Gasification Studies

Task 4 Topical Report, Utah Clean Coal Program

Reporting Period Start Date: August 2011

Report Period End Date: November 2013

Principal Authors: Kevin Whitty, Thomas Fletcher, Ronald Pugmire, Philip Smith, James Sutherland, Jeremy Thornock, Babak Boshayeshi, Isaac Hunsacker, Aaron Lewis, Travis Waing, and Kerry Kelly,

Issue date: February 6, 2014

DOE Award Number: DE-NT0005015
Project Officer: David Lang

University of Utah
Institute for Clean & Secure Energy
380 INSCC
155 South, 1452 East
Salt Lake City, UT 84112
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
ABSTRACT

A key objective of the Task 4 activities has been to develop simulation tools to support development, troubleshooting and optimization of pressurized entrained-flow coal gasifiers. The overall gasifier models (Subtask 4.1) combine submodels for fluid flow (Subtask 4.2) and heat transfer (Subtask 4.3) with fundamental understanding of the chemical processes (Subtask 4.4) processes that take place as coal particles are converted to synthesis gas and slag. However, it is important to be able to compare predictions from the models against data obtained from actual operating coal gasifiers, and Subtask 4.6 aims to provide an accessible, non-proprietary system, which can be operated over a wide range of conditions to provide well-characterized data for model validation.

Highlights of this work include:

- Verification and validation activities performed with the Arches coal gasification simulation tool on experimental data from the CANMET gasifier (Subtask 4.1).
- The simulation of multiphase reacting flows with coal particles including detailed gas-phase chemistry calculations using an extension of the one-dimensional turbulence model’s capability (Subtask 4.2).
- The demonstration and implementation of the Reverse Monte Carlo ray tracing (RMCRT) radiation algorithm in the ARCHES code (Subtask 4.3).
- Determination of steam and CO$_2$ gasification kinetics of bituminous coal chars at high temperature and elevated pressure under entrained-flow conditions (Subtask 4.4). In addition, attempts were made to gain insight into the chemical structure differences between young and mature coal soot, but both NMR and TEM characterization efforts were hampered by the highly reacted nature of the soot.
- The development, operation, and demonstration of in-situ gas phase measurements from the University of Utah’s pilot-scale entrained-flow coal gasifier (EFG) (Subtask 4.6). This subtask aimed at acquiring predictable, consistent performance and characterizing the environment within the gasifier.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DISCLAIMER</td>
<td>1</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>2</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>5</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>9</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>10</td>
</tr>
<tr>
<td>EXECUTIVE SUMMARY</td>
<td>13</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>16</td>
</tr>
<tr>
<td>METHODS</td>
<td>17</td>
</tr>
<tr>
<td>Subtask 4.1 – Entrained-Flow Gasifier Simulation and Modeling</td>
<td>17</td>
</tr>
<tr>
<td>Experimental Data</td>
<td>17</td>
</tr>
<tr>
<td>The Equilibrium Model</td>
<td>18</td>
</tr>
<tr>
<td>LES Tools for Gasification Modeling</td>
<td>18</td>
</tr>
<tr>
<td>Surrogate Modeling</td>
<td>19</td>
</tr>
<tr>
<td>Subtask 4.2 – Subgrid Mixing and Reaction Modeling</td>
<td>21</td>
</tr>
<tr>
<td>Fluid Dynamics</td>
<td>23</td>
</tr>
<tr>
<td>Particle Dynamics</td>
<td>24</td>
</tr>
<tr>
<td>Coal Sub-Models</td>
<td>25</td>
</tr>
<tr>
<td>Evaporation</td>
<td>25</td>
</tr>
<tr>
<td>Devolatilization</td>
<td>26</td>
</tr>
<tr>
<td>Char Oxidation</td>
<td>26</td>
</tr>
<tr>
<td>Char Gasification</td>
<td>26</td>
</tr>
<tr>
<td>Simulation Conditions</td>
<td>27</td>
</tr>
<tr>
<td>Subtask 4.3 – Radiation Modeling</td>
<td>28</td>
</tr>
<tr>
<td>Subtask 4.4 – Char and Soot Kinetics and Mechanisms</td>
<td>29</td>
</tr>
<tr>
<td>Characterization of Coal Feed Stocks</td>
<td>29</td>
</tr>
<tr>
<td>High-Pressure Flat-Flame Burner Reactor</td>
<td>30</td>
</tr>
<tr>
<td>Re-Injection Strategy for Char Gasification Experiments</td>
<td>32</td>
</tr>
<tr>
<td>Coal Soot Structure Analysis for Use in Soot Model</td>
<td>33</td>
</tr>
<tr>
<td>Coal Analysis by SAXS and PDF</td>
<td>33</td>
</tr>
<tr>
<td>Extension of Sub Models and Gasification Experiments of Soot</td>
<td>34</td>
</tr>
<tr>
<td>Subtask 4.5 – Slag Formation and Slag-Wall Interactions</td>
<td>34</td>
</tr>
<tr>
<td>Subtask 4.6 – Acquisition of Validation Data in an Entrained-Flow Gasifier</td>
<td>34</td>
</tr>
<tr>
<td>Subtask 4.6a: Characterization of Injector Spray Behavior</td>
<td>35</td>
</tr>
<tr>
<td>Injector Design and Modeling</td>
<td>35</td>
</tr>
<tr>
<td>High-Speed Imaging and Image Analysis</td>
<td>36</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 1. Measured syngas flow and reactor temperature .............................................................. 18

Figure 2. Example results from myGPR for evaluating this function at a variety of values, including the error estimate ................................................................. 20

Figure 3. Example of evaluating myGPR a variety of values. The colored surface shows the desired interpolating values, and the error estimate is shown with the translucent grey surfaces. .......... 21

Figure 4. Coal constituents and sub-models .................................................................................. 25

Figure 5. External and cutaway views of BYU’s HPFFB reactor (Shurtz 2011) ........................................ 31

Figure 6. SEM images of (a) sooty and (b) soot-free coal char .................................................... 32

Figure 7. Co-axial, annular, two-stream injector cross-section. Flow is downwards. Red denotes slurry, blue denotes oxygen and yellow denotes the mixing zone .............................................. 36

Figure 8. Redlake high-speed camera ............................................................................................ 37

Figure 9. Threshold adjustment of an image with ImageJ, with the droplets are colored red ............ 37

Figure 10. First (left) and second (right) versions of the patternator ............................................. 38

Figure 11. Laser sheet analysis of injector spray ........................................................................ 39

Figure 12. Low pressure (left) and high pressure (right) test vessels ............................................. 40

Figure 13. Probe extension and rod mount brace ......................................................................... 41

Figure 14. Exploded view of flange assembly and components .................................................... 41

Figure 15. Photograph of the entire probe assembly including (from left to right) flange assembly and cooling lines, stabilizer, probe extension and cooling lines, ball joint guide, threaded rod extensions and U-brace, pneumatic cylinder, support stand, and pneumatic control box ... 42

Figure 16. Flow fields and velocity vectors in the CANMET gasifier .............................................. 43

Figure 17. Carbon conversion effects on gasification ................................................................ 44

Figure 18. Effect of heat loss on gasification ................................................................................ 44

Figure 19. Effect of coal slurry concentration on gasification ........................................................ 45

Figure 20. Scaling analysis ............................................................................................................. 46

Figure 21. Particle temperature and gas-phase temperature (at particle position) vs. time for Black Thunder coal with an initial furnace temperature of 1200 K ............................................ 47

Figure 22. Fractional consumption of coal constituents vs. time for Black Thunder coal with an initial furnace temperature of 1200 K ............................................................... 47

Figure 23. Species evolution ........................................................................................................ 48

Figure 24. Ignition delay criterion – 800K, inflection point and maximum upslope of CO₂ production; a) gas phase at centerline and particle temperature b) consumption fraction of moisture, volatile and char ......................................................... 49

Figure 25. Ignition delay vs. furnace temperature for Pittsburgh (Pt) and Black Thunder (BT) coal particles injected into 20 vol% O₂ in N₂ diluent. Thick and thin lines represent Pittsburgh and Black Thunder coal types and simulation results, respectively. Dashed and solid lines show experimental and simulation results, respectively ....................................................... 50
Figure 26. a) Simulation predictions: particle temperature at ignition point vs. furnace temperature. b) Consumption fraction of volatile and char at ignition point vs. furnace temperature. The thin and thick lines represent Black Thunder and Pittsburgh coal, respectively. .................................................. 50

Figure 27. Ignition delay vs. particle size for Pittsburgh coal. Dotted lines with circles show the boundaries of particle size cuts that were used in the experiments (Liu et al. 2011b). The solid line represents the simulation prediction using the corresponding fixed particle size. .................. 51

Figure 28. Pittsburgh coal in 12 vol% O$_2$ with N$_2$ diluent. a) gas and particle temperature at ignition point. b) consumption fraction of volatile and char at ignition point. ............................................................ 52

Figure 29. Agreement between flux results from RMCRT (red) and the numerically exact solution of Burns and Christon (blue). .................................................................................................................. 53

Figure 30. Ray convergence of the numerical solution compared to the analytical solution of the Burns and Christon case. The ray convergence rate is approximately the expected rate of $-\frac{1}{2}$ .......................... 53

Figure 31. Strong scaling analysis of RMCRT on 8 to 1728 processors using 100 rays per cell on a domain of 150$^3$. ................................................................................................................................. 54

Figure 32. Strong scaling of RMCRT on the Titan GPU cluster................................................................................................................................. 54

Figure 33. Agreement between results from RMCRT (green) and the analytical solution of Michael Modest (blue). .................................................................................................................. 55

Figure 34. Ray convergence of RMCRT relative to an analytical solution. Note the ray convergence rate is approximately the expected rate of $-\frac{1}{2}$ ........................................................................ 56

Figure 35. Converged solution of the radiative flux divergence (blue) for a benchmark case compared to the radiative flux divergences from various grid resolutions (other). Notice that at the locations of interest (cell centers) there is good agreement even for the coarsest meshes. What is not well represented in the coarse meshes, however, is the detail between the cell centers. ...................... 57

Figure 36: RMCRT (*) vs. exact solution (-) for varying optical thicknesses and scattering albedos for Siegel’s benchmark case (Siegel 1987). ................................................................. 58

Figure 37. Grid convergence of the L1 error norms for the Siegel case where the scattering coefficient is 8 m$^{-1}$, and the absorption coefficient is 2m$^{-1}$. ............................................................................. 59

Figure 38. Radiative flux as computed by RMCRT (+) vs. DOM SN8 (-) for varying positions along the z direction of a center-line through the boiler. ........................................................................ 59

Figure 39. Radiative flux as calculated by RMCRT (-) vs. DOM (+) for varying positions along the z direction of a center-line through the boiler. ........................................................................ 60

Figure 40. Filtered solution of the radiative flux as calculated by RMCRT(-) vs. DOM(+) for varying positions along the z direction of a center-line through the boiler. ............................ 60

Figure 41. Temperature field of a center-slice of an oxy-coal furnace simulation. The radiation model used in this simulation incorporates entrained coal particles. .................................................. 62

Figure 42. SEM images of sieved (a) Utah Skyline (b) Pitt #8, and (c) IL#6 chars that acted as feed stock material for 15 atm steam gasification HPFFB re-injection experiments. ................................. 63

Figure 43. Centerline gas temperature profiles of the HPFFB steam conditions corrected for radiation losses from the thermocouple bead. ................................................................................ 67
Figure 44. Centerline gas temperature profiles of the HPFFB CO\textsubscript{2}/steam conditions corrected for radiation losses from the thermocouple bead.................................................................68
Figure 45. Effect of mass loss by H\textsubscript{2}O and CO\textsubscript{2} gasification when feeding 75-106 μm IL ........................................73
Figure 46. Effect of mass loss by H\textsubscript{2}O and CO\textsubscript{2} gasification when feeding 45-75 μm Utah Skyline coal char in the HPFFB reactor at the 15 atm 1830 K steam condition.................................................................74
Figure 47. Parity plots of HPFFB H\textsubscript{2}O gasification data for (a) Illinois #6 and (b) Utah Skyline coal chars using mass loss data attributed to H\textsubscript{2}O gasification.................................................................76
Figure 48. Measured and predicted values of daf mass release of IL#6 coal char at the.................................77
Figure 49. First-order model predictions for the distribution of mass loss caused by H\textsubscript{2}O and CO\textsubscript{2} gasification using kinetic parameters in Table 12 for IL#6 char reacting at the 15 atm 1812 K H\textsubscript{2}O/CO\textsubscript{2} HPFFB condition..................................................................................................................78
Figure 50. First-order model predictions for the distribution of mass loss caused by....................................79
Figure 51. Original HRTEM image of Kentucky #9 soot at a magnification of 716,000x .......................... 80
Figure 52. Image after increasing the contrast...............................................................................................81
Figure 53. Painting the FFT of an image to improve texture. (Images taken from www.skeller.ch/ps/fft_action.php).........................................................................................................................81
Figure 54. FFT filtered image........................................................................................................................82
Figure 55. Binary image..................................................................................................................................82
Figure 56. Carbon skeleton image................................................................................................................83
Figure 57. Pruning an unreasonable shape out of the carbon skeleton image ...........................................83
Figure 58. Fully processed HRTEM image after rejecting the small features...........................................84
Figure 59. Components of the coaxial atomizer (left) and face of several micro-hole atomizers (right). The labels on the micro-hole injectors indicate the number of holes as well as the diameter of each hole in thousands of an inch. .................................................................87
Figure 60. Digitally adjusted photo of water spray through a micro-hole injector with oxygen flow through eight holes of 0.015 inch diameter. 2.3 lb/hr air flow and 38 gph liquid flow. No inner air channel..............................................................................................................87
Figure 61. Patternation of various slurries at 45 liter per hour liquid flow using the 8-MH-0.023 injector. Mass flow rates of air are indicated on each plot. .................................................................88
Figure 62. Effect of inner and outer airflow on the average droplet diameter with a level inner tube. The inner air flow is shown along the x-axis while the different colored curves represent the different outer air flows. The left chart shows presents results when the inner tube was flush with the face of the main body of the atomizer. The right chart shows results when the inner tube was recessed approximately 0.25 inches from the face.................................................................89
Figure 63. Schematic of edge position evaluation with PSV........................................................................90
Figure 64. Two-factor histogram (droplet diameter and angle of travel, with 180° facing straight down) for the 12 gph, 43 wt.% petcoke slurry, edge case. .................................................................90
Figure 65. Measured gas compositions for carbon monoxide (\(\text{CO}\)), hydrogen (\(\text{H}_2\)), and carbon dioxide (\(\text{CO}_2\)), vol% dry. All radial locations are shown. Error bars represent standard error.............................................91
Figure 66. Radial gas compositions as a function of temperature, dry volume percent .............................. 92
Figure 67. System temperature (maximum measured by thermocouples) and pressure during operation with petroleum coke at 2700 °F and 200 psi. ................................................................. 94
LIST OF TABLES

Table 1. Typical measured data for the CANMET gasifier .......................................................... 17
Table 2. Proximate and ultimate analysis of the coals ..................................................................... 27
Table 3. Species composition for furnace temperature impact study ......................................................... 27
Table 4. Species composition for particle size impact study ........................................................................ 28
Table 5. Ultimate and proximate analyses of the feed stocks of 45-75 μm coals ........................................... 30
Table 6. The measured syngas composition and temperature inside the furnace ........................................... 45
Table 7. Comparison of measured and predicted data .............................................................................. 45
Table 8. Timing and accuracy of RMCRT and DOM SN8 ........................................................................... 61
Table 9. Summary of re-injected feed stock coal chars ........................................................................... 64
Table 10. Summary of HPFFB steam gasification conditions ................................................................. 65
Table 11. Summary of HPFFB CO2/steam gasification conditions ............................................................ 65
Table 12. H2O and CO2 gasification kinetic parameters for use in the first-order model ............................... 75
Table 13. Composition of the Post-Flame Environment for the H2O/CO2 HPFFB ................................. 77
Table 14. List of soot samples generated in the HPFFB and analyzed using HRTEM. Eastern bituminous A and B coals are labeled as EB ‘A’ and EB ‘B’ ........................................................................................................... 80
Table 15. Comparison of NMR* and TEM/Fringe3D (TF3D) analyses of tar/soot and char samples from eastern bituminous coal ‘A’ pyrolyzed at 1350 K and 1 atm after ~35 ms using a collection height of 1.275” above the burner ........................................................................................................................................ 85
Table 16. Heating values of intermediate and outlet syngas ..................................................................... 93
Table 17. Range of operating conditions for solid fuel used ................................................................. 93
Table 18. Select operating conditions and results for gasifier tests using coal ........................................ 93
LIST OF ABBREVIATIONS

$A_2$ Arrhenius pre-exponential factor of Kobayashi devolatilization model high-temperature devolatilization reaction

$A_{bead}$ area of thermocouple bead

$A_p$ external surface area of an assumed-spherical particle

BT Black Thunder

BYU Brigham Young University

CANMET Canada Center for Mineral and Energy Technology

CBK carbon burnout kinetics code

CFD computational fluid dynamics

$C_p$ heat capacity of the particle

CPD chemical percolation devolatilization

CPMAS cross polarization with magic angle spinning

CPU central processing unit

CWS coal-water slurry

$d_0$ mass mean diameter of feed stock material

$d_f$ mass mean diameter of collected char

$D_{AB}$ binary diffusivity coefficient

DAE distributed activation energy

daf dry and ash-free

DivQ radiative flux divergence

$d_m$ mass mean of particles

DNS direct numerical simulation

DO discrete ordinates

DOM discrete ordinates method

$d_p$ mass mean diameter of coal particles

DQMOM direct quadrature method of moments

DSLR digital single-lens reflex

$E$ activation energy

$E_2$ activation energy of high-temperature devolatilization reaction

EBA Eastern Bituminous B

EBB Eastern Bituminous A

EFG entrained flow gasifier

$E_{h,CO_2}$ activation energy of char oxidation reaction by CO$_2$

FFB flat flame burner

FFT fast Fourier transform
GC  gas chromatograph
GPR  Gaussian process regression
GPU  graphics processing unit
HAB  height above burner
\( h_c \)  convective heat transfer coefficient
\( h_m \)  mass transfer coefficient
HPFFB high-pressure flat-flame burner reactor
HRTEM high-resolution transmission electron microscope
IL #6  Illinois #6 coal
\( k_{gas} \)  gas thermal conductivity
LEFR  laminar entrained flow reactor
LES  large eddy simulation
\( m_0 \)  mass of fed material on a dry basis
\( m_0^{\text{ash,feedstock}} \)  dry mass of ash in the fed feedstock
\( m_0^{\text{feedstock}} \)  dry mass of feedstock fed
\( m_1 \)  mass of collected char on a dry basis
\( m_{\text{char collected}} \)  dry mass of char collected
\( m_{\text{coal}} \)  mass flowrate of coal
\( m_p \)  mass of particle
MS  mass spectrometry
\( n \)  number of data points
NMR  nuclear magnetic resonance
\( Nu \)  Nusselt number
ODT  one-dimensional turbulence
PCA  principal component analysis
PDF  pairwise distribution function
PFFB  pressurized flat-flame burner
Pitt #8  Pittsburgh #8 coal
\( P_{\text{reactant,in}} \)  partial pressure of reactant in the bulk gas
\( P_{\text{reactant,surf}} \)  partial pressure of CO\(_2\) of H\(_2\)O at the particle surface
PSV  particle shadow velocimetry
Pt  Pittsburg coal
\( R \)  ideal gas constant
RMCRT  reverse Monte Carlo ray tracing
RTD  residence time distribution
RTE  radiative transport equation
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAXS</td>
<td>small angle x-ray scattering</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SG</td>
<td>syngas</td>
</tr>
<tr>
<td>SLPM</td>
<td>standard liter per minute</td>
</tr>
<tr>
<td>SN4</td>
<td>24-direction DOM</td>
</tr>
<tr>
<td>SN8</td>
<td>80-direction DOM</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$T_{\text{bead}}$</td>
<td>thermocouple bead temperature</td>
</tr>
<tr>
<td>TC</td>
<td>thermocouple</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TF3D</td>
<td>TEM/Fringe3D method that predicts chemical structure</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>$T_{\text{gas}}$</td>
<td>gas temperature</td>
</tr>
<tr>
<td>$T_p$</td>
<td>particle temperature</td>
</tr>
<tr>
<td>TRI</td>
<td>turbulent radiation interactions</td>
</tr>
<tr>
<td>$T_{\text{surr}}$</td>
<td>temperature of surroundings</td>
</tr>
<tr>
<td>$T_{\text{wall}}$</td>
<td>wall temperature of the gasifier</td>
</tr>
<tr>
<td>V/UQ</td>
<td>validation/uncertainty quantification</td>
</tr>
<tr>
<td>$x^0_{\text{ash, char collected}}$</td>
<td>ash mass fraction in the dried, collected char</td>
</tr>
<tr>
<td>$x^0_{\text{ash, feed stock}}$</td>
<td>ash mass fraction in the dry feed stock</td>
</tr>
<tr>
<td>$X_i^E$</td>
<td>experimental daf mass release</td>
</tr>
<tr>
<td>$X_i^M$</td>
<td>modeled daf mass release</td>
</tr>
<tr>
<td>$\Delta H_{\text{rxn}}$</td>
<td>heat of reaction</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>emissivity of thermocouple bead</td>
</tr>
<tr>
<td>$\varepsilon_b$</td>
<td>packing factor or inter-particle void fraction</td>
</tr>
<tr>
<td>$\varepsilon_p$</td>
<td>emissivity of particle</td>
</tr>
<tr>
<td>$\rho_0$</td>
<td>apparent density of dried feed stock material</td>
</tr>
<tr>
<td>$\rho_1$</td>
<td>apparent density of dried, collected char</td>
</tr>
<tr>
<td>$\rho_{\text{apparent}}$</td>
<td>apparent density</td>
</tr>
<tr>
<td>$\rho_{\text{bulk}}$</td>
<td>bulk density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stefan-Boltzmann constant</td>
</tr>
<tr>
<td>$\nu$</td>
<td>mass of carbon that reacts per mole of reactant</td>
</tr>
</tbody>
</table>
EXECUTIVE SUMMARY

A key objective of the Task 4 activities has been to develop simulation tools to support development, troubleshooting and optimization of pressurized entrained-flow coal gasifiers. The overall gasifier models (Subtask 4.1) combine submodels for fluid flow (Subtask 4.2) and heat transfer (Subtask 4.3) with fundamental understanding of the chemical (Subtask 4.4) processes that take place as coal particles are converted to synthesis gas. However, it is important to be able to compare predictions from the models against data obtained from actual operating coal gasifiers, and Subtask 4.6 aims to provide an accessible, non-proprietary system, which can be operated over a wide range of conditions to provide well-characterized data for model validation.

