Gasification Studies

Task 4 Topical Report, Utah Clean Coal Program

Reporting Period Start Date: October 2008
Report Period End Date: July 2011

Principal Authors: Kevin Whitty, Thomas Fletcher, Ronald Pugmire, Philip Smith, James Sutherland, Jeremy Thornock, Isaac Hunsacker, Suhui Li, Kerry Kelly, Naveen Puntai, Charles Reid, and Randy Schurtz

Issue date: October 2011

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 (Subtask 4.4) and physical (Subtask 4.5) 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 (Subtask 4.1). The simulation tool was expanded to handle multiphase flow, and the various submodels required for coal gasification were implemented. Several aspects of the coal gasification model were continually improved, including the numerical behavior of the multiphase model, the direct quadrature method of moments (DQMOM) and the gas-phase combustion model, as well as the parallel scalability of the simulation tool. Validation activities included exploration of several novel statistical concepts applied to constructing surrogate models for expensive functions, all extremely useful in the validation process. Several input variables were investigated, and four were of primary importance, particularly the activation energy of the high-temperature devolatilization reaction ($E_2$).

- The development of a one-dimensional turbulence (ODT) model and associated validation activities; the exploration of principal component analysis (PCA) for use in developing combustion models; and the development of interfaces to enable the use of these models (Subtask 4.2).

- The identification of data for verification of the Reverse Monte Carlo ray tracing (RMCRT) radiation algorithm (Subtask 4.3). This data includes analytical solutions to idealized scenarios as well as pseudo-exact solutions from well-accepted numerical benchmark cases. The RMCRT algorithm has proven to be an accurate way to solve for radiation under gasification conditions. This algorithm has demonstrated convergence with an increase in number of rays traced, and has been implemented into the ARCHES code.

- The use of the Pressurized Flat-Flame Burner (PFFB) to study pyrolysis and CO$_2$ gasification of four coals; the development of a model for coal swelling; and the study of soot formation from a coal tar surrogate with the PFFB (Subtask 4.4).

- The study of the char-slag transition for three different coals, focusing on the morphology of the partly converted material and associated density and internal surface area. The results indicate that at conversions higher than roughly 95%, the material is completely coalesced, resulting in limited accessibility of the remaining carbon (Subtask 4.5).

- The development, operation, and preliminary results from the University of Utah’s pilot-scale entrained-flow coal gasifier.
# TABLE OF CONTENTS

DISCLAIMER .............................................................................................................. 1
ABSTRACT .................................................................................................................. 2
LIST OF FIGURES ...................................................................................................... 6
LIST OF TABLES ......................................................................................................... 9
LIST OF ABBREVIATIONS ....................................................................................... 10
EXECUTIVE SUMMARY .......................................................................................... 11
INTRODUCTION ......................................................................................................... 13
METHODS .................................................................................................................. 13
  Subtask 4.1 – Entrained-Flow Gasifier Simulation and Modeling ...................... 14
    Simulation Tool ...................................................................................................... 14
    Direct Quadrature Method of Moments (DQMOM) .......................................... 15
    Code Improvements .............................................................................................. 17
    Uncertainty Quantification Categorization ......................................................... 17
    Verification (Determination of Numerical Uncertainty) ................................... 18
      Code Verification Procedure ............................................................................ 18
      Solution Verification Procedure ...................................................................... 19
    Validation (Determination of Empirical Uncertainty) ....................................... 20
      Evaluation Criteria .............................................................................................. 21
      Design of Computer Simulations ..................................................................... 22
  Subtask 4.2 – Subgrid Mixing and Reaction Modeling ........................................ 23
    One-Dimensional Turbulence ............................................................................ 23
    Principal Component Analysis (PCA) ................................................................. 25
    Tabular Property Evaluation in ARCHES ......................................................... 26
  Subtask 4.3 – Radiation Modeling ....................................................................... 26
  Subtask 4.4 – Char and Soot Kinetics and Mechanisms ..................................... 28
    Description of the Pressurized Flat-Flame Burner ........................................... 29
    Recent upgrades to the PFFB ............................................................................ 30
    PFFB Gasification and Pyrolysis Conditions ..................................................... 31
    Conditions for Soot Studies ............................................................................... 31
| Subtask 4.1 – Entrained-Flow Gasifier Simulation and Modeling                  | 56  |
| Veriﬁcation (Numerical Uncertainty Quantification) Results                  | 56  |
| Code Veriﬁcation Results                                                   | 56  |
| Solution Veriﬁcation Results                                               | 56  |
| Validation (Empirical Uncertainty Quantification) Results                   | 59  |
| Surrogate Model Results: Screening Study                                    | 59  |
| Surrogate Model Results: Full Factorial Design                              | 64  |
| Subtask 4.2 – Subgrid Mixing and Reaction Modeling                         | 66  |
| One-Dimensional Turbulence                                                  | 66  |
| Principal Component Analysis                                                | 67  |
| Subtask 4.3 – Radiation Modeling                                            | 68  |
| Subtask 4.4 – Char and Soot Kinetics and Mechanisms                         | 71  |
| Tar/Soot and Char Formation and Modeling Studies                            | 71  |
| Pressurized Pyrolysis                                                      | 80  |
| Coal Swelling Model                                                         | 82  |
| PFFB Gasiﬁcation and Kinetic Modeling                                      | 86  |
Subtask 4.5 – Slag Formation and Slag-Wall Interactions................................................................. 92
Identification and Analysis of Char-Slag Transition........................................................................ 92
Workshop on gasifier refractory performance, slag-wall interactions and mechanisms of refractory degradation.................................................................................................................. 106
Subtask 4.6 – Acquisition of Validation Data in an Entrained-Flow Gasifier ................................. 107
Injector Performance ......................................................................................................................... 107
Reactor Operation – High-pressure Testing .................................................................................... 111
System Balance ............................................................................................................................... 112
CONCLUSIONS ................................................................................................................................. 113
LIST OF PEER-REVIEWED PUBLICATIONS ................................................................................. 115
REFERENCES ................................................................................................................................. 115
LIST OF FIGURES

Figure 1. Results for weak and strong scaling for Arches gasification tool for initial code scaling study (black) and improved code scaling (red). .................................................. 17

Figure 2. Left: example of a triplet-map (defining an "eddy") applied to a linear function. Right: instantaneous realizations of ODT simulations of extinction and reignition in a syngas jet flame. ... 24

Figure 3. Convergence of radiation solution given by RMCRT with an increase in number of rays traced per cell. .................................................................................. 28

Figure 4. PFFB interior (left), burner face (top right), and operating burner (bottom right). .................. 30

Figure 5. Velocity profiles at 2.5 atm (left) and 10 atm (right), both at ~1700 K peak temperature .... 33

Figure 6. SEM images of an eastern bituminous char produced at 10 atm, 1722 K, 42 ms. .................. 34

Figure 7. Schematic of cyclone used to separate char from soot, including valve to char trap. ............ 35

Figure 8. SEM image of an eastern bituminous coal produced at 5 atm, 1918 K, 660 ms. ............. 35

Figure 9. SEM images of a separated bituminous char produced at 5 atm, 1702 K, 38 ms. ............. 36

Figure 10. Schematic of the laminar entrained flow reactor, configured for char/ash formation and collection ................................................................. 40

Figure 11. Schematic diagram of the coal feeder .............................................................................. 42

Figure 12. LEFR deposition probe for ash deposition experiments. .................................................. 43

Figure 13. Feeding rate calibration of the coal feeder. ................................................................. 45

Figure 14. Axial temperature profile of the reactor. ...................................................................... 46

Figure 15. Rendering of the full-scale coal slurry feed system. ...................................................... 49

Figure 16. Progressive cavity slurry pump (blue, with the gasifier in the background). .................. 50

Figure 17. Quench recirculation and filter system. ....................................................................... 51

Figure 18. Schematic of the entrained-flow gasification facility .................................................... 52

Figure 19. Rendering of the entrained-flow gasifier and split view of same .................................. 53

Figure 20. Results of the code verification grid convergence study ................................................ 56

Figure 21. Plots of significance test results for time-averaged concentration results for a centerline profile and radial profiles at x=0.10 and x=0.20. ................................................................. 57
Figure 22. Order of convergence analysis using the mean squared error (MSE) test..........................58
Figure 23. Order of convergence analysis using the R-squared test.................................................59
Figure 24. Concentration contours for Brown's experimental data (top) and Arches computations for case screen-1 (bottom) for CO concentration.................................................................60
Figure 25. Concentration contours for Brown's experimental data (top) and Arches computations for case screen-2 (bottom) for CO concentration.................................................................61
Figure 26. Concentration contours for Brown's experimental data (top) and Arches computations for case screen-3 (bottom) for CO concentration.................................................................62
Figure 27. Residuals resulting from comparison of Arches simulation results to Brown data for CO system response..........................................................62
Figure 28. Quantile plot showing the significance of various main and interaction effects. Quantities that lie closer to the center are less significant...............................................................66
Figure 29. Left: DNS calculation showing a rendering of the scalar dissipation rate. .........................67
Figure 30. Weights for the 5 largest components of the first eigenvector (corresponding to the first PC) as a function of filter width, showing that the PCA is insensitive to filtering........................................68
Figure 31. Exact solution vs. that from RMCRT for the x-direction of a non-cubic domain of size 41X31X21..................................................................................................................................................69
Figure 32. Exact Solution vs. that of RMCRT in the y-direction of a non-cubic domain of size 41X31X21. ..................................................................................................................................................70
Figure 33. Exact solution vs. that of RMCRT for the z-direction of a non-cubic domain of size 41X31X21..................................................................................................................................................70
Figure 34. A single pulse spectrum of a highly carbonized char made at 1484 K from the Eastern bituminous coal. Sample was collected at 2” HAB and 1 atmosphere pressure...........................72
Figure 35. C-13 CPMAS NMR spectra of the original Eastern bituminous coal (bottom) and two tar/soots made at 1100 K (middle) and 1300 K (Top) from the coal. .................................................73
Figure 36. C-13 CPMAS spectra of the Eastern bituminous coal (bottom), a matched tar/soot and char pair in the two (middle) spectra and a tar/soot at 1450 K (top) spectrum...............................................75
Figure 37. C-13 CPMAS spectra the Wyodak coal (bottom) and tar/soots made at 1150 K (middle) and 1300 K (top). Samples were collected at 3” HAB at 1 atmosphere pressure.........................................76
Figure 38. C-13 CPMAS spectra of the Wyodak coal (bottom) and 1350 K tar/soot and char pairs (2 and 3 from bottom) and 1450 K tar/soot and char pairs (4 and 5 from bottom)......................................78
Figure 39. Two spectra of a tar/soot made from biphenyl at 1484 K..................................................79
Figure 40. Swelling as a function of pyrolysis pressure for coals in the PFFB. .......................................................... 81

Figure 41. SEM images of Wyodak char produced at ~1700 K. Left: 2.5 atm, 33 ms. Right: 15 atm, 44 ms. .................................................................................................................................................. 82

Figure 42. BYU swelling model with BYU and Sandia data. CBK swelling model shown for comparison. .................................................................................................................................................. 85

Figure 43. Complete atmospheric swelling model with comparison to two coals. .......................................................... 86

Figure 44. Wyodak steam gasification in PFFB at 2.5 atm, ~1700 K with 1st order model ......................... 87

Figure 45. Parity plot for Wyodak CO2 gasification and 1st order model.......................................................... 88

Figure 46. 1st order CO2 gasification model of Eastern Bituminous Coal A in the PFFB................................. 90

Figure 47. 1st order CO2 gasification rate constants. Solid lines indicate PFFB particle temperatures..... 91

Figure 48. Particle densities of the parent coal, pyrolyzed char and gasified char samples. Top: Illinois #6. Middle: Pittsburgh #8. Bottom: Black Thunder PRB. .................................................................................................................. 95

Figure 49. Internal surface area evolution of the char and ash particles prepared from Illinois #6 (top), Pittsburgh #8 (middle) and Black Thunder PRB (bottom). .................................................................................................................. 97

Figure 50. SEM Photographs of Illinois #6 char during conversion to slag at 1400°C......................... 100

Figure 51. Comparison of the morphology of the ash particles (about 97% conversion) prepared under combustion conditions at different temperatures: left, 1200 °C; right, 1400 °C. ..................... 101

Figure 52. SEM Photographs of Pittsburgh #8 char during conversion to slag at 1500°C............. 102

Figure 53. SEM Photographs of Black Thunder PRB char during conversion to slag at 1400°C...... 103

Figure 54. Char–slag transition model fit to experimental data................................................................. 105

Figure 55. The injector on the left has the 65° nozzle. ...................................................................................... 108

Figure 56. Both injectors shown have the 65° nozzle and the same flow rates of water and air......... 109

Figure 57. Both injectors have the 45° nozzle tip installed. ................................................................................. 109

Figure 58: Reactor temperature profiles during operation with the 45° nozzle at specific injector oxygen pressure drops. ........................................................................................................................................ 110

Figure 59. Temperatures (left) and concentrations of major gas species (right) as a function of oxygen/coal ratio........................................................................................................................................ 111

Figure 60. Stepwise pressure increases versus time on 12/15/2010..................................................... 112
**LIST OF TABLES**

Table 1. Model input/uncertainty map: means and their associated prior uncertainties (* = log scale). .......................................................... 20

Table 2. Experimental conditions for different coals ........................................................................................................... 44

Table 3. Proximate and ultimate analyses of the coals used in this work ................................................................. 47

Table 4. Ash chemistry of the coals used in this work ................................................................................................. 47

Table 5. Ash fusion temperatures of the coals used in this work ............................................................... 47

Table 6. Entrained flow gasifier operating ranges (approximate) ........................................................................ 52

Table 7. Screening study used for the first step of sequential assembly of the Arches coal gasification model response surface. ........................................................................................................... 60

Table 8. Main effects for each variable on the three responses of interest, computed from the screening study. .......................................................................................................................... 63

Table 9. Zone I main effects for each variable on the three responses of interest, computed from the screening study.................................................................................................................................. 64

Table 10. Zone II main effects for each variable on the three responses of interest, computed from the screening study.................................................................................................................................. 64

Table 11. Full factorial design for the screening study variables with the 4 largest main effects. .................. 65

Table 12. Main effects for each variable on the three responses of interest, as determined by the factorial design ............................................................................................................................................. 65

Table 13. Two way interaction effects as determined by the full factorial design. The interaction effects are averaged over all spatial points and ranked in order of most to least significant effect. .................. 65

Table 14. Eastern bituminous coal and two tar/soots collected at 3” HAB .......................................................... 73

Table 15. Eastern Bituminous Coal and Pyrolysis Products at HAB 3/8. ............................................................. 74

Table 16. Wyodak coal and tar/soots at HAB 3 ............................................................................................................. 77

Table 17. Wyodak coal and tar/soots and chars HAB 1 1/8”. ................................................................................. 78

Table 18. Mass release, densities, and heating rates for PFFB pyrolysis experiments ........................................ 81

Table 19. Parameters for swelling model .................................................................................................................. 85

Table 20. Char and coal properties relating to the char–slag transition ............................................................... 105

Table 21. Syngas composition (dry, normalized N₂-free) from EFG testing ...................................................... 111
LIST OF ABBREVIATIONS

A$_2$  Ahrenius Pre-exponential Factor of the High-Temperature Devolatilization Reaction of the Kobayashi devolatilization model
CBK  Carbon Burnout Kinetics Code
CPMAS  Cross Polarization with Magic Angle Spinning
Daf  Dry ash free
DNS  Direct Numerical Simulation
DOM  Discrete Ordinates Method
DQMOM  Direct Quadrature Method of Moments
d$_p$  Mass Mean Particle Diameter of the Coal Particles
E$_2$  Activation Energy of the High-Temperature Devolatilization Reaction
E$_{h\cdot CO_2}$  Activation Energy of the Char Oxidation Reaction by CO$_2$
EFG  Entrained Flow Gasifier
FFB  Flat-Flame Burner
GC  Gas Chromatography
HAB  Height Above Burner
LEFR  Laminar Entrained-Flow Reactor
MS  Mass Spectrometry
m$_{coal}$  mass flowrate of coal
NMR  Nuclear Magnetic resonance
ODT  One-Dimensional Turbulence
PFFB  Pressurized Flat-Flame Burner
PCA  Principal Component Analysis
RMCRT  Reverse Monte Carlo ray tracing
RTD  Residence Time Distribution
RTE  Radiative Transport Equation
SEM  Scanning Electron Microscopy
SLPM  Standard Liter per Minute
TC  Thermocouple
T$_{wall}$  Wall Temperature of the Gasifier
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) and physical (Subtask 4.5) 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.

This report details the V&V/UQ work performed on the Arches coal gasification model. The Arches simulation tool, originally designed for single-phase combustion applications, was extended to handle multiphase physics using the direct quadrature method of moments (DQMOM). This was formulated and implemented in the Arches simulation tool, along with several coal gasification models, with continual effort to improve the numerical and physical behavior of the models. Significant improvements of the gasification model were implemented, including improvements to both the physical models and the parallel scaling of the code.

