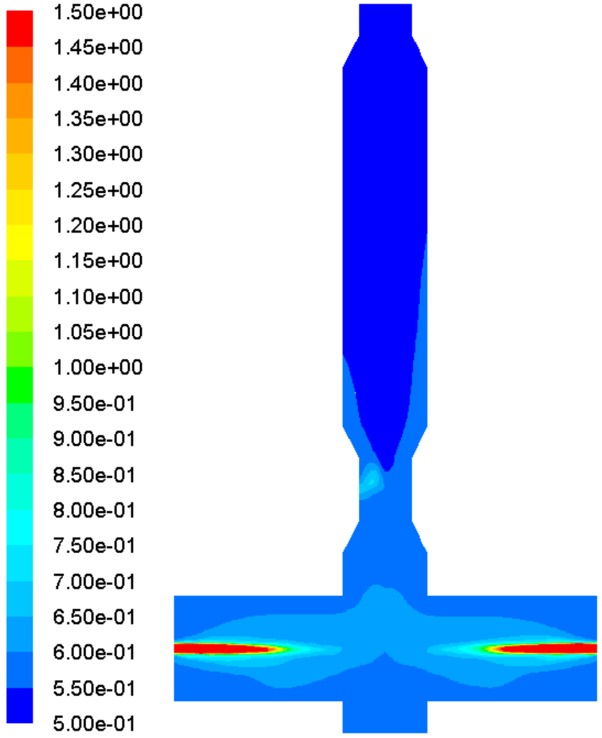
Two-Stage Gasifier Results



H_2 Mole Fraction



H_2O Mole Fraction



Stoichiometric Ratio