Subtask 4.1 focused on the collection and analysis of CANMET gasifier experimental data under the collaborative agreement between the University of Utah and CANMET. Three parameters were selected for the V/UQ evaluation matrix: O₂/coal feeding ratio, coal slurry concentration, and heat loss fraction. In addition, a cold flow LES simulation was conducted, which revealed that the injection region and recirculation region occupies 2/3 of the total furnace volume. Further, an equilibrium model was developed to study the effects of operating parameters, such as carbon conversion, heat loss ratio and coal slurry concentration, on the gasification performance. The equilibrium model showed that as heat loss increases, temperature drops rapidly, CO concentration decreases while H₂ concentration increases. As the coal slurry concentration increases from 53% to 65%, both CO and H₂ increase by 4%. The comparison between equilibrium prediction and CANMET measured data shows that temperature, CO, CO₂ and H₂ concentration agrees well. This indicates that the gasification of coal is close to equilibrium and the equilibrium assumption is reasonable although the carbon conversion is low.

Efforts surrounding Subtask 4.2 focused on the implementation of several submodels into our one-dimensional turbulence model to address the fate of coal particles in combustion/gasification processes, including: (1) moisture evaporation from coal; (2) devolatilization to describe the volatile species and their rates of evolution from the particle to the gas phase; and (3) char oxidation/gasification to calculate the char oxidation rate based on the particle temperature and oxygen partial pressure. For various furnace temperatures and particle sizes, predicted ignition delay was compared with experimental measurements for a single-particle laminar jet. The predicted and measured ignition delay in furnace temperature and particle size studies were compared.

Subtask 4.3 focused on the expansion of radiative heat-transfer algorithms in the University of Utah LES codes to include coal particles under entrained coal gasification conditions. This was accomplished by enhancing the legacy Discrete Ordinates Method (DOM) to model the combined effect of the gas-phase and particle-phase absorption coefficients.

A reverse Monte Carlo ray tracing (RMCRT) method was developed to compute accurately and efficiently the radiative heat exchange in LES combustion simulations. The capabilities and functionality of the RMCRT algorithm were extended. Capabilities include the modeling of non-homogeneous absorbing, emitting media; gray reflecting, absorbing, emitting walls; and homogeneous scattering media. The ability to compute volume flux divergences, surface fluxes on boundaries, and surface fluxes on imaginary surfaces was implemented. A virtual radiometer model that computes fluxes to small surfaces...
with arbitrary view angles and orientations was implemented for validation purposes. The maintainability of these algorithms was improved with the abstraction of redundant code into a C++ function, which can be called by various methods. The new features were tested in parallel and scaled to 1728 processors. The accuracy of the results was verified against radiative-flux results of a benchmark case described in Burns and Christen (1997). The same capability that allowed the DOM to model entrained coal particles was added to the RMCRT model.

To ensure the optimization of the RMCRT algorithm under production-scale conditions, measurements of execution time as well as accuracy were collected. The production-scale simulation was for a large furnace with a computational domain of 24 million cells, run to 70,000+ time steps, using 1300+ processors. In this simulation, the accuracy of the RMCRT algorithm was maximized while not exceeding the computation time of the DOM. A filtering technique was implemented to decrease the stochastic noise of the RMCRT solution. Filtered results show accuracy that is nearly double that of 24-direction DOM (SN4), with approximately the same computational time.

Work on Subtask 4.4 included regressing kinetic parameters for char-steam gasification for two bituminous coal chars (Illinois #6 and Utah Skyline) using measured data from an entrained-flow reactor at pressures up to 15 atm and gas temperatures up to 1830 K. Utah Skyline char was 1.6 times more reactive to steam than the Illinois #6 char. The steam gasification rate of Illinois #6 coal char was about 6 times faster than its CO\textsubscript{2} gasification rate.

The gasification of a single coal char (Illinois #6) was studied in order to gain insight about the mass loss of coal char in the presence of both H\textsubscript{2}O and CO\textsubscript{2}. Good agreement between measured and modeled mass release was obtained when using a first-order model and regressed kinetic parameters from the current study with the assumption that H\textsubscript{2}O and CO\textsubscript{2} rates are additive.

Transmission electron microscope images of coal char and soot were analyzed for structural parameters to gain insight about the maturation of coal soot. However, the structural information using TEM images was not deemed satisfactory for either char or soot after comparing to trusted nuclear magnetic resonance (NMR) measurements. In addition, only select samples could be analyzed by NMR for structural information since the high conductivity of most of the collected soot interfered with NMR magnetization.

Measurements by small angle x-ray scattering and atomic pairwise distribution function were made on char and soot samples from 4 different coals in an effort to provide size and porosity information. However, obtaining detailed structural information from these measurements was prevented by non-uniform samples in terms of particle composition and size.

Subtask 4.6 focused on developing the University of Utah’s pressurized entrained-flow gasifier, which completed construction and was brought online during Phase 2 of this program, to be a useful tool for acquiring data for validation of computational simulations. Subtask 4.6 had two primary activities: (1) development and characterization of an efficient, reliable coal-water slurry injector and (2) development of a safe probe for sampling the gas environment in the reactor during operation. Injector development and characterization is important partly because the injector represents one of the boundaries for simulations. However, having an injector that provides consistent, stable and repeatable performance is
also important to ensure the quality and to minimize the uncertainty of validation data. Under that activity, multiple injector types were explored. Most were two-stream airblast atomizers that use a high velocity annular jet to shatter a central liquid stream, similar to those developed for other liquid spray applications. Some prototypes were three-stream atomizers that incorporated a central gas channel as well. The two-stream atomizers were simpler to manufacture and operate, and were the only type used during operation of the entrained flow gasifier during this project. The most important injector modification made as determined by improvements in gasifier operation and stability was the change from an adjustable injector to a fixed injector, which allowed less flexibility but far more repeatability. The most reliable design employed 8 to 24 very small “micro-holes” directed at the liquid channel. Ex-situ characterization showed that the droplet size from this injector ranged from roughly 200 to 1000 microns, depending on conditions, and gasifier performance when using this injector was very stable. The probe developed under the second activity was water-cooled and could be quickly moved to any location across the diameter of the reactor with a pneumatic positioner. Redundant purge streams isolated the probe from the laboratory for safety. The probe was used to take gas samples at three temperatures and three radial positions during gasifier operation on coal. While little change was seen as a result of changing radial position, the temperature, as a function of stoichiometric ratio, was shown to affect the resulting syngas composition as measured by the probe. Successful operation of the University of Utah’s gasifier was accomplished at a range of operating conditions with various solid fuels. The stability and duration of these runs increased substantially as experience with the system increased, as well as with improvements in the injector design.
INTRODUCTION

Gasification of coal for power generation is recognized as a promising technology that offers higher coal-to-electricity efficiency and lower emissions than conventional pulverized coal boiler-based power generation. In addition, integrated gasification combined cycle (IGCC) systems enable concentration and separation of carbon dioxide for subsequent sequestration, which is especially attractive in light of existing and possible future legislation penalizing emission of CO$_2$. The leading coal gasification technologies for IGCC are pressurized, high temperature entrained-flow gasifiers (EFGs) offered by e.g. GE, ConocoPhillips, Siemens and Shell. There are currently five industrial-scale entrained-flow coal gasifier installations in the United States: the GE gasifiers at the world’s largest IGCC system operated by Duke Energy in Edwardsport, Indiana, the GE gasifier at Tampa Electric’s Polk Power Station, the GE gasifiers at Eastman Chemical Company’s facility in Kingsport, Tennessee, the GE gasifier at the Coffeyville, Kansas Syngas Plant and the Conoco-Phillips gasifier at the Wabash River power station in Terre Haute, Indiana. Despite increasing support for, and deployment of, entrained-flow coal gasification systems, there is still much that is not understood about processes that take place in EFGs. Considering the very high cost of coal gasification systems, it is desirable to maximize performance and coal utilization in such systems. This is most effectively achieved through a combination of computational simulation and supporting experiments for model validation.

The ultimate objective of this task is to provide simulation tools for industrial entrained flow integrated gasification combined cycle gasifiers that will predict: heat transfer by radiation and convection, coal conversion, soot formation, synthesis gas composition and slag behavior with quantified uncertainty. This will enable more rapid deployment of this carbon-capture-ready technology and will help mitigate some of the current operational challenges associated with gasifiers. For example, current coal gasifier designs suffer from low availability, which increases capital and operating costs. Improved modeling capabilities can facilitate the design of gasifiers with greater availability and reduced size. This task aims to develop modeling and associated validation capabilities as well as an improved understanding of the following processes: the heterogeneous kinetics of char gasification, changes in physical structure during coal pyrolysis, and soot formation.

Improvements in modeling capabilities include the development of a large-eddy simulation (LES) gasification tool and the development of a new radiation model, which will reduce the computing time and allow the implementation of the physics necessary to represent gasification conditions.

The University of Utah’s pilot-scale pressurized entrained-flow coal gasifier offers a unique capability for obtaining validation data, and is the only pilot-scale research facility in the United States. This task involves the collection of experimental data over for use in validation/uncertainty quantification (V/UQ) activities.
METHODS
Subtask 4.1 – Entrained-Flow Gasifier Simulation and Modeling

Experimental Data

Collaborations with CANMET began in May 2012, and CANMET shared the following data (Chui et al. 2009):

- Detailed dimensions of the gasifier and nozzle.
- Operating conditions such as pressure, and feedstock flow rate.
- Typical measured data including temperature profiles and the major components of the syngas.

These data was analyzed in detail to determine their uncertainty in preparation for a V/UQ analysis. Table 1 and Figure 1 show examples for the data. Table 1 shows the time averaged measurements as well as their variability. The maximum percent standard deviation is for the syngas flow rate, which is 15.7%, (Figure 1(a)). This level of variability is expected. Furthermore, other important measured data such as temperature (Figure 1(b)) shows that the measurement is steady enough to serve as a good validation baseline.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Average</th>
<th>Standard deviation</th>
<th>Standard deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂, %</td>
<td>56.7</td>
<td>1.64</td>
<td>2.90</td>
</tr>
<tr>
<td>O₂, %</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>CO₂, %</td>
<td>36.2</td>
<td>0.29</td>
<td>0.81</td>
</tr>
<tr>
<td>Slurry flow rate, kg/h</td>
<td>80.4</td>
<td>5.44</td>
<td>6.77</td>
</tr>
<tr>
<td>O₂ flow rate, kg/h</td>
<td>39.8</td>
<td>0.37</td>
<td>0.93</td>
</tr>
<tr>
<td>O₂ correction, kg/h</td>
<td>40.23</td>
<td>0.37</td>
<td>0.92</td>
</tr>
<tr>
<td>Syngas flow rate, kg/h</td>
<td>6.05</td>
<td>0.94</td>
<td>15.6</td>
</tr>
<tr>
<td>SG Correction, kg/h</td>
<td>6.89</td>
<td>1.08</td>
<td>15.7</td>
</tr>
<tr>
<td>Pressure, kPa</td>
<td>1482</td>
<td>29.9</td>
<td>2.02</td>
</tr>
<tr>
<td>O₂ temperature, °C</td>
<td>21.8</td>
<td>0.20</td>
<td>0.91</td>
</tr>
<tr>
<td>T1, °C</td>
<td>1474</td>
<td>6.66</td>
<td>0.45</td>
</tr>
<tr>
<td>T2, °C</td>
<td>1400</td>
<td>6.16</td>
<td>0.44</td>
</tr>
<tr>
<td>T3, °C</td>
<td>1344</td>
<td>5.03</td>
<td>0.37</td>
</tr>
<tr>
<td>T4, °C</td>
<td>1249</td>
<td>4.53</td>
<td>0.36</td>
</tr>
<tr>
<td>Slurry temp, °C</td>
<td>39.1</td>
<td>0.96</td>
<td>2.46</td>
</tr>
</tbody>
</table>
After a comprehensive evaluation of the CANMET experimental data, the investigators determined that it had insufficient detail and had some internal inconsistencies, making it difficult to perform a LES simulation with V/UQ. Consequently, this portion of the gasification task was discontinued.

The Equilibrium Model

The equilibrium model was developed based on the principle of minimum Gibbs energy using the algorithm proposed by Reynolds to solve the equations of state (Reynolds 1986). The code is specifically designed for a C, H, O, N, and Ar system. Because it is not designed for S, the S concentration was added to the N concentration to enable solution. Since the S content in coal is very low, this assumption will have a limited effect on the predicted coal gasification performance.

LES Tools for Gasification Modeling

The LES tool, ARCHES, is an open-source CFD software resulting from a 10-year partnership with the Department of Energy and the University of Utah. It is a massively parallel code that solves conserved
quantities (mass, momentum, energy, scalar) spatially and temporally in a turbulent flow field, allowing for detailed and accurate simulations of fires and flames for both gas-phase and dispersed particle-phase (Spinti et al. 2008). An Eulerian framework based on Direct Quadrature Method of Moments (DQMOM) was adopted to describe combustion and dispersion of coal particles, and details of the implementation can be found in Pedel et al. (2013). The gas-phase combustion is modeled through a mixture fraction approach, and chemical equilibrium for the gas-phase properties is assumed. A Discrete Ordinate (DO) radiation model including particle and soot radiation property calculation is used to predict radiation heat transfer inside the furnace. A simple one-dimensional wall heat transfer model is used to calculate the net heat flux absorbed by the furnace wall and wall temperature of the gasifier.

**Surrogate Modeling**

When predictive calculations are computationally demanding, as LES tools, V/UQ techniques cannot use the predictive calculations directly. In place of direct calculation within the V/UQ tool a surrogate model is used that interpolates among a limited number of LES calculations. Since each LES calculation requires one to three days to complete, the entire suite of simulations is often limited to between three and fifteen calculations. These limited number of calculations must then be situated in the parameter space according to a design of experiments. As an inexpensive interpolating function the surrogate model allows many function evaluations in a short amount of time - often dozens or sometimes even hundreds of evaluations per second.

There has been a recent flurry of activity in the realm of non-intrusive V/UQ with regards to the use of Gaussian-Process Regression (GPR) for surrogate modeling. GPR, known by a variety of names including Krigging and best linear unbiased predictors, is a probabilistic technique that depends on the spatial correlation between where source data is provided and where an interpolation or regression is to be made. A large advantage of this method is the ease with which irregular source data can be used, whereas most familiar interpolation techniques including splines become much more complicated when the source data is not on a regular grid. Another large advantage of this method is that it provides an estimate of the interpolation or regression error - even providing this estimate for extrapolation.

The investigators have developed, leveraging additional resources, an in-house python tool for generating GPR surrogate models. This tool takes advantage of python's simple object orientation to generate the surrogate by entering the source data in one step, and then to evaluate the resulting function repeatedly with very simple notation for the user. Optional intermediate steps can be taken to optimize or otherwise modify the resulting function. Two examples of using this tool are given here.

The first example demonstrates a simple one dimensional problem with three source values. The commonly used squared-exponential kernel is used to specify the spatial correlations. Also the data is assumed to have a small amount of noise, so the tool will provide a regression rather than interpolation.

In python:

```python
>>> import numpy as np
>>> from pyregress import GPR, Noise, SquareExp
```
>>> Xd = array([[0.1],[0.3],[0.6]])
>>> Yd = array([[0.0],[1.0],[0.5]])
>>> myGPR = GPR( Xd, Yd, Noise([0.1])+SquareExp([1.0,0.1]) )
>>> print myGPR( np.array([[0.2]]) )
[[ 0.54303481]]

With minimal setup and input, the tool provided the function myGPR that was easily evaluated at a new
point. Figure 2 illustrates the result of evaluating this function at a variety of values. The error estimate is
also included.

Figure 2. Example results from myGPR for evaluating this function at a variety of values, including the
correct error estimate.

The second example uses six source values scattered in a two dimensional space, and it demonstrates
several additional features of the tool.

In python:
>>> import numpy as np
>>> from pyregress import GPR, RatQuad
>>> Xd = array([[0.00, 0.00], [0.50,-0.10], [1.00, 0.00],
... [0.15, 0.50], [0.85, 0.50], [0.50, 0.85]])
>>> Yd = array([[0.10], [0.30], [0.60], [0.70], [0.90], [0.90]])
>>> myGPR = GPR( Xd, Yd, RatQuad([0.6,0.75,1.0]), anisotropy=False,
... explicit_basis=[0,1], transform='Probit' )
The rational-quadratic kernel was used for spatial correlations. Knowing that the source data is limited to a range between zero and one, a transformation was performed on the data for internal calculation of the inferred Gaussian process. A plane with unknown y-intercept and slopes was used as an underlying mean function for the Gaussian process. An additional user-driven step is demonstrated here that allows the optimization of input parameters - in this case the correlation length-scale. This example also demonstrates that the function is built to be evaluated at multiple locations for one given call. Finally, the necessary inverse transformation was automatically performed as part of the myGPR function evaluation. Figure 3 illustrates the result of evaluating this function at a variety of values.

![Example 2](image)

**Figure 3.** Example of evaluating myGPR at a variety of values. The colored surface shows the desired interpolating values, and the error estimate is shown with the translucent grey surfaces.

**Subtask 4.2 – Subgrid Mixing and Reaction Modeling**

Kerstein (1999) developed the one-dimensional turbulence (ODT) model. As a low-dimensional model, it is an inexpensive tool that can be applied to problems of practical interest. Simplicity, minimal
Empiricism, and capability to incorporate complex molecular processes without introducing additional approximations make ODT a unique model.

Combustion of coal particles was simulated in this research. Because of coal’s complicated structure, there is not a universal model to represent coal particle combustion/gasification. Understanding the life of a coal particle during combustion helps to reduce the pollutant emission and enhance combustion efficiency. Coal particles experience several step during combustion, and these steps are strongly influenced by the combustion environment. Oxygen partial pressure and temperature have a great impact on particle evolution during combustion. Several researchers have considered moving coal particles (Higaera 2009; Wang and Bhatia 2001). Coal particle structure has a big effect on the char and volatile constituents. Furthermore, oxidation of char inside the particle modifies the pore structure and leads to changing the active surface area of particle.

The combustion process in this research is divided into three steps:

1. Evaporation
2. Devolatilization
3. Char oxidation and gasification

In the evaporation step, the moisture content of coal particle evaporates.

Devolatilization (pyrolysis) is an important step in the fate of coal particle in the combustion process. Due to importance of this step, many researchers put their time and effort to understanding and modeling it. Different models from simple to highly complex models are proposed to address the devolatilization. The Arrhenius-form models such as single rate model (Badzioch and Hawksley 1970) and Kobayashi model describe devolatilization with kinetic rates. The Distributed Activation Energy (DAE) model proposed by (Anthony and Howard 1976) used a Gaussian distribution for activation energy. Determining mean value and standard deviation for the Gaussian distribution were the challenges of this model (Please et al. 2003). New models published by late 1980s demonstrated the coal thermal decomposition by break down of the macromolecular network (Brewster et al. 1988; Grant et al. 1989). Their concept was to model the devolatilization of coal's macromolecular network base on the structural constitution of coal. Chemical Percolation Devolatilization (CPD) model is one the network model that uses the percolation theory to describe the devolatilization. Recent CPD models are capable of predicting the light gas composition (Jupudi et al. 2009).

Char oxidation and gasification are heterogeneous for reactions. The time required for the combustion of the char can be several orders of magnitude larger than devolatilization. Many factors influence char oxidation, such as, coal structure, coal type, oxygen partial pressure, temperature, etc. (Smith 1982). Oxygen partial pressure and the coal temperature significantly affect the char oxidation (Ma and Mitchel, 2009; Murphy and Shaddix 2006). The products of char oxidation are mainly carbon dioxide and monoxide. There are different equations that show the ratio of these two products (Mitchel 1988; Tognotti et al. 1990).
In this work, ODT framework is employed to simulate coal combustion/gasification. Dispersed phase added to ODT helps to simulate particle motion and behavior. The governing equations for particle and gas phases are discussed in this section; however more details are included in the Appendix A.

Fluid Dynamics

The ODT model proposed by (Kerstein 1999) can be viewed as a method for simulating, with full spatial and temporal resolution, the evolution of the flow and fluid properties along a one-dimensional line of sight through a 3D turbulent flow. Restricting the domain to one-dimension (the y direction here) dramatically reduces the simulation cost. To mimic the three-dimensional nature of turbulence in one spatial dimension, mixing is modeled through a series of stochastic rearrangement events. These events may be interpreted as the model analogue of individual turbulent eddies, which are referred to as “eddy events” or simply “eddies.” After its inception as a turbulence modeling technique, different variants have been proposed and successfully applied to a broad range of problems including turbulent combustion. The details of the governing equations solved and stochastic treatment of different model variants existing in the literature are summarized in Sutherland et al. (2010).

The ODT model as formulated for multiphase reacting flows herein solves the following conservation equation set:

\[
\frac{\partial p}{\partial t} = - \frac{\partial v}{\partial y} + S_{pm}, \quad \text{Eq 4.2.1}
\]

\[
\frac{\partial pv}{\partial t} = - \frac{\partial p}{\partial y} \frac{\partial v}{\partial y} - \frac{\partial}{\partial y} \cdot \frac{\partial P}{\partial v} + S_{pv}, \quad \text{Eq 4.2.2}
\]

\[
\frac{\partial pu}{\partial t} = - \frac{\partial p}{\partial y} \frac{\partial u}{\partial y} + \frac{\partial}{\partial y} \cdot \frac{\partial u}{\partial y} + S_{pu}, \quad \text{Eq 4.2.3}
\]

\[
\frac{\partial p\rho_0}{\partial t} = - \frac{\partial p}{\partial y} \frac{\partial \rho_0}{\partial y} - \frac{\partial}{\partial y} \cdot \frac{\partial \rho_0}{\partial y} + \frac{\partial}{\partial y} \cdot \frac{\partial}{\partial y} + S_{p\rho_0}, \quad \text{Eq 4.2.4}
\]

\[
\frac{\partial p\rho_i}{\partial t} = - \frac{\partial p}{\partial y} \frac{\partial \rho_i}{\partial y} - \frac{\partial}{\partial y} \cdot \frac{\partial \rho_i}{\partial y} + \frac{\partial}{\partial y} \cdot \frac{\partial \rho_i}{\partial y} + \omega_i + S_{\rho_i}, \quad \text{Eq 4.2.5}
\]

which is completed with the ideal gas equation of state, \( p = \rho RT / M \) and with constitutive relationships for the diffusive fluxes

\[
\tau_{yy} = -\frac{4}{3} \mu \frac{\partial v}{\partial y}, \quad \text{Eq 4.2.6}
\]

\[
\tau_{yx} = -\mu \frac{\partial u}{\partial y}, \quad \text{Eq 4.2.7}
\]

\[
q = -\lambda \frac{\partial T}{\partial y} + \sum_{i=1}^{n_i} h_i J_i, \quad \text{Eq 4.2.8}
\]

\[
J_i = \frac{\rho Y_i}{X_i} D_i \frac{\partial X_i}{\partial y}, \quad \text{Eq 4.2.9}
\]
where \( u \) and \( v \) refer to streamwise and lateral velocities, respectively. \( S_{pm}, S_{pv}, S_{pu}, S_{p0} \) and \( S_{pYi} \) are particle phase source terms for mass, \( y \)-momentum, \( x \)-momentum, total internal energy and species respectively. The calculations of these source terms are discussed in detail in Appendix A.