Subtask 4.1 focused on verification and validation of the Arches gasification code. Verification included both code verification and solution verification techniques. An order of convergence with respect to two numerical parameters, grid resolution \( h \) and number of environments \( N \), was obtained. This yielded a numerical uncertainty in code predictions. In order to perform validation on an expensive simulation tool like Arches, a cheap representation of the model was created. Toward this end, the response surface methodology was selected as the approach to building surrogate models for Arches. A sequential assembly of the response surface was performed, in which each set of runs of cases in Arches were performed in phases, and decisions about subsequent phases were made based on the information obtained. This yielded the interesting result that the response surface for three responses of interest, concentrations of carbon monoxide, carbon dioxide, and hydrogen, were linear with respect to the parameters selected. The four parameters that were determined to be the most influential were \( E_2 \), the devolatilization activation energy for the high-temperature devolatilization reaction of the Kobayashi devolatilization model; \( m_{coal} \), mass flowrate of coal; \( d_p \), the mass mean particle diameter of the coal particles; and \( T_{wall} \), the wall temperature of the gasifier. Two parameters that were investigated but were found to be unimportant were \( E_{h-CO_2} \), the activation energy of the char oxidation reaction by \( CO_2 \), and \( A_2 \), the Ahrenius pre-exponential factor of the high temperature devolatilization reaction of the Kobayashi devolatilization model. These response surfaces can be used to better understand the model's behavior, and will feed into the next step of the validation process.

Efforts surrounding Subtask 4.2 have focused on: (1) development and validation of high-fidelity modeling capabilities based on the ODT model; (2) exploration of methods for parameter selection and model reduction strategies; and (3) implementation of an extensible, general methodology for implementing such models into Arches.
Subtask 4.3 focused on the acquisition of benchmark cases for verification of RMCRT and implementing this improved model into ARCHES under simplified conditions. Our RMCRT algorithm has demonstrated the ability to handle the physics involved in gasification conditions including emitting/absorbing media and emitting/reflecting boundaries. With an increase in the number of rays traced per cell, RMCRT demonstrates error convergence as expected. Additional generality has been implemented into the RMCRT algorithm to allow the user to specify non-cubic rectangular cells with any aspect ratio. This feature has also been verified against benchmark cases.

Work on Subtask 4.4 began with an upgrade to the PFFB to safely allow investigation of coal pyrolysis and CO$_2$ gasification kinetics at high initial heating rates. The PFFB was also used to study: the development of soot from a coal and from the coal tar surrogate biphenyl; coal swelling ratios during pyrolysis at total pressures of 2.5-15 atm, gas temperatures of 1700-1900 K, and heating rates of nearly $10^5$ K/s; gasification of four coals in CO$_2$ at total pressures of 2.5-15 atm and gas temperatures of 1700-1900 K.

This subtask also resulted in the development of a submodel to predict coal swelling at atmospheric pressure. Swelling observed in the PFFB was low compared to results from pressurized drop-tube reactors due to the higher heating rate. In addition, first-order kinetic modeling of gasification rates show some agreement with published rate constants, but with lower activation energies for bituminous coals. The reaction rate constants for gasification of Wyodak coal with CO$_2$ were higher than published rate constants for low-rank coals. Steam gasification of Wyodak coal was accomplished at one experimental condition and appears to occur at an unusually high rate. A model has been developed to promote further investigation of trends in gasification rates.

The investigators obtained some structural data from soot/tar and char samples from the FFB and PFFB. Obtaining sufficient sample (approximately 250 mg) for reliable carbon-13 NMR results under a given set of experimental conditions remains a problem. While the limited quantity of pyrolysis products presents severe challenges, sufficient work has been completed that the basic coal, soot, and char structural parameters can be obtained over modest ranges of temperature/residence time, e.g. ~800-1500 K. The collection points (height above burner or HAB) for the Eastern bituminous and Wyodak coals were 3” and 1 3/8”. The Wyodak and Eastern bituminous coals were pyrolyzed at 1 atmosphere while the biphenyl tar surrogate samples were pyrolyzed at 5 and 10 atm.

The results from Subtask 4.5 indicate that carbon conversion and the fate of coal particles in a gasifier depend strongly on physical characteristics of the particle. Porous, low-density char will tend to flow with the gas and offer significant internal surface area for conversion. Flow of dense molten or partly molten slag particles is more likely to be driven by inertia, and carbon conversion will be less effective if access to internal sites is less. Although many studies have focused on carbon conversion in high-temperature gasifiers, essentially all of these have focused on reactivity during the initial conversion stages, up to approximately 80% conversion. Few have considered physical transformation during late-stage conversion, and none have involved experiments at realistic high-temperature gasification conditions.
Under this program, physical transformations of individual pulverized coal particles were investigated using a high-temperature entrained-flow reactor operating under partial oxidation (gasification) conditions. Three coals were tested, and the focus was on transformations at carbon conversions greater than 80%. It was found that when the temperature of the reactor exceeds the ash fusion (melting) temperature, mineral matter within the coal begins to melt and coalesce as its concentration increases as carbon is converted. A sudden “collapse” from char to slag was not observed. Rather, both scanning electron micrographs and density measurements show a gradual shift towards molten slag. Interestingly, the specific internal surface area of the material also displayed a sudden decrease, presumably due to loss of porosity as regions with high mineral content coalesced.

The onset of the char-slag transition was very apparent, as indicated by both a sharp rise in particle density and a sharp decrease in internal surface area. An empirical model for predicting the carbon conversion at which this onset occurs was developed, and requires only the composition of the parent coal. Increasing ash content corresponds to a decrease in the conversion at which the particle begins its transition to slag. For all coals studied, most of the material had become molten slag by about 96% carbon conversion. The consequence of this is that the remaining few percent carbon will have little opportunity to be converted due to the lack of porosity and associated carbon site availability.

Under Subtask 4.6 the University of Utah’s entrained-flow gasifier (EFG) became operational. This small pilot-scale (~500 kWth) pressurized entrained-flow gasifier is located at its off-campus Industrial Combustion and Gasification Research Facility. This system was originally built in 2005 as part of a project on black liquor gasification funded by the U.S. Department of Energy’s Office of Biomass Programs. Due to shifting priorities within that office, however, the gasifier was only about 85% constructed and was never operated on black liquor. Under the University of Utah’s Utah Clean Coal Center (UC3, 2006-2008), remaining components required for operation were installed and modifications were made to allow the system to process coal instead of black liquor. Subsystems were tested under the UC3 program, but the program was of too short duration for full system shakedown and campaigns with oxygen-blown gasification of coal.

**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 CO₂. The leading coal gasification technologies for IGCC are pressurized, high-temperature entrained-flow gasifiers offered by GE, ConocoPhillips, Siemens and Shell. There are currently four industrial-scale entrained-flow coal gasifiers operating in the United States: the GE gasifier at Tampa Electric’s Polk Power Station, the GE gasifier 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. In addition, the world’s largest IGCC system, which will use GE gasifiers, is currently being constructed for Duke Energy in Edwardsport, 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 entrained-flow gasifiers. 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, 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, soot formation, and the char-slag transition.

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 modifying the Utah gasifier for high pressure operation on coal and acquisition of an initial set of data over a range of operating conditions.

**METHODS**

**Subtask 4.1 – Entrained-Flow Gasifier Simulation and Modeling**

**Simulation Tool**

The simulation tool under consideration is the Arches large eddy simulation (LES) code, which has been expanded to simulate coal combustion and gasification using a new particle tracking method. The Arches LES code is written within the Uintah framework, which is a C++ computational framework that allows Arches to scale to thousands of processors. Such computational power is required for the computationally intensive LES method, which resolves large portions of the turbulent energy spectrum. Turbulent scales increase exponentially with Reynolds number, so most computationally cheap turbulence models model all scales of the turbulent flow. In contrast, LES models resolve the largest scales of the flow, computing exact solutions to the governing equations at the resolved scales, and modeling only the small scales. This provides a significant advantage in terms of accuracy of results, as the results can be considered much closer to reality, and much more accurate solutions of the mathematical governing equations.

Combined with a novel particle method, the direct quadrature method of moments (DQMOM), the Arches LES code has been retrofit to handle multiphase (dilute solid and gas phases) physics, as well as coal
combustion and gasification particle and gas models. This involved adding the particle tracking method; particle submodels for devolatilization, char oxidation, heat transfer, and momentum transfer; gas phase models for mass transfer, heat transfer, and momentum transfer to account for two-way coupling between the gas and particles; and a method for handling multiple mixture fractions for performing gas phase equilibrium chemistry computations.

**Direct Quadrature Method of Moments (DQMOM)**

The direct quadrature method of moments is a mathematical formulation for tracking distributions of particles. It is an Eulerian model, and as such tracks the particles from a fixed perspective on a static grid. This is contrasted with the large majority of particle models, which use Lagrangian models that describe (representative) individual particles, integrate them in time, and periodically communicate the location and other information about the particles to the Eulerian grid, and propagate information from the Eulerian grid to the particles. One significant advantage of the Eulerian approach is that it can utilize elements of existing CFD frameworks, such as transport equation and source-term computation methods. For large-scale computations, such as those being done with the Arches LES code, this provides a significant cost savings, both in running and in development, as all efforts to scale the Arches transport equations apply directly to the particle tracking method as well. This is done by representing the number density function using a set of scalars, which can be transported using standard scalar transport equations. The source terms for these transport equations come from the solution to a linear system; this is another operation that is very common in CFD codes and can be easily parallelized.

The DQMOM represents a distribution by using underlying scalar quantities, called moments (defined by equation 1 in Appendix A). Moments characterize statistical characteristics of a distribution; the more moments that are known for a distribution, the better the distribution can be reconstructed with minimal loss of information. However, tracking only the moments is not possible, since the source terms for the moment transport equations are unclosed and always depend on higher-order moments. To provide closure, the DQMOM uses quadrature to approximate the integral used in equation A-1. In this way, the number of moments may be kept finite, and defined in terms of a set of quadrature scalars, called weights and abscissas. The quadrature approximation can be used to redefine approximate moments, a definition given by equation 2. Once these quantities are defined, the quadrature scalars (weights and abscissas) can be tracked in the scalar transport equation framework.

The true distribution of interest is the particle number density function (NDF), which describes the spatial and temporal distribution of particles in particle parameter space (also called internal coordinate space). Each particle is described by a set of particle independent variables, or internal coordinates, and the number density function describes how the particles are distributed in each dimension of internal coordinate space for a given location in space and time. One very common internal coordinate is length; if this is the only internal coordinate, the distribution of particles is commonly referred to as a particle size distribution (PSD). However, PSDs are limited in their ability to describe complex particles such as coal particles. Typically PSDs are used for non-reacting particles, or particles with simple physics. Coal particles, on the other hand, must be described using a large number of internal coordinates. For example, the particle temperature distribution is of direct relevance and importance when determining how much
coal is reacting at a given point in space and time. Likewise, the distribution of fuel-rich vs. burned-out particles is important. Particle velocities are also distributed, and are extremely useful quantities for the sizes and densities associated with pulverized coal particles. Coal particles on the tail ends of the pulverized coal size distribution will have differing behavior: very small particles will behave like dust, following the gas nearly exactly and not contributing any significant amount of momentum to the gas phase. On the other hand, large particles behave ballistically, with trajectories that cross fluid streamlines and pass through small eddies unaffected. This also changes as a function of composition: as particles burn out, they become less ballistic. For these reasons, it is important to know the particle NDF to perform computations of reacting coal systems.

The NDF transport equation is given by equation A-3, and consists of an accumulation term, a convection term, a phase space convection term (split into two parts, one being the particle acceleration, or “convection” in velocity phase space, and the other being particle “convection” in all other phase spaces), and a birth or death term. The birth/death term can be neglected for coal systems. This transport equation is unclosed, however, because it is a continuous distribution. In order to close it, one must rely on scalar quantities such as moments; but these have a closure problem, as mentioned above. For this reason, the NDF transport equation is converted to a quadrature-approximated NDF transport equation, given by equation 4, and the moment transform of this equation is taken. This then results in the quadrature-approximated moment transport equation. This quadrature-approximated moment transport equation results in two pieces of the DQMOM algorithm. The first piece is the transport equations for the scalar quantities (quadrature weights and abscissas) actually being tracked in the CFD code, given by equations A-5 and A-6. The second part is where the source terms for equations 5 and 6 come from: the DQMOM linear system. The construction of this linear systems is complex, with details given in several sources (Marchisio and Fox 2003, Fox 2005).

Initially, the solution to this linear system, which is the source of the transport equation source terms, was the source of many numerical issues. As formulated, the DQMOM method results in linear systems that are extremely ill-conditioned, meaning they are very sensitive to error – even to machine roundoff error, which are quantities as small as 0.0000000000000001. This numerical ill-conditioning was confirmed by several researchers, and prevented the method from being adopted for wider use. The issue hindered the development of coal gasification and combustion models because there are significant coupling effects between the particles and the gas, and numerical contamination of the scalar transport equations representing the particle distribution would immediately lead to numerical contamination of gas phase quantities like density and momentum.

The numerical issues with the DQMOM linear system were finally resolved by Fox describing a linear transform that can be done in phase space (Fox 2009). This transforms skewed and ill-behaved distributions to a new, optimal abscissa space where the distribution becomes a smooth, well-behaved normal distribution. This linear transform makes the solution to the linear system much easier. An additional advantage is that the transformation, which is possible due to the linearity of the quadrature approximation, can be factored out of both sides of the matrix equality \( AX=B \), such that the matrices A, X, and B are all transformed and constructed using the optimal abscissas. As a result, A does not change, and can be inverted once per simulation. This is a significant cost savings, since the non-transformed A matrix
is dense and different for each point in space and time. Additionally, the size of $A$ increases as the product of the number of weights and abscissas (this is also called the number of environments) and the number of internal coordinates, and as a result even moderate numbers of environments and internal coordinates would lead to huge costs incurred on the simulation due to the solution of many large, dense linear systems.

**Code Improvements**

The Arches LES code underwent several code improvements. Effort has gone into improving the table mechanisms in Arches, to make the table mechanism more flexible and able to handle several table formats. This has led to improved handling of gas-phase chemistry and multiple mixture fraction formulations for coal combustion and gasification. Additionally, effort has gone into improving code scalability. This has made a significant impact in decreasing runtimes for gasification simulations, which run for hundreds of thousands of timesteps.

![Scaling for Old (Black) vs. New (Red) Code](image.png)

**Figure 1.** Results for weak and strong scaling for Arches gasification tool for initial code scaling study (black) and improved code scaling (red).

**Uncertainty Quantification Categorization**

Uncertainty is used when the true value, and therefore the error, cannot be calculated or measured. In these cases, the error is estimated, and the uncertainty is the interval that bounds the truth with some level of belief. Uncertainty quantification applied to computer simulations of complex systems begins with a
fundamental division between the numerical and the physical (Marvin 1995). Solution verification is an activity that quantifies the uncertainty bounding the mathematical, or numerical, error; this is referred to as numerical uncertainty. Validation quantifies the uncertainty bounding the empirical error (that is, the difference between the empirical observation and the simulation prediction); this is referred to as empirical uncertainty.

Before performing any validation, it is important to first perform verification. This ensures that the code is of a sufficiently high quality that it can be stated, with confidence, that the code solves the implemented equations correctly. Verification consists of several activities, including software quality assurance, code verification, and solution verification. Only code and solution verification will be covered here.

**Verification (Determination of Numerical Uncertainty)**

Determining the numerical uncertainty is an important first step in uncertainty quantification. The size of the numerical uncertainty may be shrunk, but the cost of doing so is inversely proportional to the resulting size of the numerical uncertainty bounds. The size of the numerical uncertainty bounds help to determine the ultimate level of validation that can be achieved (“level of validation” refers to how well the simulation results match the experimental data, and depends entirely on the intended use and computational resources available; see also Coleman et al. 1997).

The most widely used verification method is grid convergence analysis, wherein numerical parameters (typically grid resolution) are successively refined for a series of simulations. These are then analyzed to determine the order of convergence with respect to the numerical parameter. Verification occurs in two steps: first, code verification, which is done to compare the computed solution to an exact analytic solution. However, this is far from the intended use of the code, so the second step, solution verification, verifies the code with problems in the regime of practical interest. This makes an exact solution impossible, so rather than quantifying numerical error, it is quantifying numerical uncertainty (that is, providing a bounds on the numerical error). For the direct quadrature method of moments (DQMOM) coal gasification model, the convergence behavior of two numerical parameters, the grid resolution \( h \) and number of environments \( N \), was investigated in solution verification.

**Code Verification Procedure**

In order to verify that the mathematical formulation of the governing equations and CFD algorithm were correct, a grid convergence study was performed using a known analytical solution. This solution was generated using the method of manufactured solutions (Roache 1998), in which a field is set equal to a function. This function is plugged into the quantity's governing equation to determine the appropriate source term, and the result is that the difference between the computed solution and the exact solution should become less and less as the grid resolution is increased. This numerical error should converge at the theoretical convergence rate, which is determined by the numerical methods used to solve the governing equations.
While this procedure is extremely useful for identifying bugs, coding mistakes, and order of convergence errors, it is not useful for a practical estimation of numerical error, since it is far from the intended use. Manufactured solutions are almost always non-physical.

Solution Verification Procedure

A grid convergence analysis of the intended-use simulation was performed in order to help quantify numerical uncertainty in the Arches gasification model. In order to perform a grid convergence analysis for the DQMOM model with respect to two numerical parameters, a multi-variable Richardson Extrapolation Estimation (REE) technique must first be described.