**Particle Dynamics**

In this work, a numerical model is developed, which captures enough of the essential physics to quantitatively predict the individual trajectories of particles (in contrast to the average location) yet is simple enough to solve problems of practical interest. The governing equations for the particle phase follow.

The motion of a single particle in gas-solid flows can be described by using Newton’s second law

\[
m_p \frac{d\mathbf{u}_p}{dt} = m_p \mathbf{g} + \mathbf{F}_{fp} + \mathbf{F}_c
\]

where \( i \) denotes the \( i \)th direction, \( m_p, \mathbf{u}_p, \mathbf{g}, \mathbf{F}_{fp} \) and \( \mathbf{F}_c \) are mass of single particle, particle velocity, gravity acceleration, force generated by fluid-particle interaction, and force generated by particle-particle interaction, respectively. For this study, particle-particle interaction is neglected \((\mathbf{F}_c=0)\), and the drag force is described by Stokes’ law so that the particle momentum equations become

\[
\frac{du_p}{dt} = \frac{f_d}{\tau_p} (u - u_p), \quad \text{Eq 4.2.11}
\]

\[
\frac{dv_p}{dt} = \frac{f_d}{\tau_p} (v - v_p) + \frac{g_i (\rho_p - \rho_g)}{\rho_p}, \quad \text{Eq 4.2.12}
\]

where \( f_d \) is the coefficient of the drag force,

\[
f_d = \begin{cases} 
1 & Re_p < 1 \\
1 + 0.15 Re_p^{0.687} & 1 < Re_p < 1000 \\
0.0183 Re_p & Re_p > 1000
\end{cases}
\]

\( \tau_p \) is the particle relaxation time (Crowe et al. 2012), and \( Re_p \) is the particle Reynolds number is given by

\[
Re_p = \frac{\rho_g d_p |u_p - u_g|}{\mu_g}, \quad \text{Eq 4.2.13}
\]

where \( d_p, \mu_g \) are particle diameter and gas dynamic viscosity respectively. Subscripts \( p \) and \( g \) indicate particle and gas phase properties, respectively.

Given the evolution of the particle velocity according to Eq 4.2.11 and Eq 4.2.12, the particle position evolves as

\[
\frac{dx_{i,p}}{dt} = u_{i,p}, \quad \text{Eq 4.2.14}
\]

where \( x_{i,p} \) is particle location in \( i \)th direction. Particle source terms on \( v \) and \( u \) velocity direction are shown by \( S_{p,v} \) and \( S_{p,u} \), respectively. The particle energy evolution is given by
\[
\frac{dT_p}{dt} = -\frac{A_p}{m_p C_p} \left[ h_c (T_p - T) + \varepsilon \sigma (T_p^4 - T_w^4) \right] + S_r \tag{Eq 4.2.15}
\]

where \( T_p, T_w, T \) are the particle, wall (Murphy and Shaddix 2006), and gas temperatures, respectively. \( C_p, m_p, A_p, \varepsilon \) are the particle heat capacity, mass, area and emissivity, respectively; \( \sigma \) is the Stefan-Boltzmann constant, \( h_c \) is the convective heat transfer coefficient. \( S_r \) is the temperature source term due to vaporization and heterogeneous reactions.

The overall mass balance on coal particle \( m_p \) is divided into three phenomenological categories describing the evolution of moisture (\( m_{H_2O} \)), volatiles (\( m_v \)), and char (\( m_c \)). This mass balance can be written as:

\[
\frac{dm_p}{dt} = \frac{dm_{H_2O}}{dt} + \frac{dm_v}{dt} + \frac{dm_c}{dt}, \tag{Eq 4.2.16}
\]

Coal Sub-Models

In the proposed model, a coal particle consists of moisture, volatile, char and ash. Figure 4 depicts the coal’s constituents and the models that describe mass exchange. For example, evaporation only adds moisture into the gas phase; however, char oxidation produces \( CO_2 \) and \( CO \) and consumes \( O_2 \). Behavior of each constituent is modeled by its corresponding sub-models.

![Figure 4. Coal constituents and sub-models.](image)

Evaporation

The moisture content evolution is given by

\[
\frac{dm_{H_2O}}{dt} = -\left( S_{p,H_2O}\right)^{Evap} = k_v \left( \frac{P_{H_2O,sat}}{RT} - \frac{P_{H_2O}}{RT_k} \right) A_p M_{H_2O}, \tag{Eq 4.2.17}
\]

where \( k_v \) is the mass transfer coefficient of steam into air (Nellis and Klein 2008; Wu, 2009), \( P_{H_2O,sat} \) is the saturation pressure of \( H_2O \) at particle temperature, and \( P_{H_2O} \) is partial pressure of \( H_2O \) in gas. For the
purposes of energy coupling, the latent heat of vaporization for H$_2$O is calculated from the Watson relation (Poling et al. 2004).

**Devolatilization**

The CPD model is one of the most accurate and complex models available to predict the production rates of the species during the devolatilization (Jupudi et al. 2009). Due to the model’s complexity, details of CPD are discussed in the Appendix.

**Char Oxidation**

Char oxidation is a complex phenomenon, which depends on many factors such as temperature and oxygen concentration. The rate of consumption of char by oxidation is described by

\[
\left( \frac{dm_{c}}{dt} \right)_{\text{oxid}} = \frac{r_{c} w_{c}}{T_{c} W_{c}} n_{d} p_{o}^{\nu_{p}} \pi d_{p}^{2},
\]

where \( \nu_{p} = 2 \left( 1 + \varphi \right) \) designates the stoichiometric ratio of carbon consumption, \( \omega_{c} \) is the molecular weight of carbon, and \( r_{c} \) is the reaction rate of char.

There are several models and equations that explain char oxidation reaction rates; the Langmuir-Hinshelwood kinetic expression is frequently used. This approach describes competing adsorption (O$_2$) and desorption (CO) on the char surface that makes it more attractive than other models. There are multiple forms of Langmuir-Hinshelwood, but the version shown in (Murphy and Shaddix 2006) Eq 4.2.19 has better performance

\[
r_{c} = \frac{k_{2} k_{1} p_{o_{2,sat}}^{n_{r}}}{k_{1} p_{o_{2,sat}}^{n_{r}} + k_{2}},
\]

where \( k_{1} \) and \( k_{2} \) are Arrhenius rate constant, \( n_{r} = 0.3 \) and \( p_{o_{2,sat}} \) is the oxygen partial pressure at the particle surface.

**Char Gasification**

The char oxidation and gasification are heterogeneous reactions that consume char. The presence of carbon dioxide and H$_2$O vapor around the coal particle can increase the likelihood of gasification reactions at high temperatures:

\[
C_{(s)} + CO_{2} \rightarrow 2CO \quad \text{Eq 4.2.20}
\]

\[
C_{(s)} + H_{2}O \rightarrow CO + H_{2} \quad \text{Eq 4.2.21}
\]

The differential equation that describes char gasification is
where $k_i$ is Arrhenius constant rate. Details of the gasification model are discussed in the Appendix.

**Simulation Conditions**

In this work, experimental results reported by Liu et al. (2011a) were employed to examine the model’s ability to capture the physics of the system. Specifically, the ignition delay of two coal types under various conditions was investigated. The properties (proximate and ultimate analysis) of the coals are given in Table 2. The initial particle temperature is 367 K.

<table>
<thead>
<tr>
<th>Coal Type</th>
<th>Proximate Analysis wt% as rec’d</th>
<th>Ultimate Analysis wt% daf</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Moisture</td>
<td>Ash</td>
</tr>
<tr>
<td>Pittsburgh</td>
<td>1.4</td>
<td>6.9</td>
</tr>
<tr>
<td>Black Thunder</td>
<td>10.8</td>
<td>5.0</td>
</tr>
</tbody>
</table>

The experiments were conducted in the laminar entrained-flow reactor located at Sandia National Laboratory. Coal particles were injected at the bottom of the reactor along the centerline, which are carried with furnace gases. To provide the gas flow, the reactor uses a Hencken burner. A detailed description of the reactor is provided by (Molina and Shaddix 2007).

The simulations were performed for a laminar single-particle jet with a jet diameter of 0.75 mm and a flow of approximately 2.5 m/s. The wall temperature is 500 K as reported by Murphy and Shaddix (2006). In the gas phase, a reduced mechanism proposed by Slavinskaya et al. (2008) is utilized.

Two studies with different initial conditions were performed.

1- Initial furnace temperature impact: Pittsburgh and Black Thunder coal are used for this simulation where the mean particle diameter is 90 μm. The initial species compositions are given in Table 3.

<table>
<thead>
<tr>
<th>Species</th>
<th>CO$_2$</th>
<th>N$_2$</th>
<th>O$_2$</th>
<th>H$_2$O</th>
<th>AR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole %</td>
<td>30</td>
<td>38</td>
<td>20</td>
<td>11.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>

By changing the initial furnace temperature, simulation predictions are changing correspondingly. In this study the initial furnace temperature varied from 1200 K to 1700 K. For each coal type, 11 simulations were performed with an initial time step of 2E-7 second.
2- Particle size impact: Pittsburgh coal is used for this simulation. The initial furnace temperature is 1320 K, and the initial species compositions are reported in Table 4. In this study 22 simulations were performed with an initial time step of 2E-7 second. The particle sizes used in this study was between 20-125 μm.

Table 4. Species composition for particle size impact study.

<table>
<thead>
<tr>
<th>Species</th>
<th>CO₂</th>
<th>N₂</th>
<th>O₂</th>
<th>H₂O</th>
<th>AR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole %</td>
<td>30</td>
<td>46</td>
<td>12</td>
<td>11.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**Subtask 4.3 – Radiation Modeling**

Radiation is the dominant mode of heat transfer in high temperature combustion environments (Tieszen, 2001). Radiative heat transfer in turbulent flames affects the gas and particle phases, including all the associated combustion chemistry. The turbulence-radiation interactions (TRI) have been shown to be of great importance in turbulent flames (Hall, 1994). Modeling turbulence-radiation interactions is difficult due to the nonlinear coupling between temperature, species concentrations, and radiative intensities (Coelho, 2007). Further, coupling parallel simulations of combustion and radiation poses several numerical challenges. The fluid mechanics of combustion are local phenomena, making them amenable to domain decomposition. Conversely, radiation is a long-distance, and potentially all-to-all phenomenon, creating difficulties for domain decomposition. Further, accurate calculation of radiative transfer requires spatially resolved information regarding the temperature and species composition fields. In this work, a new numerical technique has been developed to perform large eddy simulations of large-scale combustion flows coupled with a three-dimensional reciprocal Monte Carlo ray tracing radiation model. This model has been optimized for use on high-performance super computers and achieves near-ideal strong scaling to over 16,000 processors.

In a massively parallelized framework, where the computational domain is heavily decomposed, traditional forward Monte Carlo methods suffer due to the large number of traced rays that never reach the subdomain of interest handled by a particular processor. Therefore, an emission-based reciprocity method similar to that developed by Tesse et al. (2002, 2004) was implemented. Optical paths (i.e., rays) propagate away from cells whose radiative-source terms are currently being solved, and the emission from the cells along the paths are attenuated in a reciprocal manner back to the target cells. In this manner, rays are generated only from cells where results are expected (Zhang, 2012). The governing equation for reciprocal Monte Carlo ray tracing in nonhomogeneous, participating media was developed by Walters and Buckius (1992). Specifically,
where, $I_{ik}$ represents the incident intensity at location, $k$. The intensities from each of the rays of a cell can then be weighted according to the solid angle that each ray subtends. The target locations of the rays are distributed randomly throughout the cell. A random number generator is used to select the target locations and ray orientations. In Cartesian meshes, randomly distributed ray location generation is trivial and is accomplished by scaling three random numbers with the length, width, and height of the cell, respectively. Randomly distributed ray orientation requires more treatment. Rays propagating from boundary surfaces are distributed over a hemisphere. The ray marching model adjusts the ray directions into the proper orientation based on the surface normal of the boundary cell at hand. This is accomplished by changing the order and sign of the three direction components. For the computation of the radiative flux divergence of flow cells, no re-orientation of the direction vector is necessary, as the rays are randomly distributed over the full sphere.

Ray marching proceeds in a manner similar to that described by Amanatides and Woo (1987). The location and orientation of a ray are used to calculate the distances to each of the three potential exit faces of the cell in which the ray currently resides. The shortest of these three distances is used in determining through which face the ray will pass. This information is then used to calculate the next cell in which the ray will reside. Reflections are allowed to occur on non-black boundary faces. The temperature and emissivity of the boundaries are referenced, and the intensity at the ray-boundary intersection is computed and attenuated to the target location. For non-black surfaces, the ray reflects at the surface, and the subsequently referenced intensities are attenuated both by the total optical thickness and by the absorption of the boundary. Ray marching continues until the optical thickness of a ray exceeds a predetermined threshold value. In general, the threshold is met when $fe^{t}r<0.05$, where $r$ is the current optical thickness, and $f$ is unity multiplied by one minus the absorptivity of each intersected boundary, $(1-\alpha)$. In other words, when less than 5% of the intensity from a location in the domain will reach the target cell, ray tracing of the current ray ceases. The mesh reconstruction technique described in the following section allows ray generation and propagation to occur on each processor independently, negating the passing of rays, and minimizing inter-processor communication.

At each radiation solve, the decomposed domain used for parallelism of the combustion model is recomposed, and the radiation-specific field variables from each processor are shared with all other processors. Information sharing is accomplished through a message-passing interface. The radiation model was translated from its original language of C++ into the Graphics Processing Unit (GPU) specific language, CUDA. This allowed the model to be run on the GPU processors of the super-computing cluster, Titan.

**Subtask 4.4 – Char and Soot Kinetics and Mechanisms**

**Characterization of Coal Feed Stocks**

Steam gasification experiments were conducted for 3 bituminous coals (Illinois #6, Utah Skyline, & Pittsburgh #8) in entrained flow conditions at high heating rate. Pitt #8 coal was chosen as a replacement coal to the originally proposed Indiana coal due to insufficient quantities available of pulverized Indiana coal. CO$_2$ gasification data were also available for the Pitt#8 coal and not the Indiana coal. The results of the ultimate and proximate analyses of the 3 coals used in this project are shown in Table 5.
Table 5. Ultimate and proximate analyses of the feed stocks of 45-75 μm coals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Moisture&lt;sup&gt;a&lt;/sup&gt; (wt%)</th>
<th>Ash (wt%, dry)</th>
<th>Volatiles&lt;sup&gt;b&lt;/sup&gt; (wt%, daf)</th>
<th>C (wt%, daf)</th>
<th>H (wt%, daf)</th>
<th>N (wt%, daf)</th>
<th>O&lt;sup&gt;c&lt;/sup&gt; (wt%, daf)</th>
<th>S (wt%, daf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illinois #6</td>
<td>3.45</td>
<td>8.49</td>
<td>43.37</td>
<td>75.09</td>
<td>5.21</td>
<td>1.34</td>
<td>14.02</td>
<td>4.35</td>
</tr>
<tr>
<td>Utah Skyline</td>
<td>2.41</td>
<td>7.87</td>
<td>47.06</td>
<td>77.39</td>
<td>5.57</td>
<td>1.57</td>
<td>14.87</td>
<td>0.61</td>
</tr>
<tr>
<td>Pitt #8</td>
<td>1.67</td>
<td>12.41</td>
<td>37.73</td>
<td>80.86</td>
<td>5.39</td>
<td>1.64</td>
<td>10.61</td>
<td>1.49</td>
</tr>
</tbody>
</table>

<sup>a</sup> as received basis. <sup>b</sup>daf = dry and ash-free basis. <sup>c</sup> calculated by difference.

High-Pressure Flat-Flame Burner Reactor

A high-pressure flat-flame burner reactor (HPFFB) at Brigham Young University (BYU) was used to study entrained-flow gasification of Illinois #6, Utah Skyline, and Pittsburgh #8 bituminous coals in a fuel-rich flame using particle residence times less than 250 ms. Figure 5 shows a schematic of the HPFFB. Flat-flame burners provide initial particle heating rates around $10^5$ K/s, which approaches the particle heating rates of about $10^6$ K/s which are common in commercial, entrained-flow combustors and gasifiers (Fletcher et al., 1997).

The flat-flame burner of the HPFFB reactor is roughly 1” in diameter and uses about 100 small-diameter tubes to create many diffusion flamelets by feeding gaseous fuel through the tubes while introducing oxidizer in-between the tubes. The numerous small flamelets create a flat flame a few millimeters above the burner. Particles were entrained in nitrogen and carried to the middle of the burner surface through a small metal tube (0.053” ID). The particles then reacted while traveling upward in laminar flow through a circular quartz tube for known residence times before the particles were quickly quenched with nitrogen in a water-cooled collection probe. The mass flow rate of quench N₂ was about 2 times that of the hot gas. A virtual impactor and cyclone in the collection system separated the char aerodynamically while any soot/tar collected on water-cooled micropore filters. Permanent gases traveled through the filters and released in a ventilation cabinet.
Particle residence times in the HPFFB reactor were calculated using particle velocities measured by a high-speed camera (Kodak EktaPro) and controlled by adjusting the height of the collection probe above the burner. A complete summary of all the particle velocities is included in (Lewis in progress). Additional details of the calculations for particle residence time in the HPFFB reactor can be found in (Lewis 2011).

Low particle feeding rates, less than 1.5 g/hr, were used to ensure single-particle behavior and to prevent clogging. The gaseous fuel supplied to the HPFFB was a mixture of CO and H2. Additional details of the HPFFB reactor can be found in (Lewis, 2011) and (Shurtz, 2011).

No heaters were used in the HPFFB reactor for this study, even though they are shown in Figure 5. Since the relatively small flat-flame burner was the only heat source in the reactor, the usable distance above the burner to measure char gasification was only about 6” at conditions where the peak centerline gas temperature was near 1900 K. Above this approximate height, the temperature is low enough due to heat loss that it is not possible to measure differing extents of char gasification. Therefore, collection heights above the burner in this project were limited to 6” or less, which corresponded to particle residence times < 300 ms.
Re-Injection Strategy for Char Gasification Experiments

The HPFFB gasification experiments involved re-injecting a narrow size range of fully pyrolyzed coal char. It would have been ideal to conduct gasification experiments following *in-situ* pyrolysis like occurs in commercial entrained-flow gasifiers, but soot contamination of the char prevented this. A good mass balance for an experimental run (using weights of fed and collected material) is interrupted when a significant amount of soot contaminates the char, since it is experimentally challenging to separate the soot from the char and assign accurate mass fractions to each (Shurtz, 2011). Sooty char also prevents accurate mass release values when using ash-tracer calculations. Hence, the method of re-injecting fully pyrolyzed chars to measure char gasification data was pursued, as described by (Hurt et al., 1998; Shurtz and Fletcher, 2013). The coal chars were generated by feeding raw, sized (45-75 μm) coals in the up-flow HPFFB reactor at the same total pressure that it would later be re-injected as feed stock material.

Experimental optimization studies of char-generation conditions in the HPFFB reactor were performed with the aim of generating nearly soot-free fully pyrolyzed coal char with minimal char oxidation at total pressures of 10, 12.5, and 15 atm. Different collection heights and post-flame O$_2$ concentrations were tested. Scanning electron microscope (SEM) images of the chars were also used in the determination of the optimal char-generation conditions of the HPFFB. Figure 6a shows coal char collected from a probing char-generation condition that still contained soot. Figure 6b shows coal char essentially free of soot at the finalized 12.5 atm char-generation condition of the HPFFB reactor. Note that the SEM images in Figure 6 were not taken at the same magnification.

The finalized HPFFB char-generation conditions had peak gas temperatures near 1850 K using a 0.75” collection height (~40 ms). About 2 mol% O$_2$ was used in the post-flame environment in order to oxidize the tar before soot could be formed. Low particle residence times were used in the char-generation experiments to prevent significant oxidation of the coal char.
Coal Soot Structure Analysis for Use in Soot Model

Attempts were made to gain insight into the chemical structure differences between young and mature soot for use in a soot model. Soot is a collection of small carbonaceous particles that form during coal pyrolysis. In pyrolysis runs at short residence time, the soot has less time to grow so smaller aromatic clusters are formed. In pyrolysis runs at long residence time, the soot has more time to “mature” into bigger aromatic clusters. The original idea was to collect tar/soot aerosol samples at different conditions from the HPFFB reactor and analyze the samples using NMR analysis to determine the changes in chemical structure. Surrogate tar samples using biphenyl were planned so that exact changes in chemical structure could be determined. However, the gasification conditions were at high temperatures and pressures, causing the soot particles to aromatize further and become conductive. Conductive samples cannot be analyzed by the NMR technique since the conductance interferes with magnetization, which made the NMR soot analysis impossible to perform. In addition, the yield of soot from the surrogate samples at the high temperature conditions was extremely low.

Since NMR analysis was not possible on the soot samples, an additional technique was explored to determine chemical structures of aromatic carbon using high-resolution transmission electron micrographs (HRTEM). By photographing the soot using HRTEM techniques and processing the image to reflect the carbon structure, a distribution of the fringe lengths can be determined. Fringe lengths can be used to determine soot particle composition using the Fringe3D program created by Dr. Jonathan Mathews and colleagues at Pennsylvania State University that incorporates known molecule sizes and spacing. This TEM/Fringe3D (TF3D) method was reported to work best for materials composed of aromatic clusters of large size.