The goal of the grid convergence analysis is to find a functional form for the numerical error (equation A-13). The error is assumed to be a function of two variables, the grid resolution \( h \) and the number of DQMOM environments \( N \). The form of the error function is assumed to be the form given by equation A-14. In order to confirm that this is the case, the simulation tool is run at multiple combinations of these parameters \( h \) and \( N \). The simulation with the highest spatial resolution \( h \) and the largest number of moments \( N \) is designated as a surrogate “exact solution,” and is used as the standard for comparison. The error function is then added to this high-resolution solution.

The simulation tool was run at a predetermined set of numerical parameters that were selected using an experimental design. The intention was to explore the importance of the interaction effect between \( h \) and \( N \). If the interaction effect is insignificant, the grid convergence procedure proceeds like a normal grid convergence procedure, with the numerical term of interest being isolated, the log of both sides of equation A-16 being taken, and the order of convergence with respect to \( h \) (the parameter \( p \)) and with respect to \( N \) (the parameter \( q \)) determined in this way.

However, if the interaction effects are important, the procedure becomes more complicated. The log cannot be taken, because logs do not distribute to sums. As a result, techniques given by Logan and Nitta (2005) must be used to determine the orders \( p \) and \( q \). One technique is to assume various values of \( p \) and \( q \), and fit the resulting model to the simulation results. The R-squared value, a measure of goodness of fit of a model to data, is used to determine whether this matches the observations. If so, the order of \( p \) and \( q \) have been determined. Otherwise, new values of \( p \) and \( q \) are selected, the data regressed onto them, and the goodness of fit assessed. This continues until the \( p \) and \( q \) leading to a minimum R-squared value are found.

Alternatively, Logan and Nitta propose a similar procedure that, instead of minimizing R-squared, minimizes the quantity given by equation A-18. The quantity underneath the radical is the mean square error of the presumed model, and this quantity, rather than the R-squared value, is minimized using this alternative procedure.

The details of the experimental design are discussed in further detail below (Section, “Design of Computer Experiments”).

Results of the grid convergence analysis are presented in the Results section.
Validation (Determination of Empirical Uncertainty)

In order to perform model validation, a validation framework is adopted from Bayarri et al. (2002). This is hereafter referred to as the NISS Validation Framework. This framework provides a comprehensive way of thinking about each aspect of validation and helps to reconcile several different approaches to validation presented in the literature.

The framework consists of six steps. First, an input/uncertainty map is constructed. This consists of a list of all potentially active variables, whose uncertainties are then estimated and whose anticipated importance is ranked. The second step is to evaluate the decision criteria for validation; this consists of picking which system responses and what experimental data is to be used for validation. The third step is data collection and design of experiments, which in the case of the Arches simulation model, involves designing and running sets of cases. The results are then analyzed statistically, and significant effects are identified. The output of the expensive function (Arches) is then approximated using a surrogate model, typically a polynomial response surface. Finally, this surrogate model is used as part of an analysis of model results.

Input/Uncertainty Map

For coal gasification, the process of constructing and selecting the input/uncertainty map was done with input from individuals with a wide range of backgrounds. Several modelers experienced with turbulent combustion (specifically coal combustion) systems, as well as experienced experimentalists working primarily with gasification systems, were brought to the table and consulted regarding which model parameters were expected to be the most active. Sensitivity analysis of the coal gasifier being modeled were also consulted (Smith 1990), as well as relevant experimental analysis (Soelberg et al 1984, Brown et al 1985, Nichols et al 1987, Nichols et al 1989). The final input/uncertainty map is presented in Table 1.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Mean Value</th>
<th>Uncertainty</th>
<th>Uncertainty Range</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_2$</td>
<td>$2.0 \times 10^8$ J kmol$^{-1}$</td>
<td>50%</td>
<td>$1.0 \times 10^8 \leq E_2 \leq 3.0 \times 10^8$</td>
<td>(Kobayashi 1977, Ubhayakar 1977)</td>
</tr>
<tr>
<td>$A_2$*</td>
<td>$1.0 \times 10^{11}$ s$^{-1}$</td>
<td>27%</td>
<td>$1.0 \times 10^8 \leq A_2 \leq 1.0 \times 10^{14}$</td>
<td>(Kobayashi 1977, Ubhayakar 1977)</td>
</tr>
<tr>
<td>$\overline{d}_p$</td>
<td>37µm</td>
<td>10%</td>
<td>$33.3\mu m \leq \overline{d}_p \leq 40.7\mu m$</td>
<td>Soelberg 1985, Brown et al 1985)</td>
</tr>
<tr>
<td>$T_{wall}$</td>
<td>1200K</td>
<td>16%</td>
<td>$1000K \leq T_{wall} \leq 1400K$</td>
<td>(Soelberg 1985, Smoot Brown 1987)</td>
</tr>
<tr>
<td>$\dot{m}_{coal}$</td>
<td>22.1 kg/hr</td>
<td>10%</td>
<td>$19.9$ kg/hr $\leq \dot{m}_{coal} \leq 24.3$ kg/hr</td>
<td>Soelberg 1986, Sowa thesis)</td>
</tr>
<tr>
<td>$E_{char-CO_2}$</td>
<td>$9.3 \times 10^7$</td>
<td>60%</td>
<td>$3.7 \times 10^7 \leq E_{char-CO_2} \leq 1.5 \times 10^8$</td>
<td>(Baxter 1987, Field 1967, Goetz 1982)</td>
</tr>
</tbody>
</table>
Evaluation Criteria

Determining the evaluation criteria was straightforward for the data available for the gasification system of interest. The case being modeled was a case run by Brown, reviewed by Rasband (1988). This case is oxygen-fired gasification. The experimental data consists of 90 total data points, each time-averaged concentration measurements. The concentration measurements were made at 5 radial locations and 6 axial locations, for a total of 30 spatial locations, and at each measurement, 3 species were measured: CO, CO$_2$, and H$_2$.

Analysis of Uncertainty in BYU Data

The BYU gasifier data used to validate the Arches gasification model come from Brown (Brown 1985, Brown et al 1985, Rasband 1988). The data were originally gathered to investigate the effect of coal type on gasification. As mentioned in the previous section, the data consist of time-averaged radial profiles of three species at 6 axial locations: 0.21 m, 0.36 m, 0.51 m, 0.67 m, 0.81 m, and 1.21 m. A separate study, with different operating conditions, reported carbon conversions and effluent concentrations of CO and H$_2$, but no radial concentration profiles were reported.

Sowa (1987) discusses sources of experimental uncertainty in the BYU gasifier. Sowa performed several experimental measurements: first, he performed experimental verification experiments in order to quantify instrument error and identify systematic (bias) error, and he reported the standard deviations. These measurements included species mole fractions, carbon conversion, feed mass flowrates, and solids composition measurements. Sowa also performed computations and used a Monte Carlo error propagation technique to estimate the propagation of input uncertainty and its effect on the system responses. Sowa also investigated the amount of uncertainty in the actual gasification experiments by repeating measurements over the course of the same and different experiments. He reports the pairwise differences for carbon conversion and CO concentration for a subset of these measurements.

Sowa was primarily investigating the effect of the injector, and the pairwise differences exhibit a sensitivity to the injector design (Brown did not report injector type for any experimental measurements). However, there were additional factors that were known sources of uncertainty for these pairwise differences, including the carbon conversion measurement location (near-wall vs. near-centerline), sample volume (too large a sample size would be sampling gas with sharp gradients that was not yet well-mixed), difficulty with measuring and adjusting coal feed rate, difficulty with reproducing coal feed rate conditions for different experiments, and difficulty diagnosing sampling bias, which were also impossible to rectify. However, Sowa did not specify which of these sources of uncertainty corresponded to which specific measurements.

After analyzing the pairwise differences from the experimental repeats, Sowa created an uncertainty budget, comparing them with the measurement uncertainties and the computational estimates of input uncertainty propagation. The measurement uncertainties and propagated input uncertainties were expected to balance experimental error, but Sowa found they did not. Sowa concluded there were remaining sources of uncertainty for which he had not accounted. Sowa listed several experimental
uncertainties beyond the control of the experimenters, but several were already accounted for above. These included lack of control over the coal feed rate, lack of knowledge of the effect of probe disturbances on the flow field, problems correcting for gas sampling bias, and non-steady state conditions in the reactor. The first uncertainty listed was addressed by Brown (Brown et al 1985), who stated that one type of coal had inconsistent moisture content due to being pulverized far in advance of the experiments.

Sowa also performed an interesting comparison for various instrument models - that is, the model converting the experimentally observed quantity measured by the instrument into something more physically useful (in this case, carbon conversion). Significant differences were observed in all but one model comparison, meaning that all but two models disagreed with each other. In addition to the instrument models, Brown et al. (1985) showed that there was a 7% sensitivity to a feed rate range of 20.8 – 27.3 kg/hr.

**Design of Computer Simulations**

The combinations of input parameters, presented in the input/uncertainty map, at which to run Arches was determined using design of experiment techniques. These are intended to provide maximum information with a minimal number of runs using statistical techniques. Because the cost of determining a full 6-parameter polynomial model with high-order interaction effects is prohibitively expensive and would require more than 50 simulations to be run, a different approach was adopted.

The process of running simulations (step 3 in the NISS validation framework) and the construction of the response surface surrogate model (step 4 in the NISS framework) were performed iteratively. This process is referred to as sequential assembly of response surfaces (Box Draper 1987). In order to maximize the number of parameters investigated, the first step in assembling a response surface is to run a screening study with a large number of parameters. Screening studies, such as highly fractionated factorial and Plackett-Burman designs, are intended to identify variables with the most important main effects with a minimal number of runs. This does, of course, limit the amount of information that can be obtained. For example, variable interaction effects are aliased with main effects, so that if the main effect of a parameter A and the interaction effect of two other parameters B and C are aliased, the only information the simulation results will reveal is whether the sum of these effects is significant – it does not reveal information about which of the two are important. A screening study for 6 parameters requires 8 total simulations.

Once the important main effects are determined, the list of parameters is reduced to those of primary importance. A full factorial design is then performed for the reduced set of parameters, greatly reducing the cost and re-using the information from the screening study. A reduction in the number of variables from 6 to 4 is desired, as a full factorial design for 4 parameters requires 16 runs. This means that an additional 8 runs will provide full information about linear variable interaction effects of up to four variables.
Once the full factorial was performed, the Arches simulation results were regressed to a polynomial response surface and the goodness of fit of the response surface was analyzed. This provided a convenient branching point, at which either (a) the validation could move forward if the surrogate model is deemed “good enough,” and this surrogate model could be used in the results analysis, or (b) further Arches simulations could be run to supplement the response surface and determine coefficients for higher order terms.

Results are presented below for the ongoing process of response surface design. The statistical analysis of the screening design results, as well as the analysis of the factorial design, have yielded very useful information. However, further simulations are being run to investigate construction of better response surfaces.

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

Multi-scale simulations in coal combustion, in gasification and in oil shale/sands processing require hierarchical models to address the nonlinear coupling across the multitude of length and time scales, many of which remain unresolved. It is widely recognized that low-dimensional attractive manifolds exist within these multi-scale systems. The effect of such manifolds is to produce correlations in state variables (e.g. temperature and composition). Direct Numerical Simulation (DNS) remains the most detailed method to analyze turbulence-chemistry interactions, and hence the manifestation of manifolds in the thermochemical state. However, due to the high cost of DNS simulations, such data is limited to small problems that may not be entirely representative of practical applications. The One-Dimensional Turbulence (ODT) model is a low-cost alternative where the full range of length and time scales are resolved (as in DNS) but only in a single spatial dimension. The effects of turbulent motion along this one-dimensional “line of sight” are modeled as stochastic rearrangement events that mimic the effects of the three-dimensional turbulent cascade. Because of this, the ODT model can be used as a relatively inexpensive way of obtaining DNS-like statistics.

In general, the thermochemical state of a single-phase reacting system with \( n_s \) chemical species is uniquely determined by \( n_s + 1 \) parameters (e.g. \( T, p \), and \( n_s - 1 \) mass fractions, \( Y_i \)). However, it is widely recognized that in turbulent combustion, lower dimensional manifolds exist in this \( (n_s + 1) \)-dimensional space (Maas and Pope 1992). All of the models which reduce the number of thermochemical degrees of freedom rely, either directly or indirectly, on the existence of a low-dimensional attractive manifold to which the state quickly relaxes. Identification of the controlling parameters for such a low-dimensional manifold is a key question. We have evaluated Principal Component Analysis (PCA) as a means to identify correlations among state variables in reacting flow systems. PCA provides a rigorous and systematic methodology to construct reduced models from large data sets (e.g. DNS data).

**One-Dimensional Turbulence**

The One-Dimensional Turbulence (ODT) model originally proposed by Kerstein (1999) resolves the full range of length and time scales in the flow (analogous to direct numerical simulation), but in one spatial
dimension. In ODT, turbulent mixing is represented by instantaneous, stochastic rearrangement events that are driven by velocity gradients. These “eddy events” cause a rearrangement of the fields in a way that mimics the action of a three-dimensional eddy (see Figure 2).

![Figure 2](image-url)

Figure 2. Left: example of a triplet-map (defining an "eddy") applied to a linear function. Right: instantaneous realizations of ODT simulations of extinction and reignition in a syngas jet flame (Punati et al. 2009, 2011).

The triplet map that defines an eddy has many desirable properties to ensure conservation, preserve scale locality, etc. (Kerstein 1999, Kerstein et al. 2001). Many realizations are combined to obtain statistical information of the flow. Figure 2 shows instantaneous temperature profiles at three different times from a single ODT realization of a reacting syngas-air jet flame.

Despite its one-dimensional nature, ODT has been shown to be highly effective at reproducing statistics from three dimensional flows and has been successfully applied to a wide variety of applications including homogenous turbulence, wall-bounded flows, free shear flows, buoyant-driven flows (Kerstein 1999; Kerstein et al. 2001), particle-laden flows (with and without reaction) (Schmidt 2004; Schmidt et al. 2009; Wu 2009) and turbulent combustion (Echekki et al., 2001; Hewson and Kerstein 2001, 2002; Ricks et al. 2009; Punati et al. 2009, 2011). In ODT, eddy events are driven by the local energetics of the flow field, and the ODT model can accurately reproduce critical features of the flow field such as the $-5/3$ energy cascade (Kerstein 1999).

We have developed a new formulation of the ODT model that uses an Eulerian frame of reference rather than a Lagrangian frame where the model was originally formulated. The details of this formulation are not presented here due to space limitations, and the interested reader is directed to (Punati and Sutherland 2009; Sutherland et al. 2010) for more detailed information. This new formulation facilitates direct comparison with DNS data since both the ODT and DNS use the same mesh resolution and solved the same equations.
Principal Component Analysis (PCA)

Here we present a brief overview of PCA. More details can be found elsewhere Sutherland and Parente (2007); Parente et al. (2007); Parente (2008); Parente et al. (2009b); Sutherland and Parente (2009); Parente et al. (2011). Consider $m$ observations of $n$ variables arranged in an $n \times m$ matrix $X$ whose columns represent individual observations and rows correspond to different variables. PCA determines a basis for the data $X$ such that the data are well-represented by a truncated basis Jackson (1991); Jolliffe (2002). The covariance matrix is defined by $R = \frac{1}{n-1}X^TX$ and the eigenvector decomposition of $R$ may be obtained as $\Lambda = Q^{-1}RQ$ where $Q$ are the orthonormal eigenvectors of $R$, with $Q^{-1} = Q^T$. The eigenvectors (columns of $Q$) form a new basis, and the principal components (PCs) of the data in $X$ are defined as $\eta = QX$. The full set of PCs exactly reproduces all observations in the original data, by definition.

The real utility in PCA comes by exploiting the fact that PCA maximizes the variance of the data in each PC direction. The rotated coordinate system has the property that the first dimension (corresponding to the largest eigenvalue) is selected to best represent the variance in the data. Subsequent directions each represent the next-largest variance in the data. Therefore, a truncated basis, i.e. a subset of the columns in $Q$, can approximate the original data remarkably well. We define a transformation matrix $A$ as a rank-deficient subset of the $Q$ matrix with $n$ rows and $n_s$ columns. The columns of $A$ correspond to the columns of $Q$ with the $n_\eta$ largest eigenvalues. We may then approximate $X$ as $X = \eta A^T$. This approximation by a reduced set of variables $\eta$ is precisely what the modeling approaches discussed earlier are trying to accomplish.

In the context of combustion applications, the $n$ variables comprising the rows of $X$ are the $n_s + 1$ variables $[T, p, Y_1, Y_2, \ldots, Y_{n-1}]$. Performing a PCA on this set of variables yields a new $(n_s + 1)$-dimensional basis, $\eta$, which is a rotation of the original basis. Retaining $n_\eta < (n_s + 1)$ columns of $Q$ with the largest eigenvalues defines a basis for a $n_\eta$-dimensional parameterization of the thermochemical state of the system.

Once a PCA has been defined, transport equations for the PCs may be derived by applying the PCA transformation to the original governing equations as described in Sutherland and Parente (2007, 2009). Initial and boundary conditions may be likewise transformed to be expressed in terms of the PCs. However, for such an approach to succeed, the truncated basis (where $n_\eta < n_s + 1$) must not only

$^1$Here we have assumed that the data is centered (its mean is zero) and scaled by constant factors $\gamma_i$. These are common procedures that can strongly influence the results of the PCA. For results here, we chose vast scaling (see Jolliffe (2002)).
parameterize the thermochemical state (which has been successfully demonstrated) but the source terms as well. This remains an area where further research is required.

In summary, for a PCA to be used as a combustion modeling approach, a canonical system (e.g. opposed jet flame, ODT, LBMS, DNS) is chosen to produce data, $\phi$, to be used as a surrogate for the true system of interest. This system is solved over the relevant range of its natural parameters to obtain a large set of data. This data is then gathered in its entirety to define $\mathbf{X}$ and PCA is applied to $\mathbf{X}$ to determine the PCs, which are the parameterizing variables. A truncated set of PCs, $\eta$, is then defined (with $n_\eta \ll n_x$), along with the mapping between $\phi$ and $\eta$, and $\eta$ is then transported in the CFD application.

**Tabular Property Evaluation in ARCHES**

Many of the models employed in LES and RANS calculations are pre-computed and tabulated. There are a wide range of such models, but all have the characteristic that they estimate variables $\phi = \{T, y, \mu, \ldots\}$ as functions of some set of variables $\eta$, $\phi = \mathcal{F}(\eta)$. Typically, $\mathcal{F}(\eta)$ is obtained at discrete points through solution of algebraic or differential equations, and an interpolant is required. We have developed a methodology to facilitate interpolation of structured data in up to five independent variables using basis functions of arbitrary order. This approach employs B-Splines for the basis functions, thereby allowing arbitrary smoothness of the interpolants. Named TabProps, this software supports the following models natively:

- Thermochemical equilibrium with and without heat loss,
- Infinitely fast chemistry with and without heat loss,
- Nonreacting mixing of two streams.

Other models may be easily implemented by providing an interface to the main TabProps library. There are two such models currently supported through this approach. In addition, convolution of a single independent variable over a presumed-shape PDF function is supported, with $\delta$-PDF and clipped-Gaussian PDF functions provided.

This code is available for anonymous public access through a Git repository (Sutherland 2010b). Online documentation is available in the form of a wiki (Sutherland 2010a) as well as doxygen documentation of the code itself (Sutherland 2010c).

**Subtask 4.3 – Radiation Modeling**

The existing radiation solver used in the Arches algorithm is the Discrete Ordinates Method (DOM). This method is expensive and consumes over 50% of computation time during a typical simulation. Furthermore, adding the physics necessary to represent gasification conditions such as scattering is prohibitively difficult to implement. We believe RMCRT has the ability to accurately and efficiently handle these physics. Under this task, we have written and verified a RMCRT algorithm that
demonstrates both scalability and error convergence. Because the RMCRT scheme lends itself to easy parallelizability, it is competitive, or potentially cheaper than DOM for solving the radiative transport equation (RTE) in addition to offering additional complicated physics for coal combustion in a straightforward manner.

Research into the Reverse Monte Carlo Ray Tracing (RMCRT) included effective random number generation, efficient sampling schemes, and ray-tracing techniques along with studying the important radiation models such as the concepts of reflectance, absorptivity, and transmissivity. These models are important in solving the RTE under entrained flow gasification conditions.

Background work included analyzing previous models created by a former PhD student, Xioxing Sun, who worked on laying the foundation for RMCRT calculations to solve the RTE. This work included understanding her models and the output of her codes, many of which have been verified against benchmark cases.

We have met with ray tracing expert Steven Parker, who has consented to join our student’s supervisory committee and assist in formulating an efficient RMCRT model.

We have written, compiled, and verified a code that uses Monte Carlo ray tracing to solve the RTE within a 3D enclosure. The code has been written in an object-oriented manner, and is amenable to the addition of other physics including scattering.

The RMCRT code requires tracing of a large set of rays (500-1500) emitted per cell within the ARCHES computational domain. The basic algorithm randomly picks a starting point of a ray within a cell, and traces that ray through the domain until some criterion is met (e.g., the ray arrives at a physical boundary). The current algorithm is using state-of-the-art methods for generating random numbers and tracing the rays. Care was taken to avoid unnecessary statements and computations to obtain an efficient code.

Verification testing using benchmark 1 (discussed in the Results Section) was performed, and the RMCRT algorithm gives accurate results to within 1% of benchmark values. The L2 error norm decreases as expected with an increase in number of rays traced per cell. An L2 error represents the square root of the square of the difference between the exact solution at a point and the computed solution at the same location. The L2 error norm is the average of the ensemble of these L2 errors from all data points. This trend continues above 1,000 rays per cell, such that 1024 rays per cell, the L2 error norm is less than 0.5%, as demonstrated in Figure 3.
Figure 3. Convergence of radiation solution given by RMCRT with an increase in number of rays traced per cell.

It is often beneficial to not be restricted to domains that contain only cubic cells. Recently, we have implemented generality into the RMCRT code to allow for rectangular prismatic cells of any aspect ratio. This generality will give the user more flexibility in the refinement ratios of the domain. The algorithm that includes this non-cubic generality has been verified against benchmark 1 (see Results Section).

Subtask 4.4 – Char and Soot Kinetics and Mechanisms

Char gasification reactivity is known to vary with coal rank, temperature, heating rate, and pyrolysis pressure. There have been many studies of chars prepared at low heating rates and atmospheric pressure. However, the particle size and physical structure developed during pyrolysis significantly influences observed reaction rates through mass-transfer effects. Heat transfer by convection and radiation are also influenced by particle size. The preparation conditions also influence the reactivity of the char through the development of its chemical structure. Therefore, gasification kinetics suitable for modeling pulverized coal gasifiers should be studied through experiments conducted at high heating rates and pressures that are representative of industrial conditions. The BYU PFFB has been developed for this purpose, with particle heating rates of \( \sim 10^5 \) K/s, gas temperatures of up to 2000 K, and pressures of up to 15 atm.

The parameter that is most commonly used in combustion modeling to describe the change in coal structure during pyrolysis is the swelling ratio \( d/d_0 \). There are also detailed systems that have been developed for the classification of char based on morphological characteristics (Yu et al., 2007). These structural characteristics of char are of great interest, but the swelling ratio is the parameter most commonly used to describe char structure in combustion modeling because of its simplicity and because particle size is thought to influence the heterogeneous reaction rates more strongly than the pore structure.

Maximum swelling occurs for high-rank bituminous coals at heating rates slightly below \( 10^4 \) K/s and at pressures of 8-15 atm (Lee et al., 1991; Zygourakis, 1993; Solomon and Fletcher, 1994; Gale et al., 1995;
Consequently, swelling ratios measured in many laboratory experiments may not be very representative of industrial conditions, which for a pulverized coal gasifier are $\sim 10^6$ K/s at pressures of 20-30 atm, with pressures of 60-80 atm being contemplated for new designs (Liu and Niksa, 2004). The ability to make reasonable estimates of the swelling ratio at industrial conditions and to relate the predictions to laboratory measurements is of great practical interest in combustion and gasification modeling.

Soot is known to influence gasifier operation through radiation heat transfer. In heat transfer calculations, soot may lower predicted gas temperatures by 200-300 K (Brown and Fletcher, 1998). Lowering the gas temperature greatly reduces gasification rates. Soot is known to originate mainly from coal tar, but the mechanisms governing the transformation of tar to soot are not well understood. Soot gasification rates may limit carbon burnout in some cases, and it is likely that soot reactivity varies with coal type and preparation conditions. The ability to predict the location and characteristics of soot as it develops and gasifies is important for the development of advanced gasification models.

**Description of the Pressurized Flat-Flame Burner**

The BYU pressurized flat-flame burner (PFFB) was redesigned and rebuilt over the last 3 years to conduct pyrolysis and gasification studies on coal at pressures of up to 15 atm and heating rates of $\sim 10^5$ K/s. Flat-flame burners consist of an array of tubes that deliver a gaseous fuel to a surface (Figure 4). An oxidizer-rich gas is fed through the spaces in between the tubes. The resulting flat flame is $\sim 1$ mm thick. A tube at the center of the array contains coal entrained in a stream of N$_2$ at solid feed rates of $\sim 1$ gram/hr to ensure single-particle behavior. The coal particles are heated convectively by the post-combustion gases, achieving heating rates 2-10 times higher than an electrically heated drop-tube reactor. Increasing the heating rate in this regime has been observed to decrease coal swelling at atmospheric pressure. The flame stoichiometry can be altered to produce an oxidizing or gasifying environment. The PFFB also has supplemental heaters to maintain high gas temperatures for longer residence times.

At the end of the quartz reaction tube is a water-cooled collection probe that quenches the hot gases and particles with jets of N$_2$ (Figure 4). The probe can be moved up and down to adjust residence time. Soot is separated from char in a virtual impactor and a cyclone. Tar and soot are collected on polycarbonate filters. Tar/soot yields are determined by weighing the filters, and the tar/soot samples are recovered by scraping the filters. High static on the filters often prevents accurate weights from being measured. In these cases, the tar/soot is scraped from the filter and then weighed afterward. Char and soot can be analyzed separately. The change in particle mass is determined by tracer techniques for regression of gasification kinetic parameters. The change in particle size is calculated from the measured changes in mass and bulk density, with the assumption that the particle shape does not change enough to alter the packing factor.
Figure 4. PFFB interior (left), burner face (top right), and operating burner (bottom right).

Recent Upgrades to the PFFB

Previous attempts to conduct steam gasification studies in the PFFB met with limited success. CH₄ fuel makes soot at elevated pressures unless it is diluted with copious amounts of H₂. With 85% H₂ in the fuel mixture, the high flame speed caused the burner surface become very hot, causing two undesired effects. First, high-temperature corrosion degraded the surface of the burner. Second, preheating of the coal feeder tube occurred. This caused premature pyrolysis and clogging, particularly for bituminous coals. Safety upgrades were implemented in the lab to allow the use of CO as a fuel. Switching to CO eliminated the soot problem without increasing the flame speed. The resulting flame conditions are appropriate for studies of CO₂ gasification in the presence of CO inhibition.

Initial tests of the CO flame in the PFFB were very expensive due to the high cost of CO fuel. The original burner had a diameter of 42 mm. An existing 25 mm burner was repaired and upgraded to replace the 42 mm burner, which had been corroded during the attempted steam gasification studies. This had the effect of reducing the fuel cost to a more reasonable level. A crank system was also designed and installed to move the small burner up and down. This had the effect of reducing the labor requirement for the lab. Burner removal for maintenance (typically a daily process) previously required 2 people and could take several minutes with the 42 mm burner. More time was often required to replace quartz tubing because it was easily broken during removal of the large burner. The 25 mm burner can now be removed in a few seconds by a single person with no risk of breaking quartz.
Centerline gas temperatures were measured by inserting a thermocouple through an o-ring attachment at the top of the probe. These measurements were corrected for radiation effects. These temperature measurements were difficult and hazardous to make due to the high pressure and the fragility of the ceramic sheath that protected the thermocouple wires. Frequent thermocouple repairs and replacements were required. Recently another set of upgrades was implemented to make temperature measurement safer and easier. The top half of the ceramic sheath was encased in a metal tube and the wires were fed through a pressure-tight fitting. The metal tube was attached to a crank system to move it through o-rings at the top of the probe. This modification eliminated the possibility of the thermocouple becoming a projectile and releasing CO into the lab. The probe is sufficiently long to permit the thermocouple to be moved all the way down to the burner surface while keeping the metal portion of the protective sheath above the location where cold nitrogen quenches the burner gases.

**PFFB Gasification and Pyrolysis Conditions**

The Wyodak coal was gasified in the PFFB in 27% H$_2$O at 2.5 atm. The peak gas temperature was about 1700 K. There was 3% CO$_2$ and less than 2% each of CO and H$_2$. These conditions eroded the surface of the 42 mm burner and caused clogging when bituminous coals were attempted. These challenges delayed further H$_2$O gasification experiments; the focus was shifted to CO$_2$ gasification.

Pyrolysis of the Wyodak and 3 bituminous coals was conducted in the PFFB at pressures of 2.5, 5, 10, and 15 atm. The peak gas temperatures were about 1700 K, and residence times were ~40 ms. CO was used to fuel the flame, which led to gas compositions of 16% CO$_2$, 11% CO, and less than 2% H$_2$O. The remainder of the gas was N$_2$.

The pyrolysis gas conditions at 5 atm, 15 atm, and in some cases 10 atm were used with extended residence times (up to 690 ms) for gasification studies. Other conditions with peak temperatures near 1900 K were also used. The gas composition for these conditions was 20% CO$_2$, 8% CO, and less than 2% H$_2$O. A few conditions at gas temperatures of about 2050 K were attempted, but this led to excessive thermal degradation of the coal feeder tube.

**Conditions for Soot Studies**

Part of the objectives of the work was to study the structural changes associated with pyrolysis under varying conditions in at least two coals of different rank. The coals chosen for study were Wyodak sub-bituminous and an eastern bituminous coal. The pyrolysis conditions included variations of temperature, sample HAB. Different HAB correspond to variations in the residence time in the pyrolysis zone. The Wyodak and eastern bituminous coals were pyrolyzed at 1150 K and 1300 K using the atmospheric flat-flame burner. The effects of pressure on a surrogate tar (pyrolyzed biphenyl) and the eastern bituminous coal were studied using the PFFB.

In order to gain a better understanding of the behavior of tar/soot formation we considered a number of model compounds. One of the major challenges was securing sufficient quantities of very costly model compounds with coal related functional groups. We compromised and selected biphenyl as the surrogate...
of choice. A gas condition at 5 atm with a peak temperature of ~1400 K was developed in the PFFB for use in soot formation studies. The collection probe was set 2 inches above the burner, which should give a residence time of less than 100 ms. This condition was used with the model compound and also for a bituminous coal. The tar/soot samples were recovered on filters and sent with the bituminous char for NMR analysis. The samples produced from coal were sent quite recently; the data will not be included in this report.

Another PFFB condition at 10 atm was also used to produce tar/soot from biphenyl, but the yield was very low. Approximately 20 mg of product was analyzed by GC/MS. Other tar surrogate experiments were attempted at atmospheric pressure, but the yields of the selected compounds were too low for practical analysis.

**Investigation of Char-CO$_2$ kinetics and H$_2$O reactivity**

TGA tests of CO$_2$ reactivity were postponed until the PFFB char could be collected. In addition, the H$_2$O reactivity tests were not completed because the development of steam capability in the pressurized TGA was too time consuming to be completed within the project timeframe. Most of the time was spent developing and upgrading the PFFB system, which was more difficult than originally anticipated. H$_2$O gasification studies in the PFFB may require further modifications as well.

**Determination of Residence Times**

A high-speed video camera has been used previously to measure particle velocities in the luminous zone of the atmospheric flat-flame burner (FFB). The same technique was applied on a more limited basis in the PFFB using a window located near the burner (below the heaters, Figure 4). Lens effects of the windows and the layers of quartz tubing in the PFFB were measured and taken into account.

In the PFFB particle velocities were measured at two locations for each flame condition (Figure 5). The higher location was usually 1 inch above the burner and the lower location was close to the beginning of the luminous zone, usually less than ½ inch. For comparison, theoretical particle velocities were calculated for a non-reacting spherical particle based on an average gas velocity calculated at the local temperature from the gas flow rates. A momentum balance was performed on the particle using a drag coefficient. The theoretical particle velocity rapidly approached the average theoretical gas velocity. The difference between the particle and gas theoretical velocities was ~30% at 10 ms and ~10% at 30 ms. However, the optical particle velocity exceeded the theoretical velocity by a factor of 1.4-3.1 at the 1 inch location (Figure 5). This high centerline velocity can be attributed to rapid development of flow and perhaps a minor contribution from channeling.
A scaling scheme was applied to reconcile the theoretical trends with the measured velocities. The 1 inch location was close to the maximum flame temperature, and the theoretical particle velocity was nearly flat from about ¼ inch to 3 inches above the burner. Therefore, it was assumed that the optical velocity at the 1 inch location represented a maximum velocity. The ratio of the maximum optical particle velocity at 1 inch above the burner to the theoretical velocity at the same location was denoted as $m$. The gas temperature was used to scale post-peak velocities because the difference between the theoretical particle and gas velocities after the peak velocity was only ~8%. The particle velocity at the burner surface was determined by calculating the terminal particle velocity in the coal feeder tube (0.041 inch ID) at room temperature using N$_2$ gas properties. At this location the theoretical velocity should be a reliable estimate. A linear scaling factor between the surface theoretical velocity and the 1 inch optical velocity was attempted, but it resulted in a velocity profile with an artificial sharp corner at 1 inch and underestimated velocities closer to the burner surface. A closed-form quadratic scaling scheme was adopted. The theoretical velocity at locations up to 1 inch above the burner was multiplied by the following scaling factor:

$$SF(x) = ax^2 + bx + c \quad \text{(Equation 1)}$$

where $SF$ is the scaling factor and $x$ is the distance above the burner. To be consistent with theory at the surface, $SF(0) = 1.0$, which means $c=1.0$. To be consistent with the optical velocity, $SF(l) = m$, where $l$ is the height where the maximum optical velocity was measured (usually 1 inch). The derivative of $SF$ at $x = l$ was set to zero to prevent an artificial sharp corner and other physically unrealistic shapes in the velocity profile. These last two conditions result in:

$$a = \frac{1-m}{l^2} \quad \text{and} \quad b = -2al \quad \text{(Equation 2)}$$

Thus, the quadratic scaling factor requires no optimization of parameters and uses a single measurement to yield a smooth velocity profile that is consistent with the theoretical velocity at the burner surface and
the maximum measured velocity. If the 95% confidence interval of both measured points is taken into account then the scaled velocity profile could be made to pass through the point that was not used for scaling every time (Figure 5). In almost all cases, the agreement with the second measurement was still excellent even without taking into account the statistical error of the measurements.