Coal Analysis by SAXS and PDF

In a previous quarterly report we reported that small angle x-ray scattering (SAXS) and atomic pairwise distribution function (PDF) measurements were obtained at the Advanced Photon Source at Argonne National Laboratory on 14 samples from 4 different coals:

- Eastern Bituminous A (EBA) (5 samples) – coal, a char/soot pair formed at 1 atm, a 3 minute 15 atm pyrolysis, and a 10 minute 15 atm pyrolysis
- Eastern Bituminous B (EBB) (3 samples) – coal, a 3 minute 15 atm pyrolysis, and a 10 minute 15 atm pyrolysis
- Wyodak (3 samples) – coal, a 3 minute 15 atm pyrolysis, and a 10 minute 15 atm pyrolysis
- Kentucky #9 (3 samples) – coal, a 0.75 minute 15 atm pyrolysis, and a 10 minute 15 atm pyrolysis

The quarterly report also contained some preliminary analysis of the scattering curves, specifically power law fits of the slope of the curve for portions of the scattering curves was indicative of roughening of the surface of the particle when moving from the coal to the pyrolysis product. However attempts at fitting the entire scattering curve and obtaining any more detailed information on the structure from these results were complicated by the fact that we were dealing with such a complex mixture in terms of both the composition and particle size. This led us to the conclusion that any further analysis was productive.
Extension of Sub Models and Gasification Experiments of Soot

The original statement of work discussed extensions of sub models for coal swelling and pyrolysis, as well as TGA gasification experiments of soot. However, these sub models and TGA experiments did not receive any attention due to time constraints primarily caused by the many delays encountered in the HPFFB char gasification experiments.

Subtask 4.5 – Slag Formation and Slag-Wall Interactions

This subtask was completed prior to initiation of this project phase.

Subtask 4.6 – Acquisition of Validation Data in an Entrained-Flow Gasifier

The University of Utah’s entrained-flow coal gasifier (EFG) offers unique opportunities to acquire new performance data to aid with validation of simulation models under development. While there are many operational issues that impact EFG performance and operation, performance of the coal-water slurry (CWS) injector is the most critical. Ideally, the reactants (CWS and oxygen) would very rapidly mix upon entering the reactor. Mixing is achieved thorough CWS atomization resulting in small, uniform droplets of CWS whose carbon reacts in the shortest possible time. As the pressure drop across the nozzle is increased (the gas velocity from the injector nozzle is increased), the degree of atomization increases and stability and conversion efficiency improve. How the two phases contact each other greatly influences how the slurry will atomize. Under this subtask several previously developed injector geometries that have been shown to provide better atomization with higher pressure drops have been explored (Lefebvre 1980). The limits and, more importantly, optimal pressure drop, must be determined for a given geometry. Subtask 4.6a focuses on slurry spray characterization and modeling, and associated development of an efficient injector for the University of Utah pilot-scale system.

The other component of this work aims to characterize the environment within the gasifier itself. Pressurized entrained flow gasifiers operate at high temperature and high pressure, contain poisonous gases including carbon monoxide and hydrogen sulfide, and have molten slag flowing down the walls, so characterizing the interior environment presents significant challenges in terms of penetration and safety. Subtask 4.6b focuses on development of a safe, reliable and controllable method for measuring the gas environment within the gasifier during operation at high pressure. Tests with the University of Utah’s 1 ton/day gasifier were conducted at pressures to 265 psig (19 atm absolute pressure) and at temperatures to 2900°F in order to confirm performance of the injectors and to demonstrate successful measurement of gas-phase composition with the new sampling probe.

This task involved developing the University of Utah’s pilot-scale, pressurized, entrained-flow coal gasifier to serve as a tool for evaluating performance, syngas quality and conditions within the system under well-specified, industrially relevant conditions. Aside from the distributed control system used to monitor temperatures, pressure, and the various flows, the methods employed in operating and analyzing EFG operation focused on measuring all inputs and as many outputs and possible, and verifying those measurements. An ultrasonic flow meter was used to measure the coal slurry flow rate. This measurement was validated by periodic measurements of the liquid slurry level height in the slurry tank.
Combined with measured solids loading and slurry density measurements, this provides a measurement and check of the solid fuel input to the reactor. A Varian gas chromatograph was used to measure the syngas composition coming from the EFG. The syngas is sampled immediately downstream of the pressure control valve which is used to maintain a desired pressure inside the EFG. For several EFG tests, a metered helium flow was used to purge two small ports used for flame detection via two ultraviolet flame detectors. The known helium flow was then paired with the GC-measured syngas composition (including He concentration) to determine the overall dry syngas flow rate.

In addition to the measurement of the system inputs and outputs, numerous thermocouples were used to determine the system temperature and flame position. Five thermocouples were positioned axially at different lengths below the injector in the reaction zone. Also, twelve thermocouples were positioned along the shell of the EFG to ensure no “hot spots” developed during operation, which could indicate unstable operation within the reactor. The system pressure was measured with a pressure transducer at the syngas exit from the EFG quench zone EFG.

System startup was always performed with isopropyl alcohol in order to raise the system temperature after switching from the gas standby burner to the gasification injector. Once the system pressure reached 50 psig, the fuel was switched from isopropyl alcohol to coal or petcoke slurry, depending on the tests to be run. Two specific tasks within this subtask, described below, complement the overall objective.

**Subtask 4.6a: Characterization of Injector Spray Behavior**

**Injector Design and Modeling**

Fluid flow and associated breakup dictate the efficiency of atomization and ultimately, gasifier performance. Given the relatively small size of the University of Utah gasifier, nozzle design has been limited to relatively simple geometries with relatively large channels for the slurry in order to minimize risk of plugging. The basic injector developed an externally mixed, 2-stream design in which a central channel of coal slurry is atomized by a high velocity oxygen flow entering around the slurry channel. This design is common in fuel systems such as an entrained-flow coal gasifier (Lefebvre 1989). The geometry of the injector is such that the oxygen and CWS do not contact each other until both fluids have left the confines of the injector. When dealing with reacting flows and high temperatures, the use of an internal mixing injector could lead to a reaction inside the injector, which would likely compromise the injector’s structural integrity and could lead to other problems that could be catastrophic.

The gas and liquid flow within the injector were analyzed using a Microsoft Excel-based model, which incorporates fluid properties and injector geometry to predict exit velocities and liquid breakup and resulting droplet size. Using stagnation properties, the pressure drop is calculated for a given mass flow rate of gas and a given outlet geometry. This approach considers the gas flow to be isentropic and adiabatic, and the gas is assumed perfect with constant specific heats. The equations used to determine the pressure drop are based on established relations (John 1984).

The model also calculates nozzle efficiency. By accounting for the kinetic energy of the gas stream and the minimum required energy to atomize the given liquid, efficiency is calculated. The minimum
required energy to atomize a given liquid is evaluated using the liquid’s surface tension and the change in surface area. The initial surface area is taken to be a cylindrical jet of the same diameter as the slurry/liquid tube. A volume basis is taken and it is assumed that no liquid volume is lost. The final surface area is calculated using the average drop diameter and the total volume of liquid taken as an equivalent basis. The available kinetic energy of the gas stream is calculated using the angle at which the gas stream approaches the liquid stream. This gives radial and axial components of the oxygen kinetic energy. In addition to this 1-D *Microsoft Excel* model, some *Fluent* modeling was performed to identify the gas flow fields associated with each nozzle design.

Figure 7 shows the general regions of a co-axial, annular, two-stream injector. Slurry flows through the central (red) channel. Oxygen flow is denoted in blue in the annular region. The two fluids mix in the yellow area near the tip of the injector. The schematic exaggerates the contact area between oxygen and slurry for the sake of illustration. In reality, the exit gap for oxygen in the blue “impinging region” is on the order of one hundredth of an inch, which provides the high pressure drop and associated high velocity necessary to achieve good atomization.

![Figure 7. Co-axial, annular, two-stream injector cross-section. Flow is downwards. Red denotes slurry, blue denotes oxygen and yellow denotes the mixing zone.](image)

The challenge of injector design at this scale is the very small amount of oxygen available for atomizing. Relative to a typical air-atomized combustion injector, a gasifier has only about 10% as much gas due to the use of pure oxygen and sub-stoichiometric operation. Consequently, much of the development focuses on achieving (1) high pressure drop, which corresponds to high gas velocity, (2) efficient atomization, (3) concentric spray patterns, and (4) repeatable performance. Achieving these requires very small gaps, on the order of one hundredth of an inch, for the oxygen to flow through, so precision machining is key.

In order to characterize the spray resulting from the slurry injector, a suite of imaging and measurement techniques was developed at the University of Utah. These are described below.

**High-Speed Imaging and Image Analysis**

A *Redlake* high-speed camera (PCI 2000 SC) is used to photograph cold-flow operation of different nozzles and is shown in Figure 8. A camera setup of 2000 frames per second decreases the amount of light available for high-quality images. In order to capture worthwhile images, multiple sources are used to illuminate the atomizing liquid.
A DSLR camera was also used to capture images of the cold-flow atomization. Decreasing the exposure time and providing some backlighting to the cold-flow set up stops the motion of each droplet in the resulting images. *ImageJ* software analyzed the captured video and images, and provided information about the spray, e.g. droplet size information. Consecutive high-speed images with a known shutter speed approximated droplet velocities.

*ImageJ* has built-in algorithms that determined the boundaries of droplets, using one of the built-in thresholding methods. Figure 9 shows a pre-processing image next to a post-processing image. When processing the image, the nozzle is cropped out of the picture before analyzing to avoid an error in the droplet analysis. Once the image’s threshold has been adjusted, the particles are analyzed. The unit of length is specified and referenced to a distance in the image. *ImageJ* then produces statistical information about the droplets it identified in the image.
**Particle Shadow Velocimetry (PSV) Analysis**

In addition to the DSLR/ImageJ analysis method, PSV equipment became available during the project. PSV utilizes a diffuse laser light source paired with a high-speed camera. The set-up and image analysis method has been described in detail elsewhere (Tóth et al. 2013; Waind et al. 2013). The object to be imaged (the spray) is positioned in-line between the light source and the camera. The light source is pulsed at a high frequency allowing for the spray to appear to be stopped in the obtained images. The high frequency pulses (of a known time difference) allow for drop velocity and direction to be obtained relative the camera orientation.

**“Patternator” Spray Distribution Measurements**

A patternator, consisting of multiple deep tubes for capturing liquid sprayed from an injector, was used to assess spray distribution and concentricity. The patternator was placed underneath the nozzle during cold-flow testing and the liquid level collected in each of the tubes was measured providing spatial distribution of the liquid spray. Two designs were used. The first version (left photo in Figure 10) was not ideal. It was challenging to fabricate the system so that it did not leak, and the tight positions of the tubes relative to each other did not allow liquid to properly flow as it would if there were no patternator. A second, improved design (right photo in Figure 10) was constructed. This design used a very coarse wire mesh with a lipped test tube in every other hole in the mesh. This less restrictive design more closely approximated the actual liquid spray behavior.

![Figure 10. First (left) and second (right) versions of the patternator.](image-url)
**Laser Sheet Spray Pattern Imaging**

In addition to the patternator, the spray angle and associated distribution was evaluated using photography and a laser. The laser was forced into a sheet by passing it across a glass rod and directed so that the nozzle is perpendicular to the plane occupied by the laser sheet. As the spray passes through the sheet, the droplets illuminate (Figure 11). Capturing this process with a camera set to a long exposure, images could be analyzed further. The positioning of the laser sheet was easily moved and allowed for analysis of the spray at varying distances from the nozzle’s tip.

![Figure 11. Laser sheet analysis of injector spray.](image)

**Flow and Pressure-Drop Measurements**

Two pressure chambers (Figure 12) were built to verify the pressure drop across a nozzle when flowing gas into a pressurized vessel. One vessel was designed for lower pressures (< 50 psig) and was made of clear plastic to enable some visualization of the spray. During operation the recirculation of water droplets coated the inside walls of the vessel, making thorough visualization difficult. The other vessel was designed for higher pressures. This vessel did not have optical ports, but was used with nitrogen or air to experimentally verify pressure drop predictions made by the injector model described previously.
Subtask 4.6b – Development of Probe for In-Situ Measurements

The aim of this activity was to develop a probe to for in-situ sampling from a pressurized gasifier in order to increase the understanding of the chemical processes that drive entrained-flow coal gasification. Spatial analysis of gas-phase composition in the gasifier can improve characterization of the environment and has the potential to provide useful validation data for advanced simulation techniques like reactive flow computational fluid dynamics.

The primary consideration in design of the probe was safety, since the interior of the gasifier contains hot, high-pressure, toxic gases. Materials of construction, pressure sealing, appropriate purges and backup systems were part of the design. In addition, it was deemed important that the probe is able to be inserted and retracted from the reactor rapidly, so as to minimize exposure time in the hot environment.

A schematic of the final design for the main part of the probe is shown in Figure 13. The cylindrical portion that traverses the gasifier is water-jacketed and made from three-quarter inch, one-half inch, and one-quarter inch stainless steel tubing. The one-quarter inch tube protrudes from the tip of the extension and has a one-eighth inch hole drilled on the under side of the protuberance for gas-phase extraction. The end of the ¼-inch tube is closed off in order to deter slag buildup. The small hole on the underside also serves as the purge for the sample system when sampling procedures are not being undertaken. The probe
extension travels through a flange assembly called the seal housing and stabilizer. The seal housing consists of two pieces, one for the hot-face, or gasifier side, of the extension, and one for the cold-face of the extension. Each side has a machined stainless steel cooling trough welded into a two inch, 300 class stainless steel slip-on flange. The hot-face seal housing has an additional recessed edge for the precise placement of the pressure seal. An adjustable guide resides at the nonreactor end of the seal housing to support the weight of the probe extension and offer rigidity to the apparatus. Figure 14 shows the whole flange assembly as an exploded view, including the stabilizer and cooling trough flange assembly. Figure 15 shows the full assembly of the probe, including flange assembly, probe extension, and position feedback cylinder/position control systems.

![Figure 13. Probe extension and rod mount brace.](image1)

![Figure 14. Exploded view of flange assembly and components.](image2)
RESULTS AND DISCUSSION

Subtask 4.1 – Entrained-Flow Gasifier Simulation and Modeling

LES Simulations for the Gasifier

Using the given operating conditions (as shown in Table 1 but without coal), a cold-flow LES simulation for CANMET gasifier was completed. The resolution was 2mm for the y and z directions and 4mm for the x direction. Based on such resolution, the total cell number is $416 \times 254 \times 254$. The simulation domain replicates the CANMET gasifier structure and is shown in Figure 16. This simulation required a total of 10368 CPU hours to get 0.2 s of LES results with 144 processors. Figure 16 shows the flow fields and the velocity along a planar cross section. As the high-speed fuel-oxidizer mixture is injected into the furnace, it expands as it proceeds down stream. The velocity decays quickly as the recirculating fluid is entrained into the main jet. The velocity field shows that the injection region as well as the recirculation flow region occupies 2/3 of the total gasifier volume. The remaining 1/3 is plug flow, where the momenta are well mixed, and the flow field is smooth. The cold-flow simulation shows the ability of LES simulations for the simulation of large-scale limited injection flow problems.
Equilibrium Model for Coal Gasification

An equilibrium model was developed to study the effects of important operating parameters, such as carbon conversion, heat loss ratio and coal slurry concentration, on the gasifier performance. Figure 17, Figure 18 and Figure 19 show the effects of these operating parameters. As carbon conversion increases, temperature drops quickly since gasification reactions are endothermic. At the same time, H$_2$ concentration increases due to the water-gas shift reaction. For this reason, CO production from the water-gas shift reaction decreases. However, the char gasification reaction rates increase as the carbon conversion increases at the same time. Such competition causes the CO concentration to reach a maximum value when the char carbon conversion rate is about 80%. Figure 18 shows the major species and temperature changes with the heat loss rate. As the heat loss increases from 0% to 4%, the temperature decreases to about 200K. Such a change will have a strong effect on the carbon conversion rate. At the same time, both H$_2$ and CO$_2$ concentrations increase due to the water-shift gasification reaction. It is obvious that heat loss has a negative effect on the carbon conversion rate. On the other hand, higher coal-slurry concentrations always have a positive effect on the coal gasification process, as is shown in Figure 19.
Figure 17. Carbon conversion effects on gasification.

Figure 18. Effect of heat loss on gasification.
The simulation results show that carbon conversion is in the range of 64% to 84%. Table 7 shows that the measured temperature ranged from 1500~1750K, while the equilibrium predictions ranged from 1400~1700K. The possible reason is that the assumed carbon conversion is higher than the real value.

### Table 6. The measured syngas composition and temperature inside the furnace.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>average</th>
<th>standard deviation</th>
<th>standard deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂, %</td>
<td>56.7</td>
<td>1.64</td>
<td>2.90</td>
</tr>
<tr>
<td>O₂, %</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>CO₂, %</td>
<td>36.2</td>
<td>0.29</td>
<td>0.81</td>
</tr>
<tr>
<td>T1, °C</td>
<td>1474</td>
<td>6.66</td>
<td>0.45</td>
</tr>
<tr>
<td>T2, °C</td>
<td>1400</td>
<td>6.16</td>
<td>0.44</td>
</tr>
<tr>
<td>T3, °C</td>
<td>1344</td>
<td>5.03</td>
<td>0.37</td>
</tr>
<tr>
<td>T4, °C</td>
<td>1249</td>
<td>4.53</td>
<td>0.36</td>
</tr>
<tr>
<td>Slurry Temp. °C</td>
<td>39.1</td>
<td>0.96</td>
<td>2.46</td>
</tr>
</tbody>
</table>

### Table 7. Comparison of measured and predicted data.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Prediction</th>
<th>Equilibrium Calculation</th>
<th>Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, K</td>
<td>1725</td>
<td>1400~1700</td>
<td>1500~1750</td>
</tr>
<tr>
<td>CO₂, % (vol)</td>
<td>43.8</td>
<td>36~41</td>
<td>56.7</td>
</tr>
<tr>
<td>CO₂, % (vol)</td>
<td>11.5</td>
<td>20~30</td>
<td>36.15</td>
</tr>
<tr>
<td>H₂ (% Vol)</td>
<td>19.5</td>
<td>32~40</td>
<td>-</td>
</tr>
</tbody>
</table>
Simulations were performed to investigate the effect of furnace temperature, particles size and coal type on the predicted ignition delay of coal particles. The simulation experiments were conducted to understand the behavior of single particles, which relies on the assumption that subsequent particle interaction was neglected. A scaling analysis helps to justify this assumption. The distance between two subsequent particles can be obtained by following equation:

\[ z_p = \Delta t \times u_p \]  
Eq 4.2.23

where \( z_p \) and \( \Delta t \) are the distance and time between two subsequent particles. The \( \Delta t \) can be calculated in the following:

\[ \Delta t = \frac{m_p}{m_p} \]  
Eq 4.2.24

where \( m_p \) is the mass flow rate of particles. The characteristic length represents the length required between subsequent particles to avoid any interaction. The characteristic length is:

\[ z_c = \sqrt{D \times \Delta t} \]  
Eq 4.2.25

where \( D \) and \( z_c \) are the gas diffusion coefficient and characteristic length respectively. In Figure 20 the results of this scaling analysis as a function coal feed rate are illustrated.

Figure 20 shows the comparison between the \( z_c \) and \( z_p \), and that the distance between subsequent particles is bigger than the characteristic length for all simulated coal feed rates. This confirms that the subsequent particles do not affect each other’s behavior and the observed physics are for one particle.
Particle Fate

A coal particle experiences different stages during its lifetime in combustion/gasification process. These steps are discussed in the Approach section.

In Figure 21 the particle temperature profile along with gas phase temperature at the centerline of the furnace (particle position) are illustrated as a function of time. This simulation was performed with a 90 \( \mu m \) Black Thunder coal particle with an initial furnace temperature of 1200 K and 20 vol\% of oxygen in nitrogen diluent. The journey of the particle through furnace starts with gaining heat from the surrounding environment. This heat first causes moisture in the coal particle to evaporate. Figure 22 illustrates the consumption of each coal constituent. After the moisture content was evaporated, the particle starts to heat up.

![Particle temperature and gas-phase temperature](image1.png)

**Figure 21.** Particle temperature and gas-phase temperature (at particle position) vs. time for Black Thunder coal with an initial furnace temperature of 1200 K.

![Concentration profile](image2.png)

**Figure 22.** Fractional consumption of coal constituents vs. time for Black Thunder coal with an initial furnace temperature of 1200 K.

The devolatilization rate increases as the particle temperature rises.
Char oxidation is a heterogeneous process that occurs at the particle surface. Consequently, char oxidation affects particle temperature more than gas-phase temperature.

In Figure 21, when the char oxidation becomes highly active, the particle temperature exceeds the gas temperature. However, due to homogenous reaction of CO (produced by char oxidation) and the lower heat capacity of gas than particle, the temperature of gas becomes higher than particle as the combustion process proceeds.

**Species Evolution**

For a furnace temperature of 1320 K, Figure 23 shows contours plots of simulated temperature and mass fractions of O\textsubscript{2}, CO, OH.

As the particle enters the furnace chamber at (367 K), it absorbs heat from the surrounding gas, as shown in Figure 23a. Additionally, evaporation and devolatilization release mass at the particle temperature into the gas phase, which also contributes to a decrease the gas-phase temperature.

The production of CO is contributed by devolatilization and char oxidation, which at high temperatures char oxidation is more dominant than devolatilization. The maximum in CO concentration (t~0.027 ms) indicates the initiation of char oxidation. The CO is a potential fuel that homogenously reacts with oxygen and produce CO\textsubscript{2}.

In Figure 23c the contours of O\textsubscript{2} mass fraction are illustrated. Homogenous reactions of fuels produced by devolatilization and heterogeneous reaction of char consume the O\textsubscript{2}. The amount of O\textsubscript{2} consumed by char oxidation is higher than other processes.

![Figure 23. Species evolution.](image-url)
Ignition Delay

There are different ways to validate the simulation predictions such as comparing the species profiles, flame stand-off, ignition delay, etc. In this work, the validity of models was examined by comparing ignition delay predicted by simulation and experimental data.