Measurements at longer residence times on the FFB were used to validate the technique of scaling the particle velocities with the temperature and the scaling factor $m$. The residence times derived with the scaling technique agreed within 15% of the measurements at 100 ms. The accuracy of this method should be better for the PFFB because the PFFB appears to have fully developed flow at the 1 inch scaling point, but the FFB does not ($m \approx 1.5$). Residence times between 40 ms and 690 ms are possible in the PFFB.

**Char Size and Purity**

A challenge encountered with using bituminous coals in the PFFB was that a significant portion of the collected char was fragmented, making it very difficult to determine the original particle sizes. Some of the char collected was less fragmented, apparently due to small variations in the char collection method (Figure 6).

![Figure 6. SEM images of an eastern bituminous char produced at 10 atm, 1722 K, 42 ms.](image)

The char was collected in a pressurized horizontal cyclone and was periodically moved to a low pressure collection chamber or char trap by opening a valve (Figure 7). Two causes of fragmentation were found, both involving high-velocity collisions of char particles. First, allowing too much char to collect in the cyclone before removal caused fragile cenospheric char particles to collide with each other. This problem was reduced by emptying the char trap more frequently. Second, opening the valve from the cyclone quickly at elevated pressures caused the char particles to impact the wall of the char trap. This is probably the more significant source of fragmentation. This source of fragmentation was reduced by partially pressurizing the char trap before venting the cyclone so that a sonic shock wave did not occur when the valve was opened.
Many of the char samples collected were contaminated with large soot particles. SEM images showed that the collection system was unable to separate the very large soot agglomerates from the char (Figure 8). The aerodynamic separation system was designed with a 5 μm diameter cut point for char particles, which explains why large soot agglomerates would be collected with char particles. The soot needs to be removed from the char because char containing a significant quantity of soot cannot be accurately analyzed for mass change via elemental or ash tracer techniques. Also, accurate determination of swelling by the tap density technique is hindered by the presence of large, low-density soot agglomerates. Soot contamination increased with increasing temperature and residence time, and was much more pronounced at elevated pressures than at atmospheric pressure.

Figure 8. SEM image of an eastern bituminous coal produced at 5 atm, 1918 K, 660 ms; note that soot (which appears to have a “fuzzy” texture compared to char) is present in very large soot agglomerates and sometimes as a coating on the char particles.
The primary cause of the increased yield of soot and especially of large soot agglomerates with increasing pressure is the increased molar concentration of tar at elevated pressures. Higher concentrations promote polymerization of the tar into soot particles. The formation of more primary soot particles at lower residence times promotes the development of larger soot agglomerates.

Attempts to improve the separation of char and soot by changing the operating conditions of the aerodynamic separation system were not successful. Density separation was attempted next. In a previous study, Veranth et al. (2000) separated soot from fly ash using a liquid-suspension gravity separation technique in which soot floated to the top of an ethanol supernatant and ash settled to the bottom. Such was not the case with the current samples; many of the cenospheric char particles floated. In early separation attempts, soot agglomerates remained intact and settled to the bottom of the liquid with the dense fraction of the char. After trials with several different liquids, a mixture of 2 parts ethanol with 3 parts water (by volume) was adopted for the separation procedure (density = 0.94 g/mL). A low-intensity custom vibrator was used because fragmentation of the char particles occurred when sonication was attempted.

Char samples split into two fractions, which were filtered separately. The top fraction contained whole cenospheric char particles, and the bottom fraction contained smaller cenospheres, denser particles (from high-ash and/or non-swelling coal particles), and particle fragments. With 2 hrs of vibration, negligible amounts of soot were observed in SEM images of both the top and bottom fractions (Figure 9). It appears that the soot agglomerates broke down into fragments smaller than 5 microns and passed through the filter. The top fraction was then dried and subjected to bulk density and ash tests to determine extent of reaction and swelling. The extent of reaction determined from ash content of the top fraction can be considered a lower bound, because particles with high ash content should be too heavy to collect in the top fraction. Similarly, the density determined from the top fraction can be viewed as a lower bound on the sample density.

Figure 9. SEM images of a separated bituminous char produced at 5 atm, 1702 K, 38 ms.
The bottom fraction was also subjected to an ash test to determine an upper bound for the extent of reaction. A mass-weighted average ash content was calculated from the ash content of the two fractions. The bulk densities were not measured for the bottom fraction of the separated char because the presence of char fragments changes the packing factor. A swelling ratio determined from a bulk density on a sample with a high extent of fragmentation and an unknown packing factor has little or no physical meaning.

**NMR and GC/MS Analysis**

Solid-state carbon-13 cross polarization with magic angle spinning (CPMAS, standard magic angle spinning rate of 5 KHz) nuclear magnetic resonance (NMR, 100 MHz Chemagnetics) has been used to analyze pyrolysis products from two coals, an Eastern bituminous and the sub-bituminous Wyodak coal. In addition, a tar/soot surrogate obtained by pyrolysis of biphenyl was also examined by both carbon-13 NMR and GC/MS. The biphenyl tar/soot samples were collected at conditions 1405 K, 10 atm pressure, and 2” HAB and at 1484K, 2” HAB and 5 atmosphere. Details of the experimental nuclear magnetic resonance (NMR) techniques have been described elsewhere in the literature (see for example Solmn et al. 1989).

The term cross polarization refers to a standard method for transferring magnetization from the proton spins to the carbon spins by means of two radio frequency pulses in order to increase the sensitivity of the carbon-13 signal. Magic angle spinning refers to the orientation of the spinning rotor filled with the sample to that of the magnetic field. The term commonly used is CPMAS. Another method for carbon-13 detection when the proton population is small compared to that of the carbon atoms is single pulse where a single radio frequency pulse is used to obtain the carbon-13 spectrum. One of the key structural parameters mentioned in the report section deals with the average size of the aromatic cluster in the parent coal, tar/soot, or char samples. An important condition to note is that the growth of the average cluster size in pyrolysis reactions produces organic free radicals, and as the free radical content increases the conductivity of the tar/soot and char samples increase. As the conductivity increases the NMR probe detunes (looses sensitivity), and the carbon-13 line width increases.

The PPM scale in NMR spectra represents the $^{13}$C chemical shift in parts per million which is referenced to an external standard (tetramethyl silane). The chemical shift values define the types of carbons (both aromatic and aliphatic) that are found in well-defined chemical shift values. When data is taken under quantitative conditions, the intensity of the lines or defined chemical shift regions provide the relative amount of a given functional/structural group that is present in the sample of interest.

The biphenyl tar surrogate tar/soot samples (~10-15 mg each) collected at 10 atm on the same date were analyzed by electron impact ionization on an Agilent 6850/5975 gas chromatograph/mass spectrometer (GC/MS). Samples were diluted in methylene chloride and 1 µL was introduced via a Agilent 7683B injector. Chromatographic separation was accomplished using a Hewlett Packard-5MS capillary GC column (0.25µm, 30mX0.25mm) and an initial temperature of 60°C. After 2 minutes a temperature gradient of 60°C to 300°C at a rate of 10°C/min. was used.
Gasification Models

The first method used to derive gasification kinetics from PFFB data is a spreadsheet-based model with 1st order kinetics. Kinetic parameters were optimized using the Excel Solver. A pseudo-steady state energy balance containing convection, radiation, and reaction terms was used. The energy balance solved using the secant method is:

\[
0 = h A_p \left( T_g - T_p \right) - \alpha \varepsilon_p A_p \left( T_p^4 - T_w^4 \right) - \frac{dm}{dt} \Delta H
\]  
(Equation 3)

where \( \varepsilon_p \) is the emissivity of the char (0.8), \( h \) is the convection coefficient evaluated from a Nusselt number of 2, and graphite properties were assumed for char when calculating the heat of reaction \( \Delta H \). \( A_p \) is the surface area of the particle, \( T_p \) is the particle temperature, \( T_g \) is the gas temperature, \( T_w \) is the wall temperature for radiation heat transfer, \( \sigma \) is the Stefan-Boltzmann constant, and \( dm/dt \) is the mass rate of pyrolysis. The 1st order steam gasification rate expression based on external surface area and accounting for film diffusion is:

\[
r^n = \frac{P_{CO_2,B}}{R \frac{T_g T_g}{v h_m} + \frac{T_g}{T_p k_{rxn}}}
\]  
(Equation 4)

where the expression for steam gasification is identical with the partial pressure of H\(_2\)O in the bulk \( P_{H2O,B} \) substituted for the corresponding partial pressure of CO\(_2\), \( P_{CO2,B} \). \( R \) is the universal gas constant, \( T_g \) is the gas temperature, and \( T_p \) is the particle temperature. The parameter \( \nu \) is a unit conversion factor with units of (grams carbon reacted)/(mol gasification reactant). The mass transfer coefficient \( h_m \) is evaluated assuming a Sherwood number of 2. The parameter \( k_{rxn} \) is the reaction rate constant evaluated at the particle temperature in units of [mass reacted]/[time]/[external surface area]/[partial pressure gasification reactant].

Two more advanced gasification models have been developed. The first model is entitled BYU-CBK/G. It is based on the CBK/E code and follows an approach similar to the published version of CBK/G (Niksa et al., 2003; Liu and Niksa, 2004). CBK/E is an advanced char oxidation code with three-step semi-global kinetics that can predict different reaction orders in different temperature regimes and decreased reaction rates at high extents of reaction. The decreased rates at late burnout are modeled using ash inhibition and thermal annealing sub-models along with an effectiveness factor. CBK/G includes 5 additional semi-global reactions for gasification and effectiveness factors for each gasification reactant.

In the development of BYU-CBK/G, the methods of the previously published CBK/G were followed closely. Thermodynamic and transport properties were updated to include the required species and ensure reasonable values at temperatures above 2000 K that exist near the coal injector regions of gasifiers (Mitchell, 1980; Bird et al., 2002; McBride et al., 2002; Rowley et al., 2010). A simple mixture diffusivity was included to account for multi-component diffusion without adding the computational
burden associated with the use of Maxwell-Stefan theory (Fairbanks and Wilke, 1950; Hill and Smoot, 1993). As in previous versions of CBK, thermodynamic properties of graphite were used for char. The heats of combustion of graphite deviates by less than 5% from values predicted using the Dulong formula with compositions of bituminous and subbituminous chars generated at Sandia National Laboratory (Green and Perry, 1984; Fletcher and Hardesty, 1992). The magnitude of these deviations of char properties from graphite is similar to the error introduced by using the Dulong formula instead of calorimetric measurements.

The second gasification code developed is a simplified version of BYU-CBK/G, which uses \( n \)th order kinetics and is entitled CBK-GN. Optimization methods for kinetic parameters have been implemented using OptdesX software for both of the new codes. Neither model has yet been applied to data from the PFFB.

Subtask 4.5 – Slag Formation and Slag-Wall Interactions

Experiments were designed to investigate physical changes of coal char during the char-slag transition and to provide data for an ash deposition model that can be incorporated into CFD modeling of entrained-flow slugging coal gasifiers. Therefore, experiments were mainly focused on the ash deposition behavior as well as the changes in physical characteristics of char particles during the char-slag transition.

Three coals were selected for the experiments: Illinois #6, Pittsburgh #8 and Black Thunder from the Power River Basin (PRB). Two types of experiments were carried out: char and ash formation experiments and ash deposition experiments. The purpose of the char and ash formation experiments was threefold: (1) prepare and collect char and ash particles with different conversions that cover the range of the char–slag transition, (2) evaluate the physical changes of char and ash particles and the transformations of mineral–carbon association in the char–slag transition, and (3) identify an indicator for the char–slag transition. The goal of ash deposition experiments was to assess the intrinsic propensity of particle deposition during the char–slag transition. This is valuable for determining whether a particle is inclined to “stick” upon contacting a surface such as a refractory wall or injector face.

All the experiments were conducted in a high-temperature laminar entrained-flow reactor (LEFR). This type of device has been widely used for studying coal conversion and ash deposition behavior because it can provide well controlled experimental conditions while closely representing the environment in a practical combustion or gasification system.

Laminar Entrained Flow Reactor Experiments

Reactor Description. The LEFR, as configured for char/ash formation experiments, is shown schematically in Figure 10. The experimental setup for conducting ash deposition experiments is essentially the same as that for char and ash formation experiments except the manner of sample collection, which will be described later. The LEFR comprises five components: an electrically heated furnace, a coal feeder, a water-cooling loop, a gas supply unit and a sample collector.
Figure 10. Schematic of the laminar entrained flow reactor, configured for char/ash formation and collection.

The design of the LEFR followed the principles established in the classic work of Flaxman and Hallett (1987) and also took into account previous designs of entrained-flow reactors (Gullett 1988; Brown et al. 2001) and drop tube furnaces (Ouyang and Yeasmin 1998).

The furnace is a single zone vertical furnace (Carbolite, STF 16/610), electrically heated by six rod-shaped SiC heating elements. A type R thermocouple is installed at the axial midpoint of the furnace to provide a temperature measurement signal for the temperature controller. The maximum operating temperature is 1600°C. The heated length of the furnace is 610 mm.

Two coaxial alumina tubes (CoorsTek, 99.8% Al₂O₃) were installed inside the furnace. The inner tube serves as a plug flow reactor. The annulus between the inner and outer tubes is used to preheat the reaction gas before flowing into the inner tube. The outer tube is 8.89 cm o.d. × 7.94 cm i.d. × 137 cm length. The inner tube is 5.72 cm o.d. × 5.08 cm i.d. × 102 cm length. Porous insulation material with low thermal conductivity is used to fill the gap between the furnace wall and the outer tube to minimize heat loss and to dampen thermal shock at high temperatures. Reaction gas is injected through three ports.
on the bottom flange of the furnace and is preheated while flowing upwards in the annulus between the two coaxial alumina tubes. The gas then makes a 180° turn and flows through an alumina honeycomb flow straightener and enters the inner reactor tube. As shown in Figure 10, the honeycomb sits on the top of the inner alumina tube and is flush with the bottom of the injection probe, which is the end of the injecting section and the start of the reacting section. The o.d. of the honeycomb flow straightener fits the i.d. of the outer alumina tube, and the i.d. of the flow straightener fits the o.d. of the injection probe. A groove is cut on the bottom of the flow straightener so that it can center the inner alumina tube. The honeycomb has a configuration of 16 cell/cm², an open frontal area of 72%, a hydraulic diameter of 0.216 cm and a height of 5.08 cm. This configuration provides sufficient pressure drop for generating a laminar flow, which is essential for the entrained particles traveling along the centerline of the reaction tube to undergo identical reaction conditions. Both of the ends of the two alumina tubes sit on aluminum flanges and are sealed with silicone o-rings. The flanges hang on a triangle bracket.

A schematic diagram of the coal feeder is presented in Figure 11. The coal feeder consists of an infusion syringe pump (Harvard Apparatus, 552222) and a coal container. The coal container is made of an acrylic tube (2.54 cm o.d. × 1.90 i.d. × 25.40 cm length). The bottom of the coal container is attached to the syringe holder of the infusion pump. The coal container is connected to the injection probe via a stainless steel feeding tube. The bottom of the feeding tube is mounted on the injection probe and the top of the tube flushes with the coal bed in the container. A loose Swagelok fitting with Teflon ferrules is used to connect the feeding tube and the coal container to allow the coal container sliding along the feeding tube. When the pump infuses, the coal container is pushed upwards so that the coal bed is raised above the feeding tube and those particles near the tube fall into it. Meanwhile, the coal container is vibrated by an engraver to make the coal bed level. Coal particles that jump into the feeding tube are entrained into the injection probe by a carrier gas. The feeding rate is controlled by the travel rate of the syringe pump, which is in the range of 1–10 ml/hr.
Coal particles are pneumatically transported into the reaction zone of the reactor via a water-cooled injection probe, which connects the feeder and the reaction zone through a hole in the upper flange of the reactor. The injection probe is made of three coaxial stainless steel tubes, which form two annuluses. Cooling water flows through the two annuluses to prevent the coal particles from being devolatilized before entering the reaction zone. The probe has a dimension of 1.27 cm o.d. × 0.22 cm i.d. × 86 cm length. Indeed, the selection of the cross sectional area of the annulus is a compromise between cooling capacity and gas flow stability. Although a larger annulus can provide higher cooling capacity, the annulus must be as thin as possible to minimize heat loss from the reactor and to prevent turbulence at the gas inlet of the reaction zone. An insulation plug is installed on the cooling jacket of the injection probe to avoid cooling the preheated reaction gas.