Definition

In experiments, several methods are suggested to characterize the ignition delay. The most widely used methods are based on visual observation (Jovanovic et al. 2011) or by measuring the intensity of visible light emission (Liu et al. 2011b). Computationally, ignition delay can be obtained by various criteria. A threshold value for particle temperature (e.g., 800 K) or the inflection point in particle temperature-time history \( \left( \frac{d^2T_p}{dt^2} = 0 \right) \) have been proposed as criteria to identify the ignition delay time. Alternatively, half of the \( CO_2 \) maximum production in the gas phase or the maximum rate of \( CO_2 \) production can be used to determine the ignition that represents the change in intensity of light emission.

In Figure 24, these criteria are illustrated with green dotted lines. The black boxes show the ignition delay identified in the experiments using visual observation. The inflection point in particle temperature history shows closer ignition delay to experiments than other criteria in Figure 24. The inflection point in the particle temperature history is used as the ignition criteria for the rest of this section of the report.

![Figure 24. Ignition delay criterion – 800K, inflection point and maximum upslope of CO2 production; a) gas phase at centerline and particle temperature b) consumption fraction of moisture, volatile and char](image)

The Impact of Furnace Temperature

The furnace temperature has a significant impact on the particle’s heating rate, which is illustrated in Figure 25. Black Thunder coal contains 11\% moisture, which is almost one order of magnitude more than Pittsburgh coal’s moisture content. Vaporization of this much moisture delays Black Thunder coal ignition compared to Pittsburgh coal. Considering the uncertainty contributed by the definition of ignition delay, the agreement between simulation predictions and experimental data are satisfactory.
Figure 25. Ignition delay vs. furnace temperature for Pittsburgh (Pt) and Black Thunder (BT) coal particles injected into 20 vol% O\textsubscript{2} in N\textsubscript{2} diluent. Thick and thin lines represent Pittsburgh and Black Thunder coal types and simulation results, respectively. Dashed and solid lines show experimental and simulation results, respectively.

Characterizing ignition delay by inflection point in the particle temperature history gives different particle temperatures. In Figure 26a, particle temperature at ignition as a function of furnace temperature is illustrated. Furthermore, consumption fractions of char and volatiles at the ignition point for Pittsburgh and Black Thunder coal types are illustrated in Figure 26b. As furnace temperature increases, the reaction rate of volatiles around the particle increases, which leads to faster ignition in the gas phase. Black Thunder coal has more moisture than Pittsburgh coal. Evaporation of coal moisture dilutes the oxidizer around the particle, therefore, causes slower reaction of volatile and put more delay in the ignition. Also, increasing the ignition delay provides particles with more time for devolatilization before ignition.

Figure 26. a) Simulation predictions: particle temperature at ignition point vs. furnace temperature. b) Consumption fraction of volatile and char at ignition point vs. furnace temperature. The thin and thick lines represent Black Thunder and Pittsburgh coal, respectively.
**Effect of Particle Size**

Figure 27 illustrates the effect of particle size on ignition delay. The experiments were performed on cuts of particle sizes; however, the initial particle size is fixed in our simulations. As shown, the one-dimensional model, in the laminar case, demonstrates a reasonable ability to capture the particle’s behavior at the low coal feed rates. Furthermore, Figure 27 is consistent with the expectation that in coal flames with distributed particle sizes, the smaller particles cause the ignition, since smaller particles heat faster and start to produce volatiles sooner than bigger particles.

![Graph](image)

Figure 27. Ignition delay vs. particle size for Pittsburgh coal. Dotted lines with circles show the boundaries of particle size cuts that were used in the experiments (Liu et al. 2011b). The solid line represents the simulation prediction using the corresponding fixed particle size.

In this work, ignition was identified as the inflection point in the particle temperature history. The change in the curvature of the particle temperature curve could happen for two reasons: 1) reactions of fuel (mostly volatile matter) in the gas phase (homogenous reactions), 2) surface reactions of char in the particle phase (heterogeneous reactions). As particle size diminishes, the amount of volatile matter that is produced around the particle decreases and does not let the ignition occur in the gas phase. In this case, heterogeneous reactions of char in the particle phase initiate ignition. In Figure 28a at the point where heterogeneous reactions become the dominant process in heating of the particles, consumption of char rapidly increases as particle size decreases. Char oxidation produces greater heat than volatile reactions, and particle heats up faster. Higher particle temperature leads to an increasing rate of volatile production; in Figure 28a there is rapid change in volatile consumption when the ignition regime changes from homogeneous to heterogeneous. Figure 28b illustrates the char and volatile consumption fraction at ignition. Char oxidation is strong function of oxygen partial pressure at the particle surface.
Subtask 4.3 – Radiation Modeling

Accuracy of surface flux computations of RMCRT were compared with a converged solution given by (Burns and Christen 1997). Agreement between the RMCRT algorithm and the numerically exact solution was obtained (see Figure 29). Ray convergence tests were performed on this benchmark case. Similar to prior results for flux-divergence convergence, the solution for radiative fluxes converged with an increase in the number of rays at the expected rate of ½ order (see Figure 30).

Parallel Central Processing Unit (CPU) scaling studies were conducted on the Ember cluster using 8 to 1728 processors. Strong scaling was achieved in this range as shown in Figure 31.

Parallel GPU scaling studies were conducted on the Titan cluster using 128 to 16384 processors as shown in Figure 32. Strong scaling was achieved in this range.
Figure 29. Agreement between flux results from RMCRT (red) and the numerically exact solution of Burns and Christon (blue).

Figure 30. Ray convergence of the numerical solution compared to the analytical solution of the Burns and Christon case. The ray convergence rate is approximately the expected rate of $-\frac{1}{2}$. 
Figure 31. Strong scaling analysis of RMCRT on 8 to 1728 processors using 100 rays per cell on a domain of 150°.

Figure 32. Strong scaling of RMCRT on the Titan GPU cluster.

Reflection and wall emission capabilities were tested by comparison with an analytical solution given by Modest (2003). Figure 33 shows excellent agreement between the RMCRT algorithm and the analytical solution. Ray convergence tests were performed on this benchmark case. Error was quantified using an L2 error norm defined as the average of the absolute value of the difference between the exact solution
and the model. The solution converged with an increase in the number of rays at the expected rate of \( \frac{1}{2} \) order (see Figure 34).

Grid convergence analyses were performed for several benchmark cases, including the Burns and Christon flux and flux divergence cases. All cases showed relatively small sensitivity to grid resolution. For an example of one of the benchmark grid convergence tests see Figure 35.

Figure 33. Agreement between results from RMCRT (green) and the analytical solution of Michael Modest (blue).
Figure 34. Ray convergence of RMCRT relative to an analytical solution. Note the ray convergence rate is approximately the expected rate of $-\frac{1}{2}$. 

\[ y = -0.52478x - 0.18482 \]
Figure 35. Converged solution of the radiative flux divergence (blue) for a benchmark case compared to the radiative flux divergences from various grid resolutions (other). Notice that at the locations of interest (cell centers) there is good agreement even for the coarsest meshes. What is not well represented in the coarse meshes, however, is the detail between the cell centers.

RMCRT scattering results were compared with a case in which scattering, absorbing, emitting media resides between two parallel, cold, black plates (Siegel 1987). Figure 36 demonstrates the agreement between the resulting radiative fluxes of the model and those of the exact solution for various optical thicknesses and scattering albedos.
Good agreement was obtained for all cases, particularly for low to moderate optical thicknesses. For $\tau = 10$, the model gave fluxes that were slightly higher than the exact solution. This is most likely due to the fact that the current RMCRT algorithm allows for scattering only at cell boundaries. Therefore, scattering is limited to occur at most once per cell length. For cases with low to moderate optical thicknesses and scattering coefficients, this is not a problem, due to the relatively long mean free paths between scattering events. However, for cases where the distances between scattering events are smaller than the grid resolution, scattering will not be allowed to occur frequently enough, and the model will produce fluxes that exceed those of the exact values. A solution to this problem involves decreasing the cell size of the mesh to allow for more frequent scattering events. As Figure 37 indicates, the error norm, again defined as the average of the absolute value of the difference between the model and the exact solution, indeed decreased with an increase in mesh refinement.
Figure 37. Grid convergence of the L1 error norms for the Siegel case where the scattering coefficient is 8 m^{-1}, and the absorption coefficient is 2 m^{-1}.

RMCRT accurately represented both the radiative flux, and the radiative flux divergence of a large, production-quality simulation. Figure 38 shows the comparison between RMCRT and 80-direction DOM (SN8) for the radiative flux divergence.

Figure 38. Radiative flux as computed by RMCRT (+) vs. DOM SN8 (-) for varying positions along the z direction of a center-line through the boiler.
Figure 39 shows the comparison between RMCRT and DOM for the radiative flux. Because of the directionality of radiative fluxes, more rays are required to reach a converged solution compared to that required for radiative flux divergences. To reduce the stochastic noise of the solution, a box filter was applied to the solution to obtain the results shown in Figure 40.

Figure 39. Radiative flux as calculated by RMCRT (-) vs. DOM (+) for varying positions along the z direction of a center line through the boiler.

Figure 40. Filtered solution of the radiative flux as calculated by RMCRT(-) vs. DOM(+) for varying positions along the z direction of a center-line through the boiler.
The L1 error norms of the RMCRT solutions were reduced by approximately 50% by using a simple box filter with a width of 5. The filtered results of using 100 rays had L1 error norms that were 40% lower than those of 24-direction DOM (SN4). RMCRT with 100 rays required approximately the same amount of processor time.

Various filtering options for post-processing RMCRT calculations were explored. 1D, 2D, and 3D filters of varying filter widths were implemented. Filtering results indicated that an increase in accuracy was achieved with a negligible increase in computation time. For example, a 1D filter with a 5-cell stencil increased the accuracy of radiative flux results by a factor of 2, while increasing the compute time by less than 0.1%.

Timing and accuracy calculations were carried out on an industrial scale methane-fired boiler simulation. Results indicated that for a given level of accuracy, and a given level of parallelism, RMCRT calculations may require less computational time than the discrete ordinates method (see Table 8).

<table>
<thead>
<tr>
<th></th>
<th>Computational Time (s)</th>
<th>$\text{div}Q$ L1 error norm</th>
<th>Q L1 error norm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtered RMCRT calculations</td>
<td>1033</td>
<td>1.07</td>
<td>.0311</td>
</tr>
<tr>
<td>DOM SN8 calculations</td>
<td>2949</td>
<td>2.05</td>
<td>.0271</td>
</tr>
</tbody>
</table>

Enhancement was carried out to allow the gas-phase absorption coefficients to be modified to include the effect of the coal-particle absorption coefficients. An oxy-coal furnace simulation was selected as a demonstration case for the new capability. Results are shown in Figure 41.
Subtask 4.4 - Char and Soot Kinetics and Mechanisms

Feed Stock Chars for Gasification Experiments

As described in the approach section, pyrolyzed coal char was generated in the HPFFB reactor to serve as feed stock material for gasification re-injection HPFFB experiments. The generated coal chars from the HPFFB were sieved, and the size fraction of char used during gasification re-injection experiments was determined solely by which size fraction contained the highest yields. The Utah Skyline steam gasification experiments used the 45-75 μm fraction, while both the Illinois #6 and Pittsburgh #8 experiments utilized the 75-106 μm fraction. As an aside, char swelling during high heating-rate pyrolysis had a greater effect on the Illinois #6 and Pittsburgh #8 coals than the Utah Skyline coal since 45-75 μm raw coal was fed during the generation of all 3 pyrolyzed chars. The chosen size fractions of char (45-75 μm or 75-106 μm) were used in order to simulate pulverized coal sizes used commercially, but also allowed particle temperature gradients to be ignored in modeling.

Figure 42 shows SEM images of sieved coal chars that acted as feed stock material for steam gasification HPFFB re-injection experiments at 15 atm total pressure. These coal chars were generated in the HPFFB reactor at the 15-atm char-generating conditions.
Table 9 provides a summary of all the coal chars that served as feed stock material for HPFFB steam gasification experiments. Particle diameters were measured from optical microscope pictures of the sieved coal chars using ImageJ software. The mass mean diameters ($d_m$) reported in Table 9 were calculated from Equation (4.4.1) where $w_i$ is the mass fraction of particles in a narrow bin size of diameter $d_i$, using a total of ~500 measured particle diameters for each char feed stock sample.

$$d_m = \sum_{i=1}^{n} d_i \cdot w_i$$

(4.4.1)
<table>
<thead>
<tr>
<th>Condition at which Char was Feed Stock Material (atm)</th>
<th>Feed Stock</th>
<th>Total Pressure (dm)</th>
<th>Sieved Size (μm)</th>
<th>Mass Mean (dm)</th>
<th>Apparent Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam / low CO₂ Utah Skyline char 10 atm</td>
<td>45-75</td>
<td>61.7</td>
<td>0.252</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam / low CO₂ Utah Skyline char 12.5 atm</td>
<td>45-75</td>
<td>62.7</td>
<td>0.213</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam / low CO₂ Utah Skyline char 15 atm</td>
<td>45-75</td>
<td>68.6</td>
<td>0.193</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam / low CO₂ Pitt #8 char 10 atm</td>
<td>75-106</td>
<td>85.9</td>
<td>0.164</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam / low CO₂ Pitt #8 char 12.5 atm</td>
<td>75-106</td>
<td>86.0</td>
<td>0.175</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam / low CO₂ Pitt #8 char 15 atm</td>
<td>75-106</td>
<td>82.3</td>
<td>0.159</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam / low CO₂ IL #6 char 10 atm</td>
<td>75-106</td>
<td>84.5</td>
<td>0.149</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam / low CO₂ IL #6 char 12.5 atm</td>
<td>75-106</td>
<td>89.3</td>
<td>0.149</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam / low CO₂ IL #6 char 15 atm</td>
<td>75-106</td>
<td>78.2</td>
<td>0.150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam / high CO₂ IL #6 char 15 atm</td>
<td>75-106</td>
<td>86.3</td>
<td>0.150</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Apparent density is the mass of the particle divided by the volume of the particle and includes voids inherent in the material.

The apparent densities \( \rho_{\text{apparent}} \) in Table 9 were calculated using its relationship to bulk density:

\[
\rho_{\text{apparent}} = \frac{\rho_{\text{bulk}}}{1 - \epsilon_b}
\]  

(4.4.2)

where \( \rho_{\text{bulk}} \) and \( \epsilon_b \) are defined as the bulk density and inter-particle void fraction or packing factor. Bulk densities of the coal feed stock chars were measured using a technique similar to that used by Tsai and Scaroni (1987), where particles were added to a graduated cylinder of known volume. The bulk density was then calculated by dividing the mass of particles added by the volume of the bed. The graduated cylinder was also tapped repeatedly to ensure the minimum volume of the bed. The value for \( \epsilon_b \) was taken as 0.45 (Tsai and Scaroni, 1987; Gale et al., 1995). The error associated with this method of calculating apparent densities is estimated to be 10-20% (Tsai and Scaroni, 1987).

**HPFFB Gas Conditions for Gasification Experiments**

The reaction environment for HPFFB coal steam gasification experiments was determined by the post-flame environment above the burner. The composition of this post-flame region in this study was estimated by thermodynamic equilibrium calculations.

Previous experience has shown that increasing the steam concentration in the post-flame gases much beyond 10 mol% compromised the burner of the HPFFB reactor. This is due to the fact that steam was generated in the post-flame environment by feeding extra H₂ gas to the burner, which caused the flame to
‘sit’ closer to the burner surface due to the relatively high flame speed of H₂. The close proximity of the hot flame to the top of the metal burner head greatly reduced the life of the burner. In addition, previous experience has shown that bituminous coals consistently clog a few millimeters below the burner surface when high flow rates of H₂ are delivered to the burner due to pre-heating of the entrained coal due to conduction through the burner face.

Two different sets of gas conditions were used in the HPFFB coal steam gasification experiments. The first set had measurements of the extents of coal gasification for 3 coal chars (Utah Skyline, Pitt #8, & IL#6) at conditions where the coal char conversion was primarily due to steam gasification, while minor mass release was due to CO₂ since it is not possible to completely eliminate CO₂ in the post-flame HPFFB environment. Table 10 provides a summary of these gas conditions.

<table>
<thead>
<tr>
<th>Total Pressure (atm)</th>
<th>Peak Gas Temperature (K)</th>
<th>mol% H₂O in Post-Flame Environment</th>
<th>mol% CO₂ in Post-Flame Environment</th>
<th>mol% CO in Post-Flame Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1814</td>
<td>7.5</td>
<td>14.21</td>
<td>1.89</td>
</tr>
<tr>
<td>12.5</td>
<td>1782</td>
<td>7.7</td>
<td>14.13</td>
<td>2.26</td>
</tr>
<tr>
<td>15</td>
<td>1611</td>
<td>7.3</td>
<td>11.43</td>
<td>2.75</td>
</tr>
<tr>
<td>15</td>
<td>1830</td>
<td>8.6</td>
<td>13.74</td>
<td>2.45</td>
</tr>
</tbody>
</table>

The second set of HPFFB gas conditions studied the gasification of a single coal char (IL#6) at varying H₂O and CO₂ concentrations to determine the rate of reaction in a mixture of two gasification agents using significant concentrations of CO₂. Table 11 provides a summary of this second set of HPFFB gas conditions.

<table>
<thead>
<tr>
<th>Total Pressure (atm)</th>
<th>Peak Gas Temperature (K)</th>
<th>mol% H₂O in Post-Flame Environment</th>
<th>mol% CO₂ in Post-Flame Environment</th>
<th>mol% CO in Post-Flame Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1879</td>
<td>7.5</td>
<td>33.3</td>
<td>10.51</td>
</tr>
<tr>
<td>15</td>
<td>1812</td>
<td>7.7</td>
<td>83.2</td>
<td>7.88</td>
</tr>
</tbody>
</table>

The measured gasification rates of coal char in this study are still valuable even though CO is known to be an inhibitor to the CO₂/char gasification reaction since commercial gasification most always occurs in an environment containing both CO₂ and CO. In addition, the retarding influence of CO on the CO₂/char gasification reaction has the most pronounced effect at lower temperatures and higher CO/ CO₂ atomic ratios than studied here (Turkdogan and Vinters 1970).

Centerline Temperature Profiles of the HPFFB

The non-isothermal centerline gas temperature profiles were measured at each gas condition in the HPFFB reactor (see Table 10 and Table 11) using a B-type thermocouple with a spherical diameter of 65
422 μm. Although silica or alumina non-catalytic coatings were deposited on B-type thermocouple beads for previous HPFFB studies, an uncoated B-type thermocouple bead was used here after verifying that there was essentially no difference between measured temperature profiles with or without the use of a coating on the B-type thermocouple bead. Additional details of the experimental setup required to measure centerline gas temperatures in the HPFFB reactor were described in (Shurtz 2011).

The gas temperature was solved using an energy balance on the thermocouple bead. The bead is heated by convection and is cooled by radiating heat away to the cooler reactor walls. Conduction through the thin, relatively long wires coming off from the thermocouple bead was ignored. Assuming that the thermocouple bead was at equilibrium, the following energy balance was used:

\[ Q_{\text{convection}} = Q_{\text{radiation}} \]  
\[ h_c A_{\text{bead}} (T_{\text{gas}} - T_{\text{bead}}) = A_{\text{bead}} \sigma \varepsilon (T_{\text{bead}}^4 - T_{\text{wall}}^4) \]

where \( h_c \) is the convective heat transfer coefficient, \( A_{\text{bead}} \) is area of the thermocouple bead, \( T_{\text{gas}} \) is the gas temperature, \( T_{\text{bead}} \) is the temperature of the thermocouple bead, \( T_{\text{wall}} \) is the wall temperature of 500 K, \( \sigma \) is the Stefan-Boltzmann constant (\( 5.67 \times 10^{-8} \) W/m\(^2\)/K\(^4\)), and \( \varepsilon \) is the emissivity of the thermocouple bead. A temperature dependent emissivity expression for a S-type thermocouple bead was used (Shaddix 1999):

\[ \varepsilon = -0.1 + 3.24 \times 10^{-4} T - 1.25 \times 10^{-2} T^2 + 2.18 \times 10^{-11} T^3 \]

where \( T \) is the bead temperature in Kelvin. The emissivity expression in Equation (4.4.5) predicts a value of 0.12 at 1000 K and 0.22 at 2000 K. The temperature correction is very sensitive to the emissivity value of the thermocouple bead, but using the expression in Equation (4.4.5) led to temperature corrections around 100 K at radiation-corrected gas temperatures near 1800 K.

The centerline gas temperature profiles for the 4 steam conditions of the HPFFB reactor (see Table 10) are summarized in Figure 43, and have been corrected for radiation losses from the thermocouple bead. The different conditions are identified by the total pressure and the peak gas temperature measured from the profile. For example, the 15 atm 1830 K temperature profile was measured at 15 atm total pressure and had a maximum measured centerline gas temperature of 1830 K. Note that only 3 inches of the 15 atm 1611 K temperature profile is shown in Figure 43. The greatest reaction length (i.e., distance between burner and collection probe) at this relatively cool condition was 3” since water condensation adversely affected particle feeding when collection heights greater than 3” were attempted. The 10 atm 1850 K temperature profile is also included in Figure 43. This condition essentially did not contain steam (< 1 mol%), and was used to aid in the accounting of char mass loss due to CO\(_2\) gasification at the steam conditions (see Table 10).
Figure 43. Centerline gas temperature profiles of the HPFFB steam conditions corrected for radiation losses from the thermocouple bead.

The temperature profiles corresponding to the second set of HPFFB gas conditions (see Table 11) are shown in Figure 44. These conditions were used to study the gasification of Illinois #6 coal char at conditions where significant mass release was due to both steam and CO$_2$ gasification.
Figure 44. Centerline gas temperature profiles of the HPFFB CO₂/steam conditions corrected for radiation losses from the thermocouple bead.