In the ash formation experiments, the reacted gas–solid mixture exited the reactor through a water-cooled collection probe, shown in the system schematic (Figure 10). The probe is made of three co-axial stainless steel tubes with an inverted cone-shaped head. The collection probe is 3.18 cm o.d. × 1.52 cm i.d. × 96.52 cm long. The cone has an angle of 45º with respect to its axis and an outside diameter of 4.762 cm on the top. It covers about 88% of the cross sectional area of the reactor tube, which increases the collection efficiency. A porous stainless steel tube is installed inside the collection probe to form an annulus. Nitrogen gas is introduced into the annulus and permeates through the micropores of the porous tube. This gas flow quenches the reacting stream and reduces the thermophoresis deposit of the solid particles on the probe surface. Most of the solid particles are collected in a small cyclone. The tar and fine particles are captured on a Teflon filter installed after the cyclone. The cyclone used in this study was designed to have a cut diameter of 2–4 µm depending on the gas flow rates in the LEFR.
In the ash deposition experiments, the collection probe was replaced by a specially designed deposition probe (Figure 12). The deposition probe consists of an alumina tube and a clean alumina plate. A 45° (with respect to the cross-sectional plane of the probe) V-shaped groove was cut on top of the alumina tube for housing the alumina plate. This configuration allows simulation of inertial impaction on refractory walls because: (1) the alumina plate has a ceramic surface similar to the fresh refractory wall, and (2) the uncooled plate has a surface temperature roughly the same as that of the uncooled refractory wall. A clean alumina plate was used for each experiment because this research was focused on the intrinsic particle surface stickiness and the initial stage when the slagging layer starts building up. Reacted particles struck the plate when the particle-laden gas stream approached the plate at a 45° angle. The 45° incident angle was randomly chosen because this study was focused on the particle stickiness and the incident angle only affects the rebound velocity, i.e., does not change the particle stickiness. Upon impaction, particles with sufficient stickiness adhered on the deposition plate and were designated as deposit sample. Ash particles that did not adhere onto the plate were received by a cyclone at the bottom of the deposition probe. The deposition plate could be removed from the deposition probe so that it can be weighed before and after the deposition experiment. The weight difference is the weight of particle that deposit on the plate.

![Figure 12. LEFR deposition probe for ash deposition experiments.](image-url)

The flow rates of gases were controlled by rotameters (Cole Parmer, direct reading), which have a maximum error of 5% of their ranges. Pressure regulators between gas cylinders and rotameters provided stable gas flow. Rotameters were calibrated by bubble-type flowmeters before running experiments.
The pressure inside the furnace was monitored by a Magnehelic differential pressure gauge (Dwyer, 2320) connected to the reactor through a hole on the top flange via a 3.3 mm Teflon tube. The reactor was usually maintained at atmospheric pressure by adjusting the power of the vacuum pump.

**Reactor Operation.** Experimental procedures were basically the same for the two types of experiments. Coal particles were injected from the top of the reactor into a premixed, preheated air–nitrogen gas stream and were partially converted at various residence times. In the ash formation experiments, resulting particles exit the reactor through a water-cooled, nitrogen-quenched collection probe and were collected in a cyclone. Each experiment was run for 2 hours to collect sufficient particles for further analyses.

In the ash deposition experiments, char and ash particles with different degrees of conversion approached the deposition plate before exiting the reactor. Upon impaction, particles with sufficient stickiness adhered on the deposition plate and were designated as deposit sample. Ash particles that did not adhere on the plate were received by a cyclone at the bottom of the deposition probe. After the ash deposition experiment, nitrogen was fed into the reactor to provide an inert environment for the deposit on the plate until the reactor cooled down. The deposition probe was then taken out of the reactor and the deposition plate was removed for weight measurement. The weight of deposit was determined by the weight difference of the deposition plate before and after the deposition experiment. Each deposition experiment was run for 2 hours to collect enough deposit to minimize the weighing error.

The experimental conditions were identical for char and ash formation experiments and ash deposition experiments. The pressure inside the reactor was maintained at ambient pressure, 0.85 bar (the altitude of Salt Lake City is about 1350 m). The furnace temperature was set to either 1400 or 1500 °C by using the temperature calibration curve in Figure 14. The temperature was chosen to be above the ash flow temperature of the specific coal ash. The feeding rate of coal particles was 30 mg/min to avoid particle agglomeration in the injection probe. The flow rate of air in the reaction gas mixture was varied for different coals to keep a stoichiometric ratio (oxidant/fuel, molar basis) of 0.7, which provided an overall reducing atmosphere in the reactor. The term oxidant is defined as the oxygen in the air and coal. The term fuel refers to all the combustible elements (carbon, sulfur and hydrogen) in the coal. The experimental run for preparing fresh chars by devolatilization used pure nitrogen. The residence time of the coal particles in the reactor was varied from 1 to 6 seconds. A long residence time was necessary due to the low oxygen content (0.7%–4.6%) in the reaction gas in accordance with the low feeding rate of coal. Experimental conditions for different coals are summarized in Table 2.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Oxygen (O2) to carbon (C) ratio</th>
<th>Temperature (°C)</th>
<th>Residence time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illinois #6</td>
<td>0, 0.7</td>
<td>1400, 1500</td>
<td>1–6</td>
</tr>
<tr>
<td>Pittsburgh #8</td>
<td>0, 0.7</td>
<td>1500</td>
<td>1-6</td>
</tr>
<tr>
<td>Black Thunder</td>
<td>0, 0.7</td>
<td>1400</td>
<td>1–5</td>
</tr>
</tbody>
</table>

The residence time of particles in the reactor was determined by the length of reacting pathway and the gas velocity inside it. Stokes number analysis indicates that the very small particles used in these
experiment are entrained in and follow the gas flow and have the same residence time as the gas. The length of the reaction pathway was 610 mm. The gas velocity inside the reactor could be adjusted by the flow rate of the reaction gas. For gasification experiments, a long residence (about 5 s) is desirable. For a 610 mm reacting length and a 1400 °C operating temperature, a gas velocity of 0.12 m/s is required at the axis of the reactor to achieve this residence time. The corresponding reaction gas flow rate is around 2.5 standard liter per minute (SLPM), and the corresponding Reynolds number of the gas flow is 28. The velocity of the carrier gas can be several times of that of the reaction gas while still keeping a stable laminar flow.

For a steady state gasification experiment, a constant feeding rate is necessary. The feeding rate of the coal feeder was determined by the infusion rate (ml/hr) of the syringe pump and the tap density of the coal particles. The feeding rate was calibrated at various infusion rates of the syringe pump with a coal bulk density of 0.7 g/cm³. The measured feeding rate was determined by dividing the weight loss of the coal feeder by the run time. The nominal rate was calculated by the product of the coal bulk density and the syringe pump infusion rate. The calibrated result is shown in Figure 13. The measured feed rate was 15-20% more than the calculated feed rate, which is likely due to differences in the tap density and density of the bed as it was vibrated. This calibration curve was used for calculating actual feeding rate of coal particles in the experiments.

![Figure 13. Feeding rate calibration of the coal feeder.](image)

The temperature profile at the centerline of the furnace was measured to compare with the temperature controller settings. Each measurement was taken with a nitrogen gas flow of 3 SLPM, which is a typical flow rate used in the experiments. The temperature profiles that were measured at furnace set point temperatures of 800, 1000 and 1200 °C, respectively. The measured temperature profile and the set points
are plotted in Figure 14. This temperature calibration curve provided the basis for setting the temperature controller when running experiments. For example, for an experimental temperature of 1200 °C, the temperature controller was set at 1225 °C to compensate for the difference between the actual temperature and the temperature controller signal.

**Figure 14. Axial temperature profile of the reactor.**

**Coal Sample Properties**

Coal rank plays an important role in the reaction behavior during gasification process. Three pulverized coals of different ranks were used for the experiments: Illinois #6, Pittsburgh #8 and Black Thunder (Powder River Basin). These coals are typical feedstocks in entrained-flow coal gasifiers. The Illinois #6 is a high-volatile C bituminous coal, the Pittsburgh #8 is a high-volatile A bituminous coal, and the Black Thunder is a subbituminous coal.

All the coals were sieved to a size range of 43–63 µm to minimize the effect of particle size distribution on char conversion and ash deposition. Before sieving, the coal samples were dried in a muffle furnace at 104 °C for 24 hours to remove the moisture according to an ASTM method (105). The properties of the coals and the ashes were determined by Wyoming Analytical Laboratories. The proximate and ultimate analyses, the ash chemistry and the ash fusion temperatures are listed in Table 3, Table 4 and Table 5, respectively.
Table 3. Proximate and ultimate analyses of the coals used in this work.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Moisture (%)</th>
<th>Ash (%)</th>
<th>Volatiles (%)</th>
<th>Fixed Carbon (%)</th>
<th>Ultimate Analysis (wt%, maf)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Illinois #6</td>
<td>3.63</td>
<td>10.89</td>
<td>36.42</td>
<td>52.69</td>
<td>74.52</td>
</tr>
<tr>
<td>Pittsburgh #8</td>
<td>1.08</td>
<td>9.00</td>
<td>38.22</td>
<td>52.64</td>
<td>84.07</td>
</tr>
<tr>
<td>Black Thunder</td>
<td>24.59</td>
<td>6.82</td>
<td>49.07</td>
<td>44.11</td>
<td>77.91</td>
</tr>
</tbody>
</table>

*aMoisture free, method: ASTM D5142. bMoisture ash free, method: ASTM D5142/5373. cAs received.

Table 4. Ash chemistry of the coals used in this work.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Al₂O₃ (%)</th>
<th>CaO (%)</th>
<th>Fe₂O₃ (%)</th>
<th>K₂O (%)</th>
<th>MgO (%)</th>
<th>MnO (%)</th>
<th>Na₂O (%)</th>
<th>P₂O₅ (%)</th>
<th>SiO₂ (%)</th>
<th>TiO₂ (%)</th>
<th>SO₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illinois #6</td>
<td>17.75</td>
<td>5.23</td>
<td>18.99</td>
<td>2.06</td>
<td>0.89</td>
<td>0.05</td>
<td>1.67</td>
<td>0.16</td>
<td>46.58</td>
<td>0.88</td>
<td>4.59</td>
</tr>
<tr>
<td>Pittsburgh #8</td>
<td>19.68</td>
<td>4.54</td>
<td>27.79</td>
<td>1.20</td>
<td>0.85</td>
<td>0.02</td>
<td>0.90</td>
<td>0.34</td>
<td>39.66</td>
<td>0.84</td>
<td>4.18</td>
</tr>
<tr>
<td>Black Thunder</td>
<td>16.84</td>
<td>21.61</td>
<td>5.86</td>
<td>0.50</td>
<td>5.06</td>
<td>0.02</td>
<td>1.69</td>
<td>1.00</td>
<td>36.04</td>
<td>1.32</td>
<td>9.06</td>
</tr>
</tbody>
</table>

*aMethod: ASTM D4326 (XRF).

Table 5. Ash fusion temperatures of the coals used in this work. IT = Initial deformation temperature; ST = softening temperature; HT = hemispherical temperature; FT = flow temperature.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Ash Fusion Temp. (oxidizing, °C)</th>
<th>Ash Fusion Temp. (reducing, °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IT</td>
<td>ST</td>
</tr>
<tr>
<td>Illinois #6</td>
<td>1244</td>
<td>1254</td>
</tr>
<tr>
<td>Pittsburgh #8</td>
<td>1308</td>
<td>1342</td>
</tr>
<tr>
<td>Black Thunder</td>
<td>1184</td>
<td>1188</td>
</tr>
</tbody>
</table>

*aMethod: ASTM D1857.

Experimental Analysis

Carbon contents of the collected char and ash particles (ash formation sample) were determined using a hot foil loss–on–ignition (LOI) instrument (FERCO, HF400). About 10 mg of sample was completely burned using this apparatus. The sample was weighed before and after the LOI analysis. By assuming that all the mass loss is carbon and knowing the carbon content of the original coal, the carbon content in the char could be calculated.

For the deposition experiments, the particle collection efficiency η is defined as the mass fraction of material approaching the collection plate which is actually deposited on the plate. Because the reaction conditions and sampling position of collecting particles in ash formation experiments were identical to those of ash deposition experiments, it is reasonable to assume that the carbon content of the ash formation sample is the same as the particles approaching the deposition plate. The particle collection efficiency is an averaged value of all the particles that impacted the deposition plate.
Subtask 4.6 – Acquisition of Validation Data in an Entrained-Flow Gasifier

Preparation and execution of this study was divided into three major activities, which were carried out concurrently: (1) gasification facility preparation and modifications, (2) injector development and (3) system operation. Each activity is described below.

Gasification Facility Preparation and Modifications

As indicated in the introduction, when the CASE project began, construction of the gasification facility was complete. Over the two years of the project, the system was taken through preliminary testing (“shakedown”) and methodically brought to operation at full capacity at 250 psi pressure. During the project, two major systems were added to ensure safe extended operation at high load. These are described below, along with a description of the facility in final form.

Full-Scale Coal Slurry Preparation and Transport System. This project represents the first time the University of Utah has dealt with coal-water slurry preparation or feeding. Coal-water slurries are notoriously challenging to handle and have a propensity for settling and forming a concrete-like cake. For this reason, the first slurry preparation and feed system, which was built under the earlier UC3 program, was constructed mostly from components available around the laboratory. The mix tank was a modified 20 gallon barrel and the feed pump was a progressive cavity Moyno pump from a previous project. Despite its cobbled-together nature, this system worked surprisingly well. It was possible to make and continuously feed slurries with Utah coal at 59% solids concentration, which was just shy of the 60% target concentration. The limitation of this system was simply its small size. The feed pump was not able to output more than about 100 psi pressure and had a maximum feed rate of 5-6 gallons per hour.

Based on the good experience with this feed system, a new system to match the full capacity of the gasifier was designed (Figure 15). A larger (ca. 200 gallon) tank was obtained from the university salvage department to use for slurry preparation/feed. This tank was modified to allow slurry recirculation and for easier loading of pulverized coal. A 2 hp recirculation pump and a mixer within the tank provide good agitation to keep the slurry well mixed. This tank will hold enough slurry for 6-8 hours of operation at 250 psi.
A new, much larger progressive cavity pump (Figure 16) was procured from Moyno to feed the slurry to the gasifier. This pump was sized to meet the maximum conceivable demand of the gasifier when it is operating at the vessel rated pressure of 450 psi, and is capable of feeding 42 gallons/hour of slurry at 600 psi. For a 60 wt% solids coal-water slurry, this corresponds to a thermal input of roughly 800 kW. The pump has a variable frequency drive so the speed can be adjusted with an effective 1:100 turndown ratio.
Quench Recirculation and Filter System. As testing progressed, it became apparent that the existing quench recirculation system, which was built based on black liquor slag (smelt) which dissolves in water, was not appropriate for gasification of coal. Water in the quench bath contains pea-sized particles of solidified slag, char-slag conglomerates and fine particles of char and soot. The multistage recirculation pump was not able to handle the particulate material, and valves in the quench bath drain line would get plugged with soot and fine particulate. Also, the original recirculation pump was rated to only 360 psi while the rest of the gasifier has a maximum pressure rating of 450 psi.

For these reasons a new quench recirculation and filter system was designed and installed during year 2 of the program. A new magnetic-drive centrifugal pump with a pressure rating of 600 psi was installed. This pump is much more tolerant of particulate and can handle particles up to 1/8 inch diameter. A 24-inch stainless steel rod filter was constructed and placed within the quench bath on the suction side of the pump to keep larger particles from entering the recirculation system. A pair of high-pressure bag filters (Figure 17) has been installed downstream of the pump to capture fines. These filters are configured in parallel and each can be isolated to allow continuous operation by switching between them. In addition to keeping the quench drain line valves particulate-free the filters will be useful in closing material balances on the system for longer runs.

Figure 16. Progressive cavity slurry pump (blue, with the gasifier in the background).
Final Facility Configuration. Figure 18 presents a schematic of the entrained-flow gasification facility after the modifications made above were complete. The figure shows downstream plumbing in its most flexible configuration. The hot particle filter is actually associated with the University’s pressurized fluidized bed biomass gasifier, but the piping and valving has been installed such that either gasifier can be routed either through the filter, directly to the thermal oxidizer or to an optional system for syngas cleaning. The schematic does not show all details of the system. For example, the oxygen supply system involves a pressure building system, a vaporizer, several safety valves and check valves, a regulator, flow control valve, Coriolis flow meter and three pressure transducers. In this final configuration, the system is able to operate over a wide range of conditions.
Typical and maximum operating conditions of the entrained-flow coal gasification system are presented in Table 6. Although the maximum pressure indicated is 450 psi and the reactor shell pressure and all components are rated to at least that pressure, the effective maximum pressure is currently around 250 psi. The oxygen feed system is able to deliver oxygen to the building at 325 psi, but there is 60-70 psi pressure drop across the valves, flowmeters and injector.

<table>
<thead>
<tr>
<th>Property</th>
<th>Typical Operating</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (psi)</td>
<td>250</td>
<td>450</td>
</tr>
<tr>
<td>Temperature (°F)</td>
<td>2600</td>
<td>3200</td>
</tr>
<tr>
<td>Coal feed (lb/hr dry basis)</td>
<td>85</td>
<td>170</td>
</tr>
<tr>
<td>Thermal input (kW)</td>
<td>300</td>
<td>600</td>
</tr>
<tr>
<td>Slurry feed rate (gal/hr)</td>
<td>16</td>
<td>42</td>
</tr>
<tr>
<td>Oxygen feed rate (lb/hr)</td>
<td>100</td>
<td>250</td>
</tr>
<tr>
<td>Average reactor residence time (s)</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>Syngas production rate (scfh dry)</td>
<td>2400</td>
<td>5000</td>
</tr>
</tbody>
</table>

The gasifier reactor itself is cast with two layers of refractory inside a 30-inch pressure shell. The internal dimensions of the reactor are roughly 8 inches diameter by 60 inches long. Six pairs of opposed 2-inch sample ports down the length of the reactor allow extractive sampling from or optical access through the reactor. Two additional ports near the burner can provide additional optical access or flame monitoring.
Six smaller 1-inch ports down the length are used for temperature or pressure measurements. The system currently has five B-type thermocouples down the length of the reactor, which allow measurement of the reactor temperature profile.

A water-cooled ring below the refractory initiates the transition into the quench system. Four flat spray nozzles just below this ring make up the primary quench and are responsible for cooling the syngas and slag. The product gas passes downwards through a dip tube and bubbles through the quench bath, which provides secondary cooling. Alternately, the quench bath level can be kept low enough that the gas does not bubble through, thereby achieving a partial quench. Solidified slag falls to the bottom of the quench bath, which is deep enough to hold approximately 24 hours’ inventory at full load.

**Injector Development**

Performance of an entrained-flow gasifier, whether industrial scale or pilot scale like the University of Utah’s system, is highly dependent on the efficiency of the injector. The injector introduces the high-pressure oxygen and coal slurry and is responsible atomizing the coal slurry into fine droplets/particles. The injector in the Utah gasifier presents a particular challenge, since geometries for the slurry and oxygen streams are much smaller than in industrial-scale systems. Most coal-water slurry injectors are

![Figure 19. Rendering of the entrained-flow gasifier and split view of same.](image)
“3-stream” designs, in which oxygen flows through a center channel, coal slurry flows through an annulus around that and additional oxygen flows through an outer annulus. Ideally, we would like to have a 3-stream injector for the Utah gasifier, since that provides superior atomization. However this requires that the coal slurry flows through an annulus. If typical scaling criteria were to be used, the annulus gap would end up being very small, approximately 0.1 inch, and there is concern that that injector would plug. Ensuring that the three streams would be well-centered also presents challenges.

For this reason, it was decided that the initial injectors in the Utah system would be 2-stream designs, with coal flowing through a central channel and oxygen flowing around that. Since the coal does not have to flow through an annulus, the risk of plugging with this design is minimized. The drawback, however, is that it is more challenging to atomize the coal since the single pencil-like stream can only be shattered with oxygen from the perimeter instead of both from the perimeter and the interior.

Development and improvement of injector designs will likely continue as long as the gasifier remains in operation. In order to help evaluate injector performance, a simple atmospheric-pressure ex-situ injector test system was constructed. The system uses water and compressed air to simulate slurry and oxygen, although it is possible to feed slurry into the system using the gasifier’s Moyno pump if desired. The system simply sprays into a barrel, but the injector is positioned above the opening of the barrel so that the spray pattern can be seen. Evaluation involves a combination of visual assessment, photography and measurement of spray angle as a function of air and water flows for the various designs of injectors.

The first injector tested was adjustable and allowed the spacing of the oxygen annulus, and thus the pressure drop of the oxygen, to be changed during operation. This adjustable injector was very useful for identifying suitable geometries and operating regimes. However, during campaigns in the gasifier it proved to be too instable and could not provide consistent performance. During the second year of the program, a variety of fixed injectors were constructed and displayed more consistent performance, although still not as good as desired when the system was operated at high load. Results from the injector test systems are presented in the Results and Discussion section.

System Operation

This research program represented a number of “firsts” for operation of pilot-scale equipment at the University of Utah. It was the first time the entrained-flow gasifier, including all necessary auxiliary systems, was operated as an integrated unit. It was the first time oxygen was introduced into a pressurized system, and it was the first time any system was operated at pressures exceeding 50 psi. It was the first time a coal slurry was prepared and fed into a reacting system, and it was the first time handling molten coal slag which had to be kept from plugging the reactor.

In order to ensure safe and reliable commissioning of the system, initial tests were relatively short (1-2 hours) and performed at low load and at relatively low pressure (50-80 psi). As the operators became comfortable with operation and behavior of the gasifier, it was pushed to higher load and pressure. Over time, the point was reached where it was possible to operate at the maximum system pressure of 250 psig.
(18 bar absolute pressure), which is limited by the oxygen supply pressure. Under these conditions, thermal load was approximately 1 million Btu/hr (300 kW). Much of the focus during operation was placed on startup of the reactor and transition to operation on coal slurry. The method was modified and improved over time to ensure safe and effective operation. The method described here is the final chosen procedure. Startup involved heating the reactor for 2-3 days using a natural gas burner to ensure that the refractory was sufficiently hot and that temperatures had come to steady state. Coal slurry was prepared by mixing pulverized coal (~70 micron mean size) and water, plus potentially a powdered fluxing agent such as limestone or borax. To begin operation on coal, the natural gas burner was turned off and carefully removed from the reactor. The water-cooled coal injector was placed into the reactor with a new gasket and the flange was tightened down. To begin with, an alcohol, either isopropyl alcohol or denatured ethanol, was fed through the injector. This was done because these fuels are much more volatile than coal slurry, and it was easy to get a flame going. After approximately 10 seconds of alcohol feed, oxygen flow was begun corresponding to a stoichiometric ratio of roughly 0.6 (i.e., gasification conditions). The alcohol would immediately ignite off the heat from the refractory walls and make a hot flame. Once the flows were stable and the system began to heat up again (after heat loss resulting from the burner exchange) the pressure control valve was closed and the system was allowed to pressurize to approximately 50 psig. Once the system had reached this pressure with alcohol feed, a 3-way valve was turned, which immediately replaced the alcohol feed with the coal slurry feed. The transition between fuels was smooth, and it was clear when the slurry reached the injector because the temperature in the reactor would drop a bit. At this point the oxygen flow rate was increased a bit to the desired value for the coal. The system continued to be pressurized to the desired operation pressure, usually 200 to 250 psig, as the flow rates of slurry and oxygen were increased proportionally to maintain a given residence time.

Once final operating conditions were achieved, the gasifier operated very smoothly. Maintaining pressure could be a challenge; depending on conditions it could vary by as much as 6-7 psi from the target pressure. However, the overall system was quite forgiving.

Shutdown and return to natural gas standby involved decreasing slurry and oxygen flow and allowing the pressure to fall to about 100 psi. At this point water was fed through the slurry line to clean it out. As soon as the flame was extinguished, oxygen flow ceased and the system was allowed to depressurize naturally with only nitrogen purge flowing through the reactor. Once the system was no longer under pressure the coal injector was exchanged for the natural gas burner and the system was once again placed on natural gas standby.

The biggest challenges during operation were (1) maintaining good oxygen pressure drop across the injector and (2) avoiding slag buildup in the bottom of the reactor. High oxygen pressure drop (minimum ~40 psi) is necessary to achieve good atomization. Later designs of the injector were non-adjustable, which helped with stability. Slag buildup would often limit operating time to just 2-3 hours and continues to be a challenge at high fuel input rates. The use of fluxant improves slag flow and reduces buildup, as does operating at higher O/C ratios (higher temperatures). Injector design development and slag handling will undoubtedly continue to be important research considerations.
RESULTS AND DISCUSSION

Subtask 4.1 – Entrained-Flow Gasifier Simulation and Modeling

Verification (Numerical Uncertainty Quantification) Results

Code Verification Results

The code verification procedure was performed for a manufactured solution with spatial dependence, with the function given by equation A-25. This has a source term given by equation A-26. When this field is transported in a transport equation framework, the exact solution is available and can be compared to the value computed by the CFD code.

The results of this comparison are presented in Figure 20. The observed order and error as a function of grid resolution were computed using the L-2 norm. The resulting plots show that the order of convergence of the calculation of the MMS from Arches, with respect to the grid resolution \( h \), is of order 2-2.5.

![Figure 20. Results of the code verification grid convergence study. The observed order as a function of grid resolution is plotted on the left, while the error norm as a function of grid resolution is plotted on the right. The observed order of convergence is ~2-2.5.](image)

Solution Verification Results

An analysis of the effects of the main and interaction effects of the numerical parameters \( h \) and \( N \) showed that the interaction effect between the two variables is relatively important for several concentration profiles, and therefore cannot be ignored (Figure 21). For this reason, the two procedures suggested by Logan and Nitta, mentioned above, were used to determine the order of convergence of the Arches simulations.
The solution verification was performed for a gasifier that was reduced in length, so that the domain was 0.2 m in length (the same as the diameter of the gasifier). Nine system responses were analyzed to determine the order of convergence for the system of interest: time-averaged centerline profiles of three species (CO, CO$_2$, H$_2$) and radial profiles at $x=0.10$ m and $x=0.20$ m, also for the same three species (CO, CO$_2$, H$_2$).

The two tests suggested by Logan and Nitta both suggested selecting various values of the convergence orders $p$, $q$, $r$, and $s$, and minimizing R-squared and MSE. The results of this procedure are shown in Figure 22 (MSE) and Figure 23 (R-squared). From the figures, it can be determined that the most appropriate values of $p$ and $q$ are $p=1$ and $q=1$.

![Graphs showing significance test results for time-averaged concentration results for a centerline profile and radial profiles at $x=0.10$ and $x=0.20$.]
Figure 22. Order of convergence analysis using the mean squared error (MSE) test. Using this test, the optimal values of p, q, r, and s are those values that minimize the mean squared error, given by equation A-18. The MSE is plotted as a function of p and q (r and s are held constant at 1). Each blue dot represents a value of MSE for various values of the other parameters.
Figure 23. Order of convergence analysis using the R-squared test. This attempts to minimize the R-squared value of the regressed data. Plotted are the R-squared values as a function of the parameters p and q (r and s are held constant at 1). Each blue dot represents a value of R-squared for various values of the other parameters.

Validation (Empirical Uncertainty Quantification) Results

Surrogate Model Results: Screening Study

The sequential assembly procedure described above was applied to construct a surrogate model for the Arches gasification model. The first step was to run a screening study, which was a 1/8 fractional factorial design intended to reveal important main effects with a minimal number of runs (8 total). The various combinations of parameter values for each of the 8 runs are given in Table 7. The screening study revealed some interesting results.
Table 7. Screening study used for the first step of sequential assembly of the Arches coal gasification model response surface.

<table>
<thead>
<tr>
<th>Run</th>
<th>( E_2 )</th>
<th>( A_2 )</th>
<th>( T_{\text{wall}} )</th>
<th>( E_{\text{h-CO}_2} )</th>
<th>( \overline{d_p} )</th>
<th>( m_{\text{coal}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>screen-1</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>screen-2</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>screen-3</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>screen-4</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>screen-5</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>screen-6</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>screen-7</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>screen-8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

For each of the 8 simulations, time-averaged concentration profiles were extracted from the temporally and spatially dependent concentration fields computed by the gasification model in Arches. Some preliminary comparisons to data for a selection of cases and a single response are presented in Figure 24 through Figure 26, which compare the gasifier concentration profiles measured experimentally by Brown with the concentration profiles computed in Arches (note that, because of the large number of results and data, only a selection is shown). These plots are both constructed from the same amount of data; that is, five radial points at six axial locations. Also plotted, in Figure 27, are residuals from comparison of the experimental data points to the Arches model predictions.

![Figure 24](image_url)

Figure 24. Concentration contours for Brown's experimental data (top) and Arches computations for case screen-1 (bottom) for CO concentration.
Based on a visual assessment of the comparisons of model predictions to experimental data, the results show fair agreement. Many of the features of the experimental data are captured by the Arches simulations. Furthermore, incorporating the experimental error into the comparison would certainly improve the agreement. However, how well the model prediction matches the data varies significantly with the parameter values. A qualitative comparison is insufficient to determine which parameter values are “good” and which ones are not. It is for this reason that a statistical analysis is used to investigate the main effect of each of the six screening study factors.

Figure 25. Concentration contours for Brown's experimental data (top) and Arches computations for case screen-2 (bottom) for CO concentration.
The main effects for each factor were computed, and are presented in Table 8. Determining the factors with the most significant main effects was difficult, given that there were 90 total response surfaces.
species concentrations, 5 radial location measurements, and 6 axial location measurements), with potentially different rankings of significant effects for each response. For this reason, the gasifier was divided into two zones, the near-injector region (Zone I) and the near-exit region (Zone II). In the first zone, devolatilization was the dominant mechanism, so the factors with the strongest main effects were likely to be those related to the devolatilization reaction. Char oxidation reactions were the dominant mechanism in the second zone. There is no distinct cutoff between the location of Zone I and Zone II, but it was approximated as being halfway through the gasifier (60 cm). The main effects were computed for the entire reactor, as well as separately for Zone I (first three axial locations) and Zone II (last three axial locations).

Table 8. Main effects for each variable on the three responses of interest, computed from the screening study. The main effects are averaged over all spatial locations and ranked in order of most to least significant effect

<table>
<thead>
<tr>
<th>Variable</th>
<th>[CO₂]</th>
<th>[CO]</th>
<th>[H₂]</th>
<th>Mean Main Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₂</td>
<td>0.0698</td>
<td>0.0494</td>
<td>0.0133</td>
<td>0.0441</td>
</tr>
<tr>
<td>( \bar{d}_p )</td>
<td>0.0343</td>
<td>0.0276</td>
<td>0.0070</td>
<td>0.0230</td>
</tr>
<tr>
<td>T&lt;sub&gt;wall&lt;/sub&gt;</td>
<td>0.0246</td>
<td>0.0128</td>
<td>0.0114</td>
<td>0.0163</td>
</tr>
<tr>
<td>( \dot{m}_{\text{coal}} )</td>
<td>0.0278</td>
<td>0.0104</td>
<td>0.0085</td>
<td>0.0155</td>
</tr>
<tr>
<td>E₂–CO₂</td>
<td>0.0135</td>
<td>0.0032</td>
<td>0.0025</td>
<td>0.0064</td>
</tr>
<tr>
<td>A₂</td>
<td>0.0011</td>
<td>0.0008</td>
<td>0.0010</td>
<td>0.0010</td>
</tr>
</tbody>
</table>

The residual error contour plot given in Figure 27 is also informative. This type of plot provides an initial indication of problem areas; that is, areas where the model does not match the data well. Combined with the results of a statistical analysis that identifies a factor with a large main effect in that region, problematic factors and submodels may be identified.

The main effects in Zone I computed from the screening study are presented in the table in Table 9. The devolatilization process is likely a very strong influence, as the two most significant main effects, E₂ and mean particle size, directly control the rate of the devolatilization process. This, in turn, controls the rate of fuel release in the reactor. The coal particles enter the domain at room temperature, heat up, and release all of their volatile gas along the centerline, creating local conditions rich in fuel. The first step, the heating rate, is controlled by the particle size, while the second, the devolatilization reaction, is controlled by E₂, the high-temperature devolatilization reaction activation energy. Note that the main effect for E₂ is nearly three times the main effect for mean particle size. The mass flowrate and wall temperature main effects are also significant, though about half as much as the particle size main effect. This is not surprising, as both these factors also contribute to the mechanism of particle heating and devolatilization. The mass flowrate can lead to greater amounts of fuel in the domain, but it can also contribute to thermal inertia, keeping particles from heating up as fast. It also changes the gas flow field through the axial momentum source term, which is proportional to the mass flowrate. Likewise, the wall temperature affects the temperature of the recirculation zone and indirectly controls the temperature of the first hot gas the particles encounter.

63
Table 9. Zone I main effects for each variable on the three responses of interest, computed from the screening study. The main effects are averaged over Zone I and ranked in order of most to least significant effect.

<table>
<thead>
<tr>
<th>Variable</th>
<th>[CO₂]</th>
<th>[CO]</th>
<th>[H₂]</th>
<th>Mean Main Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₂</td>
<td>-0.0998</td>
<td>0.0472</td>
<td>0.0174</td>
<td>0.0548</td>
</tr>
<tr>
<td>dₚ</td>
<td>0.0343</td>
<td>0.0231</td>
<td>0.0033</td>
<td>0.0203</td>
</tr>
<tr>
<td>Twall</td>
<td>0.0182</td>
<td>0.0126</td>
<td>0.0085</td>
<td>0.0131</td>
</tr>
<tr>
<td>mcoal</td>
<td>0.0132</td>
<td>0.0022</td>
<td>0.0144</td>
<td>0.0099</td>
</tr>
<tr>
<td>Eₕ−CO₂</td>
<td>0.0055</td>
<td>0.0031</td>
<td>0.0008</td>
<td>0.0032</td>
</tr>
<tr>
<td>A₂</td>
<td>0.0021</td>
<td>0.0015</td>
<td>0.0019</td>
<td>0.0018</td>
</tr>
</tbody>
</table>

The main effects in Zone II, the char oxidation region in the latter half of the gasifier, are also presented in Table 10. The variables appear largely in the same order, with only wall temperature and mass flowrate switching spots. This is likely due to the gas-phase chemistry; lower wall temperature can lead to slower devolatilization, which leads to fuel being released at a different location in the reactor. This affects the local concentrations of fuel and the char oxidation process. Despite the fact that much less devolatilization occurs in Zone II than in Zone I of the gasifier, the devolatilization activation energy parameter still has a strong main effect due to its influence over all aspects of the gas phase chemistry. The influence of this parameter propagates through the entire gasifier.

Table 10. Zone II main effects for each variable on the three responses of interest, computed from the screening study. The main effects are averaged over Zone II and ranked in order of most to least significant effect.