Measurement of Particle Mass Release

Mass release refers to how much of the initial mass leaves the particle and is an indicator of the extent of gasification. The typical equations used to calculate mass release on a dry and ash-free (daf) basis from a mass balance (Equation (4.4.6)) and ash-tracer (Equation (4.4.7)) follow:

\[
\text{% mass release (daf)} = \left( \frac{m^{0}_{\text{feedstock}} - m_{\text{char collected}}}{m^{0}_{\text{feedstock}} - m^{0}_{\text{ash, feedstock}}} \right) \cdot 100
\]  (4.4.6)

\[
\text{% mass release (daf)} = \left( 1 - \frac{x^{0}_{\text{ash, feedstock}}}{1 - x^{0}_{\text{ash, collected}}} \right) \cdot 100
\]  (4.4.7)

In the case of the HPFFB reactor, \( m^{0}_{\text{feedstock}} \) is the dry mass of feedstock fed during experimentation, \( m_{\text{char collected}} \) is the dry mass of char collected during the experiment, and \( m^{0}_{\text{ash, feedstock}} \) is the dry mass of ash in the fed feedstock. The mass fraction of ash in the dry feedstock fed during experimentation is \( x^{0}_{\text{ash, feedstock}} \), and \( x^{0}_{\text{ash, collected}} \) is defined as the mass fraction of ash in the dried, collected char. The coal chars collected from the HPFFB reactor often contained ~ 10 wt% moisture. It was necessary to account for the fact that the collected char was not moisture-free in order to accurately assign mass loss on a daf basis. The ash fractions required by Equations (4.4.6) and (4.4.7) came from ash tests that were performed on
samples by slowly heating dried samples to 750 °C in a muffle furnace and maintaining that temperature for 10 hours. Accurate ash test results required at least ~8 mg of ash.

Equation (4.4.7) is convenient because it does not depend on collection efficiency during experimentation, and allows accurate mass release to be calculated (assuming that original ash remains with the char) even when a mass balance is ruined by spills, clogs, etc. However, mass released calculated by Equation (4.4.7) should only be considered when the corresponding mass release values using Equation (4.4.6) are higher, assuming again that the original ash remained with the collected char. A hypothetical example is given to clarify this point. Say the mass release by Equation (4.4.7) yields a value of 20% daf mass release while Equation (4.4.6) yields a value of 10%. As long as care has been taken to account for moisture in both the feedstock material and the collected char, the hypothetical 20% daf mass release value by Equation (4.4.7) can be ignored since there is predicted mass loss above that which is clearly documented by a mass balance.

Both Equations (4.4.6) and (4.4.7) assume that ash does not vaporize from the fed feedstock during experimentation. When ash vaporizes from the fed material during HPFFB experiments, Equation (4.4.7) will underestimate the particle mass release. The use of Equation (4.4.6) also leads to incorrect values of daf mass release when ash vaporizes from the fed material during experimentation. The numerator in Equation (4.4.6) reflects the organic mass that leaves during experimentation if ash does not vaporize during experiments. However, when ash vaporizes, the numerator in Equation (4.4.6) reflects the mass of ash that vaporized in combination with the organic mass of the particle that was released. Equation (4.4.8) was derived for this research project in order to calculate percent mass release on a daf basis when ash vaporizes during experimentation. The numerator in the equation reflects the amount of organic mass of the particle that was released:

\[
\% \text{ mass release (daf)} = \left( \frac{m^0_{\text{feedstock}} \cdot (1 - x_{\text{ash, feedstock}}^0) - m_{\text{char, collected}} \cdot (1 - x_{\text{ash, char}})}{m^0_{\text{feedstock}} - m^0_{\text{ash, feedstock}}} \right) \cdot 100
\] (4.4.8)

It is important to note that Equation (4.4.8) depends on an accurate mass balance, which is regularly achieved in the HPFFB reactor. For example, the collection efficiency of the HPFFB reactor was measured to be about 98% while feeding petroleum coke using collection heights in the range 3” to 9.5”. In addition, the best mass balance was ensured by cleaning out the collection system and to most accurately assign weights of material fed and collected char.

Calculated mass release by Equation (4.4.8) was the primary value used in the gasification modeling of this study, even though mass release values by Equation (4.4.7) were also considered. Ash often vaporized from the bituminous coal chars used in this study, as determined using a mass balance of the ash. Shurtz (2011) also observed ash vaporization from coals injected in the HPFFB reactor at high heating rates, and documented that the mass release values using Equation (4.4.7) resulted in “very noisy trends.”
First-Order Gasification Model

Although more complicated models exist (Liu and Niksa, 2004; Shurtz and Fletcher, 2013), the coal char mass release data from the gasification experiments in the HPFFB reactor were modeled with a first-order global model (Sowa 2009; Lewis 2011; Shurtz 2011) where the rate is normalized by particle external surface area:

\[
\frac{dm}{dt} \cdot \frac{1}{A_p} = -k_{\text{ran}} \cdot P_{\text{reactant, surf}} = \left[A \cdot \exp\left(-\frac{E}{R \cdot T_p}\right)\right] \cdot P_{\text{reactant, surf}} 
\]  

(4.4.9)

where \(m_p\) is the particle mass, \(t\) is time, \(A_p\) is the external surface area of the assumed-spherical particle, \(k_{\text{ran}}\) is the rate constant of CO\(_2\) gasification, \(P_{\text{reactant, surf}}\) is the partial pressure of H\(_2\)O or CO\(_2\) at the particle surface, \(A\) is the pre-exponential factor, \(E\) is activation energy, \(R\) is the ideal gas constant, and \(T_p\) is the particle temperature. The rate in Equation (4.4.9) was integrated using the Explicit Euler method for integration in an Excel spreadsheet, and is negative since the particles lost mass during gasification. The kinetic parameters \(A\) and \(E\) for the model in Equation (4.4.9) were determined by minimizing the sum-squared error between predicted and measured gasification mass release data using the Excel solver.

Decrease in external surface area with increased conversion was included in the model based off of measurements used in the following equation:

\[
\frac{d_1}{d_0} = \left(\frac{\rho_0}{\rho_1}\right)^{\frac{1}{3}} \left(\frac{m_1}{m_0}\right)^{\frac{1}{3}} 
\]  

(4.4.10)

where \((d_1/d_0)\) is the diameter ratio of collected char to feed stock material, \((\rho_0/\rho_1)\) is the ratio of apparent densities (see Equation (4.4.2)) of dried feed stock material to dried collected char, and \((m_1/m_0)\) is the mass ratio of collected char to fed material on a dry basis. Equation (4.4.10) assumes spherical particles, which is often assumed in coal modeling.

Since only the gas temperature \(T_{\text{gas}}\) was measured, \(T_p\) was solved from the transient particle energy balance at each time step using the Euler method and an under-relaxed secant method:

\[
m_p \cdot C_p \cdot \frac{dT_p}{dt} = h_e \cdot A_p \cdot (T_{\text{gas}} - T_p) + \varepsilon_p \cdot \sigma \cdot A_p \cdot (T_{\text{surr}}^4 - T_p^4) + \frac{\Delta H_{\text{rxn}}}{\Delta t} \cdot \frac{dm_p}{dt} 
\]  

(4.4.11)

where \(C_p\) is the heat capacity of the particle, \(h_e\) is the heat transfer coefficient \((\text{Nu} \cdot k_{\text{gas}}/d_p\) where \(\text{Nu} = 2)\), \(\varepsilon_p\) was the emissivity of the char particle, \(\sigma\) is the Stefan–Boltzmann constant \((5.67 \times 10^{-12} \text{ W/cm}^2/\text{K})\), \(T_{\text{surr}}\) is the temperature of the surroundings \((500 \text{ K})\), and \(\Delta H_{\text{rxn}}\) is the heat of reaction for the CO\(_2\) or H\(_2\)O gasification reaction. A value of 0.8 was used for \(\varepsilon_p\) (Fletcher 1989). The left-hand side of Equation (4.4.11) was set equal to zero since steady state was assumed during the small time steps of \(\sim 0.13\) ms. The first term on the right-hand side of Equation (4.4.11) represents the particle heating up from convective heat transfer, and is positive when \(T_{\text{gas}} > T_p\). The second term in Equation (4.4.11) is the radiative heat transfer from the particle, and is negative when \(T_p > T_{\text{surr}}\). The last term in Equation (4.4.11)
takes into account heat of the reacting particle. This last term is negative due to the \( \frac{dm_p}{dt} \) term (i.e., \(-k_{rxn}P_{reactant/surf}A_p\)), and requires positive values for \( \Delta H_{rxn} \) when accounting for the endothermic steam or CO\(_2\) char gasification reactions.

Although the model does not take pore diffusion into account, it does consider film diffusion, which allowed \( P_{reactant/surf} \) to be solved for explicitly:

\[
P_{reactant/surf} = \frac{v \cdot h_m \cdot P_{reactant}}{R \cdot T_{gas} \left[ k_{rxn} + \frac{v \cdot h_m}{R \cdot T_p} \right]} \tag{4.4.12}
\]

where \( v \) is the mass of carbon (in grams) that react per mole of CO\(_2\) or H\(_2\)O reactant, \( h_m \) is the mass transfer coefficient (\( ShD_{AB}dp \) where \( Sh = 2 \) for this low velocity, small diameter experiment), and \( P_{reactant} \) is the partial pressure of H\(_2\)O or CO\(_2\) in the bulk gas. In the case of CO\(_2\) or H\(_2\)O char gasification, \( v \) was \((12 \text{ g C/ (1 mol H}_2\text{O or CO}_2))\) from the following reactions:

\[
\begin{align*}
C + CO_2 & \rightarrow 2 \text{ CO} \\
C + H_2O & \rightarrow CO + H_2
\end{align*}
\]

The heat of reaction, \( \Delta H_{rxn} \), for gasification was calculated using correlations and coefficients from the Gordon-McBride database (McBride et al. 2002), resulting in approximate values of 11,200 and 13,700 J/gm for H\(_2\)O and CO\(_2\) char gasification reactions, respectively (although \( \Delta H_{rxn} \) is dependent on particle temperature). As other researchers have assumed previously, (Hurt et al. 1998; Shurtz 2011), coal char was assumed to have the properties of graphite in the calculations for \( \Delta H_{rxn} \).

The gas thermal conductivity \( (k_{gas}) \) of a modeled condition was estimated using the \( k_{gas} \) values of individual gas species present in the HPFFB post-flame environment weighted by their respective mole fractions. The thermal conductivity of individual gas species was estimated using the empirical correlation \( k_{gas}(T) = a T^b \) with reported values of ‘a’ and ‘b’ (Mitchell 1980) evaluated at the film temperature (average of \( T_{gas} \& T_p \)) in units Kelvin.

The binary diffusion coefficients \( (D_{AB}) \) that were part of the mass transfer coefficient \( (h_m) \) calculation came from various sources including published values (Incropera and Dewitt 2002), those fit to an empirical equation based on Chapman-Enskog kinetic theory (Mitchell 1980), and those predicted by corresponding-states methods (Bird et al. 2002). The diffusion coefficient was evaluated at the film temperature, and was inversely proportional to pressure, and directly proportional to temperature raised to a power \((1.5 \text{ to } 2.33)\).

Regressing Steam Gasification Kinetic Parameters for Bituminous Coal Chars Using first-Order Model.

Steam gasification kinetic parameters were regressed for Utah Skyline and Illinois #6 coal chars using mass release data from the HPFFB reactor. As mentioned previously, these experiments utilized a re-injection strategy where fully pyrolyzed char was fed at steam conditions (see Table 10) in the HPFFB.
These steam conditions contained some CO\textsubscript{2} as well, since it is not possible to get completely rid of the CO\textsubscript{2} in the post-flame environment. However, the mass release measured during the experiments was primarily due to steam.

It was necessary to differentiate the measured mass loss between that caused by CO\textsubscript{2} gasification and that due to steam gasification. Assuming that the rates of CO\textsubscript{2} and steam gasification are additive, the mass loss predicted to occur by CO\textsubscript{2} gasification was accounted for, and any remaining mass loss was attributed to steam gasification. This method allowed steam gasification kinetic constants to be regressed for the first-order model.

Mass loss due to CO\textsubscript{2} gasification of Illinois #6 coal char was predicted using published CO\textsubscript{2} gasification rates (Shurtz and Fletcher 2013). It was convenient since the reported Illinois #6 CO\textsubscript{2} gasification kinetic parameters (i.e., \( A = 0.8876 \text{ g/cm}^2\text{s/atm} \) and \( E = 121.3 \text{ kJ/mol} \)) were for the same first-order model used in this work. Illinois #6 coal char was also fed in the HPFFB at 10 atm using a peak gas temperature of 1850 K to aid in the accounting of char mass loss due to CO\textsubscript{2} gasification. The temperature profile of this condition was shown in Figure 43. This 10 atm 1850 K condition was specifically chosen since it provided a data point of mass loss solely due to CO\textsubscript{2} gasification since this condition essentially did not contain any steam (< 1 mol%). The 10 atm 1850 K condition also had a similar temperature profile as the steam conditions (see Figure 43), yet contained the highest partial pressure of CO\textsubscript{2} (i.e., \( P_{\text{CO}_2} = 2.08 \text{ atm} \)). Therefore, the measured mass loss of coal char at the 10 atm 1850 K condition after ~300 ms provided an upper bound of the mass loss due to CO\textsubscript{2} gasification in the steam experiments. The mass release data point from the 10 atm 1850 K condition also allowed a quality check of the published CO\textsubscript{2} gasification kinetics (Shurtz and Fletcher 2013) before they were used to predict mass loss due to CO\textsubscript{2} in the steam gasification experiments. Since there was only a 2.4 wt% discrepancy between the measured and modeled daf mass loss at the 10 atm 1850 K condition when feeding IL#6 coal char, it was concluded that the published IL#6 CO\textsubscript{2} gasification rates (Shurtz and Fletcher 2013) provide accurate estimates of the mass loss due to CO\textsubscript{2} at the HPFFB steam conditions.

Figure 45 shows the prediction of mass loss of IL#6 char due to CO\textsubscript{2} and H\textsubscript{2}O after the first collection height at 1” at the 15 atm 1830 K steam condition. Published CO\textsubscript{2} gasification rates (Shurtz and Fletcher 2013) of IL#6 coal char were used to account for the mass loss due to CO\textsubscript{2} at this condition. From the figure, it is easily seen that most of the mass loss of IL#6 coal char was due to steam gasification. The 15 atm 1830 K steam condition resulted in the highest mass loss due to CO\textsubscript{2} of all 4 steam conditions. Therefore, the mass loss due to CO\textsubscript{2} in any of the other 3 steam conditions would be less than that shown in Figure 45.
Regressing steam gasification kinetic parameters for Utah Skyline char was made slightly more complicated since published CO$_2$ gasification rates of this coal were not found. However, published empirical correlations (Shurtz and Fletcher 2013) to predict the pre-exponential factor, $A$, at $E = 123$ kJ/mol for CO$_2$ gasification rates using the first-order model were attempted to model the CO$_2$ gasification of Utah Skyline char. This approach was abandoned after the empirical rate constants predicted mass loss about double that measured when feeding 45-75 μm Utah Skyline char at the 10 atm 1850 K non-steam HPFB condition using a particle residence time near 300 ms. Instead, CO$_2$ gasification kinetic constants were regressed for Utah Skyline char using the single data point collected at the 10 atm 1850 K non-steam condition. It would have been ideal to regress CO$_2$ gasification kinetic parameters of Utah Skyline char with a full set of CO$_2$ gasification data, but time constraints of the project prevented this. However, it is believed that using the regressed CO$_2$ gasification kinetic parameters from the limited CO$_2$ gasification data obtained in this project yielded more accurate results than if the empirical correlations were used. Setting $E = 123$ kJ/mol as was done previously for coal chars (Shurtz and Fletcher 2013), the regressed $A$ parameter was 1.0734 g/cm$^2$/s/atm for the Utah Skyline char CO$_2$ gasification data point at the 10 atm 1850 K non-steam condition. As a comparison, $A$ values of 3.006 and 2.679 g/cm$^2$/s/atm for Utah Skyline char were predicted using the aforementioned empirical correlations based on elemental coal composition and predicted NMR parameters, respectively.

Figure 46 shows the prediction of mass loss of Utah Skyline char due to CO$_2$ and H$_2$O after the first collection height at 1” at the 15 atm 1830 K steam condition. The regressed parameters ($A = 1.0734$
g/cm²/s/atm and \( E = 123 \text{ kJ/mol} \) were used to account for the mass loss due to \( \text{CO}_2 \) at this condition, as previously mentioned. From the figure, it is easily seen that most of the mass loss of Utah Skyline coal char was due to steam gasification, just as was observed for the IL#6 experiments in Figure 45. The mass loss due to \( \text{CO}_2 \) for Utah Skyline char at any of the other 3 steam conditions was roughly equal to or less than that shown in Figure 46.

In summary, the mass loss predicted for \( \text{CO}_2 \) gasification was accounted for using the first-order model, and any remaining mass loss was attributed to steam gasification, which was then used to regress first-order steam gasification kinetic parameters. The steam gasification data included mass release values from 4 gas conditions in the HPFFB at 3 residence times per gas condition, excluding the 15 atm 1611 K condition that only used 2 residence times. The maximum particle residence time of the measured data was about 240 ms.

The activation energy, \( E \), for steam gasification was kept at 121.3 kJ/mol for both Utah Skyline and Illinois #6 coal chars since changing \( E \) did not make any significant improvements to the model fit. Recall that this same value was the published first-order model activation energy of IL#6 char for the \( \text{CO}_2 \) gasification reaction. Setting \( E \) equal for both bituminous coal chars for both \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) gasification reactions allowed convenient comparisons between the rates of the 2 coal chars using ratios of pre-exponential factors. In addition, the rate comparisons of the \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) gasification reactions could be similarly performed. The regressed kinetic parameters are summarized in Table 12. The kinetic parameters in the table were derived from data where \( T_p \) and \( P_{\text{H}_2\text{O},\text{surf}} \) values ranged from about 1250-1670 K and 0.67-1.25 atm, respectively. Using data in this table reveals that Utah Skyline char is about 1.6
times (i.e., 8.457 / 5.350) more reactive to steam than the IL#6 char. Steam gasification rates were about 6 times (i.e., 5.350 / 0.8876) faster than CO₂ gasification rates.

<table>
<thead>
<tr>
<th>Coal Feed Stock</th>
<th>E (kJ/mol)</th>
<th>A (H₂O gasification)</th>
<th>A (CO₂ gasification)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Utah Skyline</td>
<td>121.3</td>
<td>8.457</td>
<td>1.0734d</td>
</tr>
<tr>
<td>Illinois #6</td>
<td>121.3</td>
<td>5.350</td>
<td>0.8876</td>
</tr>
</tbody>
</table>

(Shurtz and Fletcher, 2013)

This kinetic constant was derived in this project using very limited data.

Relative error provides a way to judge the model fit of measured data and is defined as the average percent deviation of the model using the following equation:

\[
\text{Relative Error} = \frac{\sum_{i=1}^{n} \left( \frac{X_i^M - X_i^E}{X_i^E} \right)^2}{n} \cdot 100
\]  

(4.4.13)

where \(X_i^M\) and \(X_i^E\) are defined as the modeled and experimental mass release points, respectively. The relative error was calculated using experimental steam mass loss data from the four HPFFB steam conditions and the predictions of the model using parameters in Table 12. The relative error between the Utah Skyline mass loss data due to H₂O gasification and that predicted when using the reported kinetic parameters in Table 12 was 13.2%. From a very similar calculation, the IL#6 coal char had a 9.8% error. These calculations ignored data collected at the first collection point at each of the 4 steam HPFFB conditions since mass loss was modeled after this first collection point, resulting in no error between measured and modeled values at these points. The value of \(n\) in Equation (4.4.13) was therefore 7 instead of 11.

The parity plots shown in Figure 47 show how the measured mass release data (on a char basis) due to steam compared with that predicted by the first-order gasification model using steam kinetic parameters in Table 12. The fits of the first-order model in Figure 47 are very reasonable considering the simplicity of the model.
Gasification of Illinois #6 Coal Char by Both H$_2$O and CO$_2$. The gasification of a single coal char (75-106 μm IL/#6) was studied in order to gain insight about the mass loss of coal char in the presence of both H$_2$O and CO$_2$. These conditions differed from the HPFFB steam conditions (see Table 10) since CO$_2$ was present in much larger concentrations in these second set of conditions, which allowed CO$_2$ to account for a much higher fraction of the total mass release when compared to the steam conditions. Similar concentrations of H$_2$O were used in both sets of conditions, since attempting to increase the H$_2$O fraction in the post-flame environment of the HPFFB reactor would have required increased H$_2$ flow rates to the burner, which can damage the burner. These H$_2$O/CO$_2$ experiments utilized 2 gas conditions at 15 atm, which is the highest operating pressure of the HPFFB reactor. The high total pressure was chosen in order to maximize the partial pressures of the two gasification agents, thus guaranteeing the highest extents possible of coal char gasification in the limited particle residence times inside the HPFFB reactor. The composition of the post-flame environment as predicted by thermodynamic equilibrium for the two H$_2$O/CO$_2$ conditions is included in Table 13. The non-isothermal temperature profiles of these 2 conditions were included in Figure 44.

Figure 47. Parity plots of HPFFB H$_2$O gasification data for (a) Illinois #6 and (b) Utah Skyline coal chars using mass loss data attributed to H$_2$O gasification.
Table 13. Composition of the Post-Flame Environment for the H₂O/CO₂ HPFFB Conditions for IL#6 Experiments

<table>
<thead>
<tr>
<th></th>
<th>15 atm 1879 K Mole %</th>
<th>15 atm 1812 K Mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0.56</td>
<td>0</td>
</tr>
<tr>
<td>CO</td>
<td>10.51</td>
<td>7.88</td>
</tr>
<tr>
<td>CO₂</td>
<td>33.29</td>
<td>83.16</td>
</tr>
<tr>
<td>H₂</td>
<td>0.52</td>
<td>0.17</td>
</tr>
<tr>
<td>H₂O</td>
<td>7.45</td>
<td>7.7</td>
</tr>
<tr>
<td>N₂</td>
<td>47.67</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Measured and predicted mass release values of the IL#6 coal char at the two H₂O/CO₂ conditions of the HPFFB reactor is shown in Figure 48. Note that replicates of the measured mass release values are shown in the figure and that the repeatability of mass release at the 15 atm 1812 K condition was much better than that at the 15 atm 1879 K condition. The predicted mass release values in Figure 48 came from the addition of mass loss predicted by CO₂ and H₂O gasification using the first-order model with the IL#6 kinetic parameters in Table 12, which include published CO₂ kinetic parameters (Shurtz and Fletcher, 2013) and H₂O kinetic parameters that were regressed in the current study. The prediction of the mass release values agreed well with the measured values at the 15 atm 1812 K condition.

![Figure 48](image-url)

Figure 48. Measured and predicted values of daf mass release of IL#6 coal char at the H₂O/CO₂ conditions of the HPFFB reactor.

Although there was more experimental scatter in the 15 atm 1879 K data set (see Figure 48), the predictions of the first-order model seemed to agree well with the measured IL#6 mass release (excluding 1 data point at ~ 130 ms). Although the partial pressure of CO₂ at the 15 atm 1812 K condition was 2.5 times higher than at the 15 atm 1879 K condition (Table 13), similar mass release values were measured at both conditions (see Figure 48) since rates are exponential with temperature and the 15 atm 1879 K condition was hotter (see Figure 44). In conclusion, good approximations of mass release were obtained.
when using the first-order model and the kinetic parameters in Table 12 with the assumption that \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) rates are additive.

Figure 49 and Figure 50 show the predictions of the first-order model for the distribution of mass loss due to \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) gasification using kinetic parameters in Table 12 for the case when 15-atm pyrolyzed 75-106 \( \mu \text{m} \) IL#6 coal char was re-injected at the 15 atm 1812 K and 15 atm 1879 K \( \text{H}_2\text{O}/\text{CO}_2 \) HPFFB conditions, respectively. Although the first-order model predicts similar total mass release of IL#6 coal char at the \( 2 \text{H}_2\text{O}/\text{CO}_2 \) HPFFB conditions, it predicted that 62% of the total mass loss is due to \( \text{CO}_2 \) at the 15 atm 1812 K condition when compared to only 43% at the 15 atm 1879 K condition at particle residence times near 220 ms.

![Graph showing mass release predictions](image)

**Figure 49.** First-order model predictions for the distribution of mass loss caused by \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) gasification using kinetic parameters in Table 12 for IL#6 char reacting at the 15 atm 1812 K \( \text{H}_2\text{O}/\text{CO}_2 \) HPFFB condition.
Samples Generated for Coal Soot Structure Analysis for Soot Model

In an effort to gain insight into the chemical structure differences between young and mature soot for use in a soot model, coal soot was collected from previous pyrolysis experiments from BYU’s HPFFB reactor (see Approach). The soot separated from char during HPFFB experiments through a virtual impactor and cyclone, both parts of the HPFFB collection system (see Figure 5). After this initial separation, the soot collected on water-cooled polycarbonate filters, which were positioned in-between filter flanges of the HPFFB collection system (see Figure 5). Upon completion of a HPFFB experiment, the soot was scraped from the polycarbonate filters and stored into separate bottles under argon and refrigerated until subsequent analysis was performed.

Soot samples from the pyrolysis of 4 different coals were selected. The results are presented in (Shurtz, 2011). Two residence times were selected for each of these 4 coals, emphasizing the difference in composition between young and mature soot. The adiabatic flame temperatures and the pressures were held constant in order to isolate residence time as the variable of interest. A $^{13}$C-NMR test was performed on the first sample in Table 14 (i.e., EB ‘A’ at 1 atm 1350 K, ~35 ms), providing a standard to evaluate the effectiveness of the Fringe3D analysis to estimate soot chemical structure.
Table 14. List of soot samples generated in the HPFFB and analyzed using HRTEM. Eastern bituminous A and B coals are labeled as EB ‘A’ and EB ‘B’.

<table>
<thead>
<tr>
<th>Coal Type</th>
<th>Date of Run</th>
<th>Date of TEM</th>
<th>HPFFB Pressure (atm)</th>
<th>Adiabatic T (K)</th>
<th>Collection Height Above Burner / Residence Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>EB ‘A’</td>
<td>10/1/2009</td>
<td>8/16/2011</td>
<td>1</td>
<td>1350</td>
<td>1.375” (~35 ms)</td>
</tr>
<tr>
<td>Kentucky #9</td>
<td>6/3/2010</td>
<td>7/14/2011</td>
<td>15</td>
<td>1690</td>
<td>0.75” (~35 ms)</td>
</tr>
<tr>
<td>Kentucky #9</td>
<td>6/29/2010</td>
<td>7/14/2011</td>
<td>15</td>
<td>1690</td>
<td>10” (~400 ms)</td>
</tr>
<tr>
<td>Wyodak</td>
<td>4/5/2010</td>
<td>10/17/2011</td>
<td>15</td>
<td>1690</td>
<td>10” (~400 ms)</td>
</tr>
<tr>
<td>EB ‘A’</td>
<td>1/5/2010</td>
<td>12/14/2011</td>
<td>15</td>
<td>1690</td>
<td>3” (~110 ms)</td>
</tr>
<tr>
<td>EB ‘A’</td>
<td>4/12/2010</td>
<td>11/23/2011</td>
<td>15</td>
<td>1690</td>
<td>10” (~400 ms)</td>
</tr>
<tr>
<td>EB ‘B’</td>
<td>1/27/2010</td>
<td>12/14/2011</td>
<td>15</td>
<td>1690</td>
<td>3” (~110 ms)</td>
</tr>
<tr>
<td>EB ‘B’</td>
<td>5/12/2010</td>
<td>12/9/2011</td>
<td>15</td>
<td>1690</td>
<td>10” (~400 ms)</td>
</tr>
</tbody>
</table>

*Collected from an atmospheric-pressure flat-flame burner reactor (Ma, 1996)

**HRTEM Procedure**

The soot samples were placed on lacey 200 mesh Cu grids and photographed using BYU’s Tecnai 30 TEM microscope. Images were taken at around 750,000x magnification (see Figure 51). Images were then calibrated, adjusted, filtered, and simplified.

![Figure 51. Original HRTEM image of Kentucky #9 soot at a magnification of 716,000x.](image)
Image Processing. The raw image of the soot was preprocessed in Adobe Photoshop before it could be analyzed using the Fringe3D program. First, the contrast was increased to make the fringes more defined (Figure 52 below).

Figure 52. Image after increasing the contrast.

Then, the Fast Fourier Transform (FFT) filter was brought up using Fovea Pro 4.0.1 (a Photoshop plugin), and the texture of the image was evened out by painting over the white points of the FFT (see Figure 53 and Figure 54 below).

Figure 53. Painting the FFT of an image to improve texture. (Images taken from www.skeller.ch/ps/fft_action.php)
Once the image had been contrasted and filtered, the image was converted to binary, where the threshold limit was set manually to reflect the cohesiveness of the fringes (Figure 55).

Next, the image was “skeletonized” so that the fringes of the carbon particles were more clearly represented (Figure 56) using the IP*Morphology skeletonize function of Fovea Pro 4.0.1.
To correctly analyze the image using Fringe3D, unreasonable carbon structures needed to be pruned out of the image manually (Figure 57). These included fringes that had unreasonably sharp angles or complete circles.

Finally, the features resembling structures too small to analyze using Fringe3D were rejected (Figure 58).
The processed image was then analyzed using Fovea Pro 4.0.1 to calibrate the image to the known measurement in the lower left hand corner of the HRTEM image, and then to find the distribution of fringe lengths, fringe interlayer-space, fringe stacking, and fringe orientation.

Fringe3D Analysis. The data gathered from the processed HRTEM image and the corresponding image were analyzed with the Fringe3D program to obtain the geometric centroids, fringe skeleton lengths, fringe moment angles, and fringe interlayer-space distances of each fringe. A relationship between fringe length and aromatic carbon mass developed by Mathews et al. (2010) was used to estimate the minimum and maximum fringe lengths for each suspected aromatic molecule in the image, depending on the geometric orientation of the molecule to the plane of the HRTEM image. Using this relationship and repeating it for all different aromatic structures, the image was automatically reconstructed as the most probable molecule. From this procedure, the soot composition was estimated by taking the ratio of a weight range of aromatic molecules over the total number of aromatic molecules placed on the HRTEM processed image.

Comparison of NMR and TEM/Fringe3D Analyses of Coal Soot

Before applying the TF3D method to all the soot samples generated at pressurized conditions, the quality of the results from this method was first evaluated for a single soot/char sample obtained from pyrolyzing Eastern Bituminous ‘A’ (i.e., EB ‘A’) coal in a flat-flame burner reactor at 1 atm and 1350 K (Table 14). The HRTEM images of coal and soot used in the TF3D technique were taken at BYU. These images were conditioned and processed to show the edges in a clear manner. The transformed HRTEM images were then sent to Professor Jonathan Mathews at Penn State University (where the TF3D method was developed), and the images were analyzed for both structural and lattice parameters using his Fringe3D program.

The results of the TF3D analysis for this soot/char sample were compared with University of Utah $^{13}$C NMR measurements of the same sample. The $^{13}$C NMR results can be found in Shurtz (2011), but are also
Table 15. Comparison of NMR* and TEM/Fringe3D (TF3D) analyses of tar/soot and char samples from eastern bituminous coal ‘A’ pyrolyzed at 1350 K and 1 atm after ~35 ms using a collection height of 1.275” above the burner.

<table>
<thead>
<tr>
<th>Structure Parameters</th>
<th>NMR</th>
<th>TEM/Fringe3D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tar/ Soot</td>
<td>Char</td>
</tr>
<tr>
<td>Aromatic carbon, $f_a = f_a^* + f_a^C$</td>
<td>0.91</td>
<td>0.92</td>
</tr>
<tr>
<td>Carbonyl and Carboxylic acid, $f_a^C$</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Carbonyl, $f_e^O$</td>
<td>0</td>
<td>0.01</td>
</tr>
<tr>
<td>Carboxylic acid, $f_s^{OO}$</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Aromatic carbon, carbonyl subtracted, $f_a^*$</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Protonated aromatic carbon, $f_a^{H}$</td>
<td>0.45</td>
<td>0.3</td>
</tr>
<tr>
<td>Non-protonated aromatic C, $f_a^N = f_a^P + f_a^S + f_a^B$</td>
<td>0.45</td>
<td>0.6</td>
</tr>
<tr>
<td>Aromatic carbon with O attachment, $f_a^P$</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Aromatic carbon with alkyl attachment, $f_a^S$</td>
<td>0.19</td>
<td>0.21</td>
</tr>
<tr>
<td>Aromatic bridgehead and inner carbon, $f_a^B$</td>
<td>0.21</td>
<td>0.34</td>
</tr>
<tr>
<td>Aliphatic carbon, $f_{al}$</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>Aliphatic CH and CH$<em>2$, $f</em>{al}^H$</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>Aliphatic CH$<em>3$ and non-protonated carbon, $f</em>{al}^*$</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Aliphatic with oxygen attachment, $f_{al}^O$</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>Bridgehead Carbons, $x_b$</td>
<td>0.233</td>
<td>0.378</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Lattice Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total carbons per cluster ($C_{cl}$)</td>
<td>11.2</td>
</tr>
<tr>
<td>Total attachments per cluster, $\sigma + l$</td>
<td>3.0</td>
</tr>
<tr>
<td>Bridges and loops per cluster, $B_C$</td>
<td>2.5</td>
</tr>
<tr>
<td>Side chains per cluster</td>
<td>0.5</td>
</tr>
<tr>
<td>Fraction of intact bridges per cluster, $p$</td>
<td>0.83</td>
</tr>
<tr>
<td>Average cluster molecular weight</td>
<td>393</td>
</tr>
<tr>
<td>Side chain molecular weight</td>
<td>32</td>
</tr>
</tbody>
</table>

*Taken from Appendix A (p. 234) of Shurtz’s PhD Dissertation (2011).

In general, the TF3D analysis did not have impressive agreement with the NMR measurements. The aromaticity was 1.0 in the TF3D analysis, but 0.91 and 0.92 in the tar and char, respectively. The TF3D method did not detect the aliphatic material, so the comparison of aromaticity was not a real test. Comparisons of types of aromatic carbon, such as protonated ($f_{al}^{H}$), non-protonated with alkyl attachment ($f_{al}^B$), or bridgehead or inner carbon ($f_{al}^H$) were not satisfactory for either the tar or the char.

The most desired parameter to be able to predict accurately using TF3D analysis is the aromatic carbons per cluster ($C_{cl}$). However, the average number of aromatic carbons per cluster ($C_{cl}$) in the tar/soot was 11.2 by NMR analysis, yet predictions of 11.3 and 13.5 were made by TF3D analysis. The values of $C_{cl}$ in
the char were 18.7 (NMR) and 8.2 (TF3D), which values have drastic disagreement. This discrepancy was especially discouraging, although it may have been caused by the difficulty in getting good edge plane images for char particles in the 50 to 100 μm diameter range.

Subtask 4.6 – Acquisition of Validation Data in an Entrained-Flow Gasifier

This subtask focused on extending the range of conditions for operation and characterization of the University’s 1 ton/day pressurized, oxygen-blown, EFG. For this phase of the project, two new activities were added to improve operability and analysis of system performance. The first activity involved detailed characterization of the slurry injector and associated atomization efficiency. The second aimed to develop a safe, flexible system to measure gas composition at various positions in the gasifier. These activities are described below, followed by discussion of operating experience with the gasifier.

Subtask 4.6a – Injector Design, Characterization and Performance

Injector Design and Atomization Performance

Experience at the University of Utah and elsewhere shows that overall performance of an EFG is very closely tied to performance of the slurry injector. A finely atomized slurry results in better mixing between the fuel and oxygen, a more-well attached, compact flame and overall better conversion. Earlier characterization studies involved imaging of the spray produced by the injector. More recent studies focused on developing techniques to quantify spray behavior, which will allow observed injector behavior to be used for validation of spray simulations.

Design of an injector at this scale is challenging. The only gas available for atomization is the oxygen used for reaction. With a typical airblast atomizer used for e.g. oil combustion in air, the ratio of gas and liquid mass flow rates is roughly 10 to 1. The gas fed to an entrained flow gasifier is almost pure oxygen and roughly half as much oxygen is fed as for combustion, so that the gas/liquid mass flow ratio is roughly 1 to 1. In addition, since the system operates at high pressure the gas is compressed by a factor of roughly 18 in the University’s gasifier. The net result is that there is only about 1/180th as much gas volume available for atomization as compared to a conventional combustion injector.

To achieve good atomization efficiency with such small gas flows, it is necessary to maximize gas velocities and associated gas momentum, which in turn necessitates very small gas exit geometries. Achieving small, fixed, concentric geometries is a challenge, so the design of the injector for the gasifier has undergone several iterations, which have been described in previous reports. Several annular designs (Figure 59, left) were developed and tested, and while those could achieve acceptable atomization it was challenging to maintain concentricity and pressure drop, which has been shown to be important. The latest generation of atomizer uses multiple very small “micro-holes” for oxygen flow (Figure 59, right), which has proven to give more stable flow in the hot reactor.
Figure 59. Components of the coaxial atomizer (left) and face of several micro-hole atomizers (right). The labels on the micro-hole injectors indicate the number of holes as well as the diameter of each hole in thousands of an inch.

Figure 60 shows the spray pattern resulting from water atomization through an 8-hole injector. Much of the stream, mostly towards the center of the liquid channel, appears well atomized into small droplets. Near the periphery of the liquid channel, however, the water clearly runs in ribbons, most likely resulting from the individual gas jets “slicing” the liquid. As the jets expand and cover a larger area near the center of the injector, atomization is better. This demonstrates the balance between achieving high velocity yet covering the cross section of the liquid column.

Figure 60. Digitally adjusted photo of water spray through a micro-hole injector with oxygen flow through eight holes of 0.015 inch diameter. 2.3 lb/hr air flow and 38 gph liquid flow. No inner air channel.

The patternator apparatus was used to evaluate distribution of the sprays resulting from the different micro-hole atomizers under a variety of conditions. In addition to using pure water, slurries of coal and pet coke, with different solids concentrations, were evaluated. Liquid and gas flows were varied over a
range of conditions. Figure 61 shows the resulting spray distribution for an 8-microhole injector using a liquid flow rate and gas velocities typical of gasifier operation. As the solid loading increased, so did the suspension viscosity. Consequently, as the airflow increased from 0.65 kg/hr to 0.93 kg/hr, the spray became better dispersed. This behavior was more pronounced for the higher solids loadings.

<table>
<thead>
<tr>
<th>Water</th>
<th>29% Coal</th>
<th>34% Pet coke</th>
<th>43% Pet coke</th>
<th>53% Coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65 kg/hr</td>
<td>0.65 kg/hr</td>
<td>0.65 kg/hr</td>
<td>0.65 kg/hr</td>
<td>0.65 kg/hr</td>
</tr>
<tr>
<td>0.79 kg/hr</td>
<td>0.79 kg/hr</td>
<td>0.79 kg/hr</td>
<td>0.79 kg/hr</td>
<td>0.79 kg/hr</td>
</tr>
<tr>
<td>0.93 kg/hr</td>
<td>0.93 kg/hr</td>
<td>0.93 kg/hr</td>
<td>0.93 kg/hr</td>
<td>0.93 kg/hr</td>
</tr>
</tbody>
</table>

Figure 61. Patternation of various slurries at 45 liter per hour liquid flow using the 8-MH-0.023 injector. Mass flow rates of air are indicated on each plot.

Atomization can be enhanced by promoting disruption of the liquid column in the center of the injector before it experiences impingement by the high-velocity gas jets exiting the micro-holes. Industrial injectors achieve this by introducing a second gas stream in the center of the liquid column. The central gas forces the liquid into an annulus so that the gas jets break up a film rather than a column.

An 8-hole microhole injector (8-MH-0.025) was modified to function as a 3-stream injector by centering a narrow tube for central gas within the slurry tube. Testing was performed using only water. The effect of the inner tube position was evaluated on two levels, either flush with the face or recessed approximately 0.25 inches. Measured droplet diameter is shown in Figure 62. The x-axis indicates the inner airflow, while the different colors indicate the outer airflow. Clearly, droplet size was less for the case when the inner tube was recessed from the atomizer face. Two factors may contribute to this. First, by recessing the inner gas tube, the annular sheet is given more time to develop instabilities. These instabilities have more time to grow or are provided more amplitude by the fact that the liquid spends more time in the form of an annular sheet. Second, by recessing the inner gas tube, the gas and liquid are given space to mix before leaving the atomizer. This essentially turns the atomizer into an internal mixing atomizer with an outer, external gas annulus. These results are consistent with experience from others that both internal mixing atomizers and three-stream, annular liquid sheet atomizers to be efficient in atomizing a wide variety of liquids (Lefebvre, 1989).
Figure 62. Effect of inner and outer airflow on the average droplet diameter with a level inner tube. The inner air flow is shown along the x-axis while the different colored curves represent the different outer air flows. The left chart shows presents results when the inner tube was flush with the face of the main body of the atomizer. The right chart shows results when the inner tube was recessed approximately 0.25 inches from the face.

Development of Particle Shadow Velocimetry Analysis

During this phase of the project, a new technique was developed for analysis of distribution and droplet behavior in water and slurry sprays. The PSV system described in the Approach Section was employed to study droplets along the centerline and edge of the conical spray resulting from two-stream atomization using a micro-hole injector. Multiple spray locations were imaged for two liquid flow rates, three airflow rates, two solid fuel types, and two solid loadings. Water was also considered for a comparison. Droplet sizes, drop size distributions, drop velocity, and drop displacement direction (trajectory) were obtained.

Figure 63 shows a schematic of the edge region imaged with PSV. As two consecutive images are obtained with a known time step, the droplet displacement from one image to the next can provide both the instantaneous drop velocity and trajectory. For the 12 gph 43 wt.% petcoke slurry case, Figure 64 shows a two-factor histogram where the color corresponds to the fraction of total drops identified falling within a particular diameter and direction bin. The figure illustrates a small increase in drop diameter as airflow is increased from 0.65 kg/hr to 0.79 kg/hr. For this micro-hole atomizer liquid tends to adhere to the bottom face of the atomizer, so the suspicion is that when the airflow is increased the velocity is enough to entrain more of the liquid adhering to that bottom face. The entrained liquid falls off the atomizer edge as drops that cause an increase in the average drop size for the higher airflow case.
Subtask 4.6b – Development of Probe for In-Situ Measurements

During the most comprehensive sampling campaign, nineteen gas-phase samples from were taken from within the reaction chamber of the pilot gasifier. The probe was mounted to the third sample port down (approx. 30% of the distance through the gasifier) and samples were taken at three radial positions (near wall, centerline and midpoint between these two) during operation under three different oxygen/fuel ratios (temperatures) giving nine conditions total. Duplicate samples were taken at most conditions, and one triplicate was acquired. The dry gas phase compositions are shown in Figure 65 for carbon monoxide, hydrogen, and carbon dioxide. At higher temperatures, concentrations of CO and H₂ become less while the CO₂ concentration increases. This is expected, since higher temperatures are achieved by increasing the O₂/fuel ratio, which results in more combustion of the syngas.
While there was a clear influence of oxygen/fuel ratio (temperature) on gas composition, the significance of radial sample location is not as apparent. This can be seen in Figure 66 for carbon monoxide, hydrogen, and carbon dioxide with varying target temperature. The dimensionless diameter coordinate corresponds to the location at which the sample was taken in the gasifier. The value indicates how far the probe has traveled in the reaction zone (e.g. 0 corresponds to the wall location and 0.5 corresponds to the centerline).
The heating value of the intermediate syngas was calculated from concentrations and heating values of the individual combustible components. The heating values for the intermediate (sample port 3) and final product gases differ. Centerline gas composition and gasifier outlet higher heating values (HHV) are shown in Table 16. As expected, syngas heating value decreases with temperature due to more combustion of the syngas. The syngas heating values compare reasonably well for the lower temperatures, but there was more disparity at the higher temperature. The results agree with expectations, since combustion occurs in the flame region of the gasifier, producing CO$_2$ and H$_2$O which subsequently convert the rest of the fuel through the gasification reactions $\text{CO}_2 + \text{C} \rightarrow 2 \text{CO}$ and $\text{H}_2\text{O} + \text{C} \rightarrow \text{H}_2 + \text{CO}$. 
Table 16. Heating values of intermediate and outlet syngas.

<table>
<thead>
<tr>
<th>Target Temperature (°F)</th>
<th>2500</th>
<th>2650</th>
<th>2800</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centerline HHV (Btu/SCF)</td>
<td>196</td>
<td>187</td>
<td>138</td>
</tr>
<tr>
<td>Syngas Out HHV (Btu/SCF)</td>
<td>208</td>
<td>195</td>
<td>179</td>
</tr>
</tbody>
</table>

**Operation of the Entrained Flow Gasifier**

The University of Utah’s entrained flow gasifier was operated during several campaigns, and with many different fuels, over the course of this project. Coals tested included an eastern bituminous (Illinois #6), a PRB (North Antelope), a Utah (Sufco) and an Appalachian coal. Three different petroleum cokes were also tested. The range of conditions tested for each class of fuel is shown in Table 17. Results for select campaigns, encompassing the range of fuels and conditions studied, are presented in Table 18.

Table 17. Range of operating conditions for solid fuel used.

<table>
<thead>
<tr>
<th>Solid Fuel(s)</th>
<th>Temperature (°F)</th>
<th>Pressure (psig)</th>
<th>S.R. (λ)</th>
<th>Solid Fuel Feed Rate (lb/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal (3+)</td>
<td>2250 – 3000</td>
<td>150 – 265</td>
<td>0.23 – 0.75</td>
<td>40 – 70</td>
</tr>
<tr>
<td>Petcoke (3+)</td>
<td>2400 – 2800</td>
<td>150 – 250</td>
<td>0.34 – 0.82</td>
<td>45 – 76</td>
</tr>
</tbody>
</table>

Table 18. Select operating conditions and results for gasifier tests using coal.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Fuel flow (lb/hr dry)</th>
<th>O₂ flow (lb/hr)</th>
<th>Max Temp (°F)</th>
<th>H₂ (vol%)</th>
<th>CO (vol%)</th>
<th>CO₂ (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illinois #6</td>
<td>46.1</td>
<td>42.9</td>
<td>2600</td>
<td>24.9%</td>
<td>30.0%</td>
<td>41.7%</td>
</tr>
<tr>
<td>Appalachian</td>
<td>45.6</td>
<td>53.3</td>
<td>2600</td>
<td>28.9%</td>
<td>33.9%</td>
<td>32.0%</td>
</tr>
<tr>
<td>Appalachian</td>
<td>43.8</td>
<td>52.4</td>
<td>2750</td>
<td>22.3%</td>
<td>28.8%</td>
<td>42.9%</td>
</tr>
<tr>
<td>Utah Sufco</td>
<td>69.0</td>
<td>67.3</td>
<td>2800</td>
<td>28.5%</td>
<td>36.6%</td>
<td>31.1%</td>
</tr>
<tr>
<td>Petcoke #1</td>
<td>50.0</td>
<td>45.5</td>
<td>2400</td>
<td>44.2%</td>
<td>n/a</td>
<td>49.8%</td>
</tr>
<tr>
<td>Petcoke #2</td>
<td>36.1</td>
<td>60.1</td>
<td>2450</td>
<td>32.7%</td>
<td>37.9%</td>
<td>24.4%</td>
</tr>
<tr>
<td>Petcoke #2</td>
<td>52.5</td>
<td>64.2</td>
<td>2600</td>
<td>28.6%</td>
<td>42.7%</td>
<td>25.2%</td>
</tr>
<tr>
<td>Petcoke #2</td>
<td>53.0</td>
<td>75.5</td>
<td>2800</td>
<td>26.2%</td>
<td>43.0%</td>
<td>27.9%</td>
</tr>
</tbody>
</table>

Operating a pressurized, oxygen-blown EFG at any scale is challenging, and performance is largely driven by the effectiveness and stability of the fuel injector. As this project progressed, performance of the reactor became more predictable and stable. The operating procedure, in particular the startup procedure, was refined and the operators became familiar with nuances of the reactor. Additionally, the progression of injector development allowed for more stable and predictable operation from one test to the next. Figure 67 illustrates the stable operation of the gasifier during a test with a petroleum coke over
a period of approximately 3.5 hours. The figure shows stable operation at 250 psig and 2600°F for 4+ hours. The stoichiometric ratio was roughly 0.37, which is about the same as for an industrial gasifier. Aside from the initial 30-40 minutes as the reactor was brought to the target conditions, the temperature and pressure is extremely stable for the duration of the run.

Figure 67. System temperature (maximum measured by thermocouples) and pressure during operation with petroleum coke at 2700 °F and 200 psi.

CONCLUSIONS

The long-term objective of the Task 4 has been to develop simulation tools to support development, troubleshooting and optimization of pressurized entrained-flow coal gasifiers. Significant progress has been made in each of the gasification subtasks, including the overall gasifier models (Subtask 4.1), subgrid-scale submodels for fluid flow (Subtask 4.2), heat transfer (Subtask 4.3), chemical processes (Subtask 4.4), and the development and operation of an accessible, non-proprietary system, which can be operated over a wide range of conditions to provide well-characterized data for model validation.

Entrained-flow gasifier Simulation and modeling. The investigators analyzed experimental data from the CANMET gasifier. Because this data was insufficient to perform a V/UQ analysis, the investigators focused on a cold-flow LES simulation and equilibrium modeling of the gasifier. The cold-flow simulations revealed that the injection region and recirculation region occupies 2/3 of the total furnace volume. The equilibrium model simulations evaluated the effects of important operating parameters, such as carbon conversion, heat loss ratio and coal slurry concentration, on gasifier performance. The results showed that as heat loss increases, temperature drops quickly, CO concentration decreases while H₂ concentration increases. As the coal slurry concentration increases from 53% to 65%, both CO and H₂ concentrations increase by 4%. The comparison between equilibrium prediction and CANMET measured data shows that temperature, CO, CO₂ and H₂ concentration agrees well. This indicates that the gasification of coal is close to equilibrium and the equilibrium assumption is reasonable although the carbon conversion is low.
Subgrid-scale modeling. The combustion of single particles in laminar flames was successfully simulated. Detailed kinetics in the gas phase and the high-fidelity CPD model for devolatilization of coal particles were applied in a one-dimensional framework. Simulation predictions showed that increased initial furnace temperature decreases the ignition delay, which matched experimental observations. Furthermore, studies on the impact of particle size on ignition phase revealed that decreasing the particle size shifts the phase of ignition from homogenous to heterogeneous.

Radiation. The RMCRT model developed during the course of this research allowed for the computation of radiative flux divergences, fluxes to boundary surfaces, interior surfaces, and surfaces with arbitrary view angles and orientations. Good agreement between benchmark solutions and computed solutions was obtained. The capability to model the radiative effects of entrained coal particles was attained. The RMCRT model scaled well in parallel.

Char and soot kinetics and mechanisms. Kinetic parameters for char-steam gasification were regressed for two bituminous coal chars (Illinois #6 and Utah Skyline) using measured data from an entrained-flow reactor at pressures up to 15 atm and gas temperatures up to 1830 K. Utah Skyline char was 1.6 times more reactive to steam than the Illinois #6 char in a pressurized entrained-flow reactor. The steam gasification rate of Illinois #6 coal char was about 6-times faster than its gasification rate by CO$_2$. Good agreement between measured and modeled mass release was obtained for Illinois #6 coal char when using a first-order model and regressed kinetic parameters from the current study with the assumption that H$_2$O and CO$_2$ rates are additive.

NMR analysis of the soot samples from the gasification experiments was not possible due to the conductivity of the highly reacted soot samples obtained. The TEM/Fringe3D method was investigated as a replacement for the NMR analysis, and was evaluated using samples for which the NMR analysis had been performed previously. However, the comparison between the TF3D- and NMR-derived chemical structure parameters and lattice parameters was poor.

Measurements by SAXS and PDF were made on char and soot samples from 4 different coals in an effort to provide size and porosity information. However, obtaining structural information from these measurements was prevented by non-uniform samples in terms of both particle composition and size.

Acquisition of Validation Data in an Entrained-Flow Gasifier. A key determiner of performance in entrained-flow systems is the efficiency of fuel atomization and associated mixing with oxygen. At the comparatively small scale of the Utah gasifier, design and fabrication of a suitable atomization nozzle that can handle a range of flow rates and system pressures was challenging. Introducing oxygen through a narrow annulus in theory resulted in uniform breakup of the slurry stream, but fabricating and maintaining centricity of the annulus is a challenge, and performance can vary from one day to the next. Introducing oxygen through multiple very small holes of diameter 0.015 to 0.025 inches resulted in much more stable operation both over the course of a day’s operation and from day to day. That stability did come at the expense of somewhat less uniform atomization and overall poorer performance.

Part of the usefulness of a gasifier such as that at the University of Utah is for acquisition of data on the environment within the reactor for validation of computational simulation models. The environment in
The gasifier is hot, pressurized and contains poisonous gases so that any form of in-situ sampling needs to be designed with safety as top priority. An automated piston-driven, water-cooled sampling probe and associated sample conditioning system was designed, constructed and tested on the gasifier while processing coal under pressurized conditions. Gas was extracted at three radial positions at an axial location approximately 35% down the length of the reactor. Replicate samples at the same position showed good repeatability of syngas composition measurement. Little variation in composition between the centerline and near-wall region was observed, suggesting that the reactor experiences relatively little internal recirculation.

**LIST OF PEER-REVIEWED PUBLICATIONS**


**REFERENCES**


Appendix

February 2, 2013

Coal Sub-models:

The overall mass balance on coal particle \( m_p \) is divided into three phenomenological categories describing the evolution of moisture \( m_{H_2O} \), volatiles \( m_v \), and char \( m_c \).

**Evaporation**

The moisture content evolution is given by

\[
\frac{dm_{H_2O}}{dt} = - (S_{p,H_2O})^{\text{Evap}} = k_v \left( \frac{P_{H_2O,\text{sat}}}{RT} - \frac{P_{H_2O}}{RT_g} \right) A_p M_{w,H_2O}, \tag{1}
\]

where \( k_v \) is the mass transfer coefficient of steam into air [5, 9], \( P_{H_2O,\text{sat}} \) is the saturation pressure of water at particle temperature, \( P_{H_2O} \) is partial pressure of water in gas. For purposes of energy coupling, the latent heat of vaporization for water is calculated from the Watson relation [6].

**Devolatilization**

*Chemical Percolation Devolatilization (CPD) Model*: CPD is one of the most accurate and complex available model to predict the production rates of the species during the devolatilization.

The number of ODEs required to solve this model is about 32, that make this model expensive to run. The volatile composition produced by CPD changes through the time. In CPD, reactions start with cleaving liable bridge \( l \) to form a highly reactive intermediate

\[
l \xrightarrow{k_l} l^* \tag{2}
\]

which then decomposes to form a char bridge \( c \) and gas \( g \) as well as side-chains

\[
l^* \xrightarrow{k_c} c + 2v_i \tag{3}
\]

\[
l^* \xrightarrow{k_s} 2\delta_i \tag{4}
\]
The side chains ($\delta_k$) decompose to form light gases,

$$\delta_k \xrightarrow{k_{\text{li}}} v_i.$$  \hfill (5)

We can write the balance equations for the above quantities as

$$\frac{d}{dt} = -k_{\text{li}} \quad (CPD - 1)$$

$$\frac{d}{dt} = k_{\text{li}}(k_{\delta} + k_{c})l^* \quad (CPD - 2)$$

$$\frac{d}{dt} = k_{c}l^* \sim \frac{k_{\text{li}}}{\rho^c + 1} \quad (CPD - 3)$$

$$\frac{d}{dt} = \left[ \frac{2\rho_{\delta} k_{\text{li}}}{\rho^c + 1} \right] \left[ \sum_{j=1}^{16} f_{\delta j} - k_{\text{li}} \delta_j \right] \quad (CPD - 4)$$

also for $v_i$ reaction rate is

$$\frac{dv_i}{dt} = (S_{p,v_i})_{CPD} = \left[ \frac{2k_{\text{li}}}{\rho^c + 1} \right] \left[ \sum_{j=1}^{16} f_{\delta j} \right] + k_{\text{li}} \delta_j \quad (6)$$

where $\rho_{\delta} = \frac{k_{\delta}}{k_{c}}$ and $f_{\delta j}$ are functional groups for each species. $k_l$ is reaction constant which is described as

$$k_l = \Lambda_i e^{-\frac{E_b}{R T}} \quad (7)$$

where $E_b$ is the activation energy and can be expressed by

$$F(E) = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{E} e^{-\left[ (1/2)(E-E_0)/\sigma^2 \right]} dE \quad (8)$$

where $F(E)$ is

$$F(E) = \frac{v_i}{v_{i,\text{max}}} = \frac{1}{l_0} \quad (9)$$

where $l_0$ is the initial amount of liable bridge. Also for $k_{v_i}$ same procedure is applied but the only difference is the expression for $\frac{v_i}{v_{i,\text{max}}}$,

$$\frac{v_i}{v_{i,\text{max}}} = \frac{v_i}{2(1 - c_0)\sum f_{\delta j}} \quad (10)$$

Evolution of volatile mass during the devolatilization can be expresses by following equation

$$\frac{dm}{dt} = \left( \sum_{i}^{16} \frac{dv_i}{dt} + \frac{dm_{c,CPD}}{dt} \right) \quad (11)$$

$$\frac{dm_{c,CPD}}{dt} = \frac{dc}{dt} * w_c \quad (12)$$

where $dm_{c,CPD}/dt$ and $w_c$ are the char produced by devolatilization and molecular weight of char respectively.

In Table 1 the reaction rates for each source term are stated.
Table 1: CPD composition

<table>
<thead>
<tr>
<th>Specie</th>
<th>bond</th>
<th>primary functional group source</th>
<th>( A(s^{-1}) )</th>
<th>( E/R(K) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 )</td>
<td>extra loose</td>
<td>carboxyl</td>
<td>( 0.56 \times 10^{15} )</td>
<td>30 000 ± 1500</td>
</tr>
<tr>
<td></td>
<td>loose</td>
<td>carboxyl</td>
<td>( 0.65 \times 10^{17} )</td>
<td>33 850 ± 1500</td>
</tr>
<tr>
<td></td>
<td>tight</td>
<td>carboxyl</td>
<td>( 0.11 \times 10^{16} )</td>
<td>38 315 ± 2000</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>loose</td>
<td>hydroxyl</td>
<td>( 0.22 \times 10^{19} )</td>
<td>32 700 ± 1500</td>
</tr>
<tr>
<td></td>
<td>tight</td>
<td>hydroxyl</td>
<td>( 0.17 \times 10^{14} )</td>
<td>32 700 ± 1500</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>ether loose</td>
<td>ether O</td>
<td>( 0.14 \times 10^{19} )</td>
<td>40 000 ± 6000</td>
</tr>
<tr>
<td></td>
<td>ether tight</td>
<td>ether O</td>
<td>( 0.15 \times 10^{16} )</td>
<td>40 500 ± 1500</td>
</tr>
<tr>
<td></td>
<td>extra tight</td>
<td>ether O</td>
<td>( 0.20 \times 10^{14} )</td>
<td>45 400 ± 1500</td>
</tr>
<tr>
<td>( \text{HCN} )</td>
<td>loose</td>
<td>methyl</td>
<td>( 0.17 \times 10^{14} )</td>
<td>30 000 ± 1500</td>
</tr>
<tr>
<td></td>
<td>tight</td>
<td>methyl</td>
<td>( 0.69 \times 10^{13} )</td>
<td>42 500 ± 4750</td>
</tr>
<tr>
<td>( \text{NH}_3 )</td>
<td></td>
<td>H(al)</td>
<td>( 0.12 \times 10^{13} )</td>
<td>27 300 ± 3000</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_2 )</td>
<td>extra loose</td>
<td>methoxy</td>
<td>( 0.84 \times 10^{15} )</td>
<td>30 000 ± 1500</td>
</tr>
<tr>
<td></td>
<td>loose</td>
<td>methyl</td>
<td>( 0.75 \times 10^{14} )</td>
<td>30 000 ± 2000</td>
</tr>
<tr>
<td></td>
<td>tight</td>
<td>methyl</td>
<td>( 0.34 \times 10^{12} )</td>
<td>30 000 ± 2000</td>
</tr>
<tr>
<td>( \text{H} )</td>
<td></td>
<td>H(ar)</td>
<td>( 0.10 \times 10^{15} )</td>
<td>40 500 ± 6000</td>
</tr>
</tbody>
</table>

The detail of CPD model is discussed in [1].

**Char Oxidation/Gasification**

Char oxidation is a complex phenomenon which depends on many factors such as temperature and oxygen concentration. The rate of consumption of char by oxidation is described by

\[
\left( \frac{dm_c}{dt} \right)^{\text{Oxid}} = \frac{r_cw_c}{\nu_w P_{O_2}}.
\]  

(13)

where \( \nu = 2/(1+\psi) \) designates the stoichiometric ratio of carbon consumption, \( w_c \) is the molecular weight of carbon and \( r_c \) is the the reaction rate of char.

There are several models and equations that explain char oxidation reaction rate, the Langmuir-Hinshelwood is a kinetic expression that frequently used. This approach describes competing adsorption (\( O_2 \)) and desorption (\( CO \)) on char surface that makes it more attractive. There are multiple forms for Langmuir-Hinshelwood, but it was shown by [4] that Eq.(14) has better performance,

\[
r_c = \frac{k_2k_1P_{O_2,s}^{n_r}}{k_1P_{O_2,s}^{n_r} + k_2},
\]  

(14)

where \( k_1 \) and \( k_2 \) are Arrhenius rate constants that their parameters are given in Table. 2, \( n_r = 0.3 \) and \( p_{O_2,b} \) is the partial pressure of oxygen at particle surface [4]
Table 2: Arrhenius parameters for $k_1$ and $k_2$ in Eq.(14) as suggested by [4].

<table>
<thead>
<tr>
<th></th>
<th>$A \text{ (mol} \cdot \text{m}^{-3} \cdot \text{atm}^{-n})$</th>
<th>$E \text{ (kJ/mol)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>93.0</td>
<td>0.1</td>
</tr>
<tr>
<td>$k_2$</td>
<td>26.2</td>
<td>109.9</td>
</tr>
<tr>
<td>$n_r$</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>

\[
\frac{p_{O_2}}{p} = \left( \frac{p_{O_2,inf}}{p} - \gamma \right) \exp \left( -\frac{r_{eq} \Delta p}{2C_{mix}D_{02,mix}} \right) + \gamma,
\]

where \( \gamma = (\psi^{-1}/2 \text{ and } \psi = (X_{CO2}/X_{CO})(1 + X_{CO2}/X_{CO})^{-1} \) represents the mole fraction of carbon becomes CO$_2$. \( X_{CO2} \) and \( X_{CO} \) are produced moles of CO$_2$ and CO by char oxidation. Determining the production molar ratio of CO$_2$/CO$_2$ is investigated by [3] and reported in Arrhenius form. In this work Eq. 16[7] is applied which contributed of oxygen partial pressure into the equation and estimated the ratio as:

\[
\frac{X_{CO2}}{X_{CO}} = A_0 P_{O_2}^{n_p} \exp \left( \frac{B}{T_p} \right),
\]

with \( A_0 = 0.02, B = 3070 K, n_p = 0.2 \).

Calculating char mass at a given time requires to solve equations (13), (14), (15) and (16) simultaneously.

The mass source terms from particle to the gas phase are:

\[
(S_{p,CO})^{Oxid} = -\frac{\text{dm}_c}{\text{dt}} \frac{w_{CO2}}{w_c}, \quad (S_{p,CO})^{Oxid} = -\frac{\text{dm}_c}{\text{dt}} \frac{w_{CO2}}{(X_{CO2}/X_{CO}) w_c}.
\]

The char oxidation and gasification are heterogeneous reactions that consume char. The presence of carbon dioxide and water vapor around the coal particle can increase the likelihood of gasification reactions at high temperatures:

\[
C(s) + CO_2 \rightarrow 2CO \text{ (19)}
\]

\[
C(s) + H_2O \rightarrow CO + H_2 \text{ (20)}
\]

The differential equation that describes char gasification is

\[
\left( \frac{\text{dm}_c}{\text{dt}} \right)_{\text{Gasif}} = -k_i m_c; \quad i \equiv CO_2, H_2O
\]

where $k_i$ is given by, [8]

\[
k_i = A_i p_i^{n_p} \exp \left( -E_i/RT_p \right),
\]

Here $p_i$ represent the partial pressure of CO$_2$ and H$_2$O around the particle for reactions (19) and (20), respectively,
while $A_i, E_i$ are documented in Table 3.

<table>
<thead>
<tr>
<th></th>
<th>$T &lt; 1473$</th>
<th>$T \geq 1473$</th>
<th>$T &lt; 1533$</th>
<th>$T \geq 1533$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$ ($\text{J/kmol}$)</td>
<td>$2.71 \times 10^8$</td>
<td>$1.63 \times 10^8$</td>
<td>$2.52 \times 10^8$</td>
<td>$1.40 \times 10^8$</td>
</tr>
<tr>
<td>$A$ ($\text{kg.s}^{-1}.\text{pa}^{-n_g}$)</td>
<td>$3.34 \times 10^8$</td>
<td>$6.78 \times 10^4$</td>
<td>$2.89 \times 10^8$</td>
<td>$8.55 \times 10^8$</td>
</tr>
<tr>
<td>$n_g$</td>
<td>0.54</td>
<td>0.73</td>
<td>0.64</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Table 3: Arrhenius parameters for the gasification reactions to use in Eq.(22) by [2, 8].

In the gasification process, mass exchange between gas and the particle phase. H$_2$O and CO$_2$ are consumed from the gas phase while CO and H$_2$ are released into the gas phase.

**Source Terms:**

There are numerous interactions between dispersed and gas phase that must be considered in mass and energy conservation equations. To accomplish this, source terms are considered in conservation equations.

Most of the particle mass except ash part are released to the gas phase during the combustion process. Furthermore, char oxidation and gasification requires additional species from the gas phase such as oxygen and carbon monoxide. The mass source term for single particle for species $i$ can be written as:

$$S_{pi} = (\frac{dm_i}{dt})^{\text{Evap}} + (\frac{dm_i}{dt})^{\text{Dev}} + (\frac{dm_i}{dt})^{\text{Oxid}} + (\frac{dm_i}{dt})^{\text{Gasif}},$$

The energy source term for the gas phase energy conservation equation (Eq. ??) is given in Eq.24. The source term includes the heat of char oxidation (exothermic) also CO$_2$ and H$_2$O gasification (endothermic).

$$S_{pco} = \alpha (S_{p,CO}\Delta H_{CO} + S_{p,CO_2}\Delta H_{CO_2})^{\text{Oxid}} + \alpha (\frac{dm_c}{dt})_{H_2O} \Delta H_{H_2O}^{\text{Gasif}} + \alpha (\frac{dm_c}{dt})_{CO_2} \Delta H_{CO_2}^{\text{Gasif}},$$

where $\alpha$ is heat fraction that released to the gas and $1 - \alpha$ is the heat fraction absorbed by the particle [9].
where $C_p$ is particle heat capacity and $\Delta H$ is the enthalpy of reactions.

References