<table>
<thead>
<tr>
<th>Variable</th>
<th>[CO₂]</th>
<th>[CO]</th>
<th>[H₂]</th>
<th>Mean Main Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₂</td>
<td>0.0397</td>
<td>0.0516</td>
<td>0.0092</td>
<td>0.0335</td>
</tr>
<tr>
<td>dₚ</td>
<td>0.0343</td>
<td>0.0321</td>
<td>0.0105</td>
<td>0.0257</td>
</tr>
<tr>
<td>Twall</td>
<td>0.0359</td>
<td>0.0234</td>
<td>0.0084</td>
<td>0.0026</td>
</tr>
<tr>
<td>mcoal</td>
<td>0.0373</td>
<td>0.0082</td>
<td>0.0085</td>
<td>0.0180</td>
</tr>
<tr>
<td>Eₕ−CO₂</td>
<td>0.0215</td>
<td>0.0032</td>
<td>0.0041</td>
<td>0.0096</td>
</tr>
<tr>
<td>A₂</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.0002</td>
</tr>
</tbody>
</table>

Surrogate Model Results: Full Factorial Design

Based on the screening design results, the char oxidation activation energy and devolatilization reaction pre-exponential factor were both eliminated as factors for the next step of the response surface assembly. Eight supplementary runs were performed to complete a full factorial design for the remaining four variables. The parameter combinations used for each of these runs is given in Table 11. Once the full factorial was run, a preliminary response surface could be constructed and linear interaction terms, as well as non-aliased main effects, could also be calculated. These are presented in Table 12 and Table 13.
Table 11. Full factorial design for the screening study variables with the 4 largest main effects. Table 2 contains the screening study design points, while this table contains the complementary design points, which compose a full factorial design when combined with the screening study design points.

<table>
<thead>
<tr>
<th>Run</th>
<th>E_2</th>
<th>T_wall</th>
<th>(\overline{d_p})</th>
<th>(\dot{m}_{\text{coal}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>fact-9</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>fact-10</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>fact-11</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>fact-12</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>fact-13</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>fact-14</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>fact-15</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>fact-16</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 12. Main effects for each variable on the three responses of interest, as determined by the factorial design. The main effects are averaged over all spatial points and ranked in order of most to least significant effect.

<table>
<thead>
<tr>
<th>Variable</th>
<th>[CO_2]</th>
<th>[CO]</th>
<th>[H_2]</th>
<th>Mean Main Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_2</td>
<td>0.0715</td>
<td>0.0498</td>
<td>0.0141</td>
<td>0.0451</td>
</tr>
<tr>
<td>T_wall</td>
<td>0.0344</td>
<td>0.0224</td>
<td>0.0173</td>
<td>0.0247</td>
</tr>
<tr>
<td>(\overline{d_p})</td>
<td>0.0309</td>
<td>0.0283</td>
<td>0.0080</td>
<td>0.0224</td>
</tr>
<tr>
<td>(\dot{m}_{\text{coal}})</td>
<td>0.0231</td>
<td>0.0101</td>
<td>0.0077</td>
<td>0.0136</td>
</tr>
</tbody>
</table>

Table 13. Two way interaction effects as determined by the full factorial design. The interaction effects are averaged over all spatial points and ranked in order of most to least significant effect.

<table>
<thead>
<tr>
<th>Variable</th>
<th>[CO_2]</th>
<th>[CO]</th>
<th>[H_2]</th>
<th>Mean Interaction Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_2 x (\dot{m}_{\text{coal}})</td>
<td>0.0091</td>
<td>0.0109</td>
<td>0.0055</td>
<td>0.0085</td>
</tr>
<tr>
<td>E_2 x (\overline{d_p})</td>
<td>0.0011</td>
<td>0.0223</td>
<td>0.0012</td>
<td>0.0082</td>
</tr>
<tr>
<td>(\overline{d_p}) x (\dot{m}_{\text{coal}})</td>
<td>0.0071</td>
<td>0.0029</td>
<td>0.0016</td>
<td>0.0039</td>
</tr>
<tr>
<td>T_wall x (\dot{m}_{\text{coal}})</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.0002</td>
</tr>
<tr>
<td>T_wall x (\overline{d_p})</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>E_2 x T_wall</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

A visual ranking of these effects is given for Zone I of the gasifier in Figure 28. There are several main effects that stand out from the main cluster, indicating that they are of particular significance. Most of the interaction effects, however, are clustered around the center. A few, specifically the two interaction effects with the largest significance, can be seen to deviate somewhat from the cluster of interaction effects in the center of the plots. This is an indication that they are important, but it is obvious from both these plots and the tables that the main effects are of primary importance, with interaction effects of much lower importance.
A preliminary response surface was regressed to the Arches simulation results from the full factorial design, resulting in the three response surfaces given by equations 27, 28, and 29 (Appendix A). While further statistical analysis is needed to evaluate how well this response surface represents the true function, Arches, this surrogate model is an excellent starting point. As a result of the sequential assembly of the response surfaces given in equations 27-29, much greater confidence may be invested in the resulting response surfaces and the decisions (and justifications of those decisions) that went into their assembly.

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

**One-Dimensional Turbulence**

We have assessed the ability of ODT to reproduce DNS data of nonpremixed CO/H₂ jets with extinction and reignition (Punati et al. 2009, 2011). Results of this work indicate that ODT can reproduce many statistics associated with extinction and reignition in turbulent flows. Figure 29 depicts some of the results from (Punati et al. 2011) and shows the ability of ODT to capture the flow entrainment and large scale mixing (evidenced by accurate evolution of the mixture fraction profiles) as well as its ability to reproduce the extinction and reignition present in the DNS dataset (evidenced by the time evolution of the mean OH profiles). ODT can also provide statistics of the flow such as conditional PDF evolution, etc. (Punati et al. 2011).
Work related to the ODT model development resulted in the following publications and conference proceedings (Puntai et al. 2009, 2010; Puntai and Sutherland 2010; Sutherland et al. 2010).

**Principal Component Analysis**

PCA has been applied to both DNS and ODT data. Among the most notable results obtained thus far:

- As the model dimensionality ($n_\eta$) is increased, the parameterization error decreases exponentially for all state variables (Parente et al. 2007; Parente 2008; Parente et al. 2009b; Sutherland and Parente 2009). This encouraging result suggests great potential for using PCA as a basis for combustion modeling.

- PCA can be used to identify structure in the state variables to aid in interpretation of physical phenomena in complex reacting flow systems. Recently, PCA has been applied to experimental data from MILD (flameless) combustion systems (Parente et al. 2009a, 2011) to show the variation in the structure of the thermochemical state and characterize finite-rate chemistry effects.

- As filtering is applied, the structure of the PCA remains unchanged and the accuracy of the reconstruction is insensitive to the filter width. This is shown in Figure 30, where the five largest components of $Q$ corresponding to the first PC are shown at filter widths up to 32 times the DNS grid spacing. This implies that PCA identifies structure in the system that is independent of the length scale, and is a major advantage of PCA-based methods since no turbulent closure (e.g. convolution with a joint PDF) is required.

A significant challenge remains for PCA-based modeling to become a viable modeling strategy: parameterization of source terms. When the transport equations for the PCs are derived, they contain chemical source terms, which are linear combinations of the original chemical source terms. While PCA can reproduce the original variables with good accuracy, reproduction of chemical source terms, which are highly nonlinear functions of the original variables, is significantly more challenging. Our recent efforts have focused on this area, but it is something that will certainly require more research effort.
Figure 30. Weights for the five largest components of the first eigenvector (corresponding to the first PC) as a function of filter width, showing that the PCA is insensitive to filtering.

Assuming that the data from which the PCA is constructed is relevant to the intended application, one may determine a model that satisfies a user-specified error tolerance on one or more quantities. While approaches such as ILDM (Maas and Pope 1992), CSP (Lam and Goussis 1988), etc. have this characteristic, no parameterization-based approaches currently do. Conversely, one may specify the dimensionality of the model (number of parameters) and extract a model (with a priori error estimates) that best represents the state space of the system given the specified dimensionality. Furthermore, as evidenced by Figure 30, this parameterization is unaffected by filtering, i.e., for a PCA-based mapping for $\phi = \{T, p, Y_i\}$, $\phi' = \mathcal{G}(\phi)$, $\bar{\phi}' = \mathcal{G}(\bar{\phi})$. This is a noteworthy characteristic of these methods, since the joint PDF of $\eta$ does not need to be constructed.

The following publications and conference proceedings have resulted from the work on PCA: Biglari and Sutherland (2010), Parente et al. (2009a,b; 2011), and Sutherland and Parente (2009).

**Subtask 4.3 – Radiation Modeling**

Several benchmark cases for verification have been selected. Many of these cases have previously been used by our research group and have been found to be acceptable benchmarks for our purposes. These cases will allow us to validate our data obtained via the RMCRT technique. The cases are outlined as follows.
1. Emitting/absorbing media with cold black walls. A 3D black enclosure bounds an absorbing/emitting medium. The temperature is homogeneous, but the absorption coefficient is non-homogeneous and varies linearly with position (Burns 1997). We have used this case for verification studies for serial and parallel runs of RMCRT simulations.

2. Nonblack surfaces: Two parallel plates with different reflective and emission coefficients surfaces with absorbing/emitting media (Modest 2003). This case will verify the ability of RMCRT to handle reflections off of, and emission from the bounding surfaces. The physics necessary to implement this benchmark have been added to the RMCRT algorithm.

3. Isotropic and nonisotropic scattering media: This case will be used to verify the RMCRT solver for both isotropic and nonisotropic scattering media bounded with cold black surfaces (Busbridge et al. 1967). This case will be useful for more sophisticated validation studies.

4. Isotropic scattering media bounded with gray walls: The ability of our algorithm to solve problems involving isotropic scattering media will be validated using data from a one-dimensional parallel gray plates problem and bounded with gray wall (Fiveland 1987). This case will be useful for more sophisticated validation studies.

The RMCRT algorithm has been verified against a benchmark case that represents a 3D enclosure with an emitting/absorbing medium. This case was described by Modest, and is summarized above in benchmark 2. Furthermore, the L2 error norm of the data decreases as expected with an increase in the number of rays traced per cell, such that at approximately 1000 rays, the error norm is less than 0.5% (see Figure 3).

Increased generality was added to the RMCRT algorithm to allow the user to specify any aspect ratio of rectangular cells. This feature was verified using benchmark 1 using a domain of 1m^3 with cell aspect ratios of approximately 4:3:2 using 41X31X21 cells. The radiative results obtained by RMCRT are in agreement with the exact solution as demonstrated in Figure 31 - Figure 33. In all figures below, the x axis represents in meters, the distance from the negative face of the domain.

![Figure 31](image-url) 
**Figure 31.** Exact solution vs. that from RMCRT for the x-direction of a non-cubic domain of size 41X31X21.
Figure 32. Exact Solution vs. that of RMCRT in the y-direction of a non-cubic domain of size 41X31X21.

Upon completion of the verification testing, the RMCRT code was implemented into the Arches framework for simplified gasification cases.

Figure 33. Exact solution vs. that of RMCRT for the z-direction of a non-cubic domain of size 41X31X21.

Upon completion of the verification testing, the RMCRT code was implemented into the Arches framework.
Tar/Soot and Char Formation and Modeling Studies

Pyrolysis products (tar/soots and chars) from the two coals at various temperatures were collected at three HAB (1 3/8”, 2” and 3”). The data for these samples and representative C-13 CPMAS spectra are collected in the following tables and figures.

Eastern bituminous. A 1484 K char sample from the Eastern bituminous coal, collected at 2” above the burner, appears to be too highly carbonized (all aromatic and conductive) for useful NMR analysis (see Figure 34). However, the tar soot sample (see Figure 35) provides some useful information. A standard set of structural and lattice parameters previously developed1 is used to describe these types of amorphous carbonaceous materials.

The NMR structural data for the Eastern bituminous coal and two tar/soots (1150 K and 1300 K) are given in Table 14 and the NMR spectra for these samples are shown in Figure 35. The coal has a corrected aromaticity, $f_a'$, of 0.65, the 1150 K tar/soot a value of 0.87, and the 1300 K tar/soot a value of 0.92. The average aromatic cluster size (C) is the same within experimental error (~ +/- 2) and has a value of about 16 – 17 in the three samples. Usually tars have a slightly smaller cluster size compared to the starting coal as the smaller molecules leave the lattice as tar, and the larger clusters remain in the char and are more extensively cross linked. Since the tar from this sample is the same size as the coal there may have been secondary reactions in the gas phase (these secondary reactions convert tar into soot at higher temperatures). One can also see a selective loss of phenolic groups (152 ppm shoulder on the aromatic band) as the temperature is increased. When there are large changes in aromaticity one should look at the relative phenolic content $f_a^p/f_a'$ rather than the amount per 100 carbons, $f_a^p$. If one lost all aliphatic material but did not change the aromatic content, the numbers per 100 carbons would change but the aromatic structure such as cluster size, C, would be unchanged. The aliphatic region in the coal has the highest peak at about 30 – 34 ppm where methylene groups are found but in the 1150 K tar/soot the highest peak is about 20 ppm and is due to methyl groups on aromatic rings. These aliphatic peaks and most of the remaining aliphatic material have been lost at 1300 K.
Figure 34. A single pulse spectrum of a highly carbonized char made at 1484 K from the Eastern bituminous coal. Sample was collected at 2” HAB and 1 atmosphere pressure.
Figure 35. C-13 CPMAS NMR spectra of the original Eastern bituminous coal (bottom) and two tar/soots made at 1100 K (middle) and 1300 K (Top) from the coal. Samples were collected at 3” HAB and at 1 atmosphere pressure.

Table 14. Eastern bituminous coal and two tar/soots collected at 3” HAB.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$f_2$</th>
<th>$f_2^C$</th>
<th>$f_2^H$</th>
<th>$f_2^{CO}_2$</th>
<th>$f_2^{CO}_1$</th>
<th>$f_2^O$</th>
<th>$f_2^N$</th>
<th>$f_2^a$</th>
<th>$f_2^m$</th>
<th>$f_2^{al}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>0.67</td>
<td>0.02</td>
<td>0.005</td>
<td>0.015</td>
<td>0.65</td>
<td>0.20</td>
<td>0.45</td>
<td>0.06</td>
<td>0.17</td>
<td>0.22</td>
</tr>
<tr>
<td>Tar/Soot 1150 K</td>
<td>0.89</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.87</td>
<td>0.42</td>
<td>0.45</td>
<td>0.06</td>
<td>0.10</td>
<td>0.29</td>
</tr>
<tr>
<td>Tar/Soot 1300 K</td>
<td>0.95</td>
<td>0.03</td>
<td>0.01</td>
<td>0.02</td>
<td>0.92</td>
<td>0.18</td>
<td>0.54</td>
<td>0.04</td>
<td>0.19</td>
<td>0.31</td>
</tr>
</tbody>
</table>

The NMR parameters for pyrolysis products from the Eastern bituminous coal at a height of 1 3/8” are given in Table 15, and representative C-13 CPMAS spectra are shown in Figure 36. At this height there is less time for secondary reactions in the gas phase as compared to the 3” discussed above. At 1350 K Table 15 shows the corrected aromaticity,$f_2^C$, has a value of 0.90 for both the char and tar/soot, much higher than the value of 0.65 in the coal. The aromatic cluster size, C, is smaller in the tar/soot (11.2) than in the original coal (16.8) and is largest in the char (18.7). Since this value is smaller in the tar/soot than the coal, extensive secondary gas-phase reactions probably have not taken place, probably due to a
shorter “residence time” in the reaction zone so this tar/soot sample is composed primarily of tar. The missing aliphatic material present in the coal but not in the char or tar/soot has been lost as gas or converted to aromatics. The tar/soot sample at 1450 K is essentially all aromatic carbon. From dipolar dephasing results if one assumes that all non-protonated aromatic carbons are bridge heads (and not biaryl linkages) the aromatic cluster size would be about 41 carbons and that should be taken as a maximum limit. This sample is just starting to become conductive as measured by probe detuning and one can see wings starting to extend from the aromatic band shape as is seen for samples when they become conductive and more carbonized. This tar/soot 1450 K sample is really just soot. All samples made at higher temperatures, such as the Eastern Bituminous coal at 1484 K, collected at 2” above the flat-flame burner at a pressure of 5 atmospheres, would be expected to be conductive and have larger aromatic ring systems with fewer protons. The char sample collected under these conditions cannot be studied by cross polarization NMR experiments since there are not enough protons left in the structures to facilitate the cross polarization experimental conditions. For these types of samples one must use single-pulse techniques (see Figure 34) to observe all of the carbons atoms. These types of highly carbonized samples are not particularly suitable for NMR analysis.

Table 15. Eastern Bituminous Coal and Pyrolysis Products at HAB1 3/8.

<table>
<thead>
<tr>
<th>Structural Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
</tr>
<tr>
<td>-----------------------</td>
</tr>
<tr>
<td>Coal</td>
</tr>
<tr>
<td>Tar/soot 1350 K</td>
</tr>
<tr>
<td>Char 1350 K</td>
</tr>
<tr>
<td>Tar/soot 1450 K</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Lattice Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>Coal</td>
</tr>
<tr>
<td>Tar/soot 1350 K</td>
</tr>
<tr>
<td>Char 1350 K</td>
</tr>
<tr>
<td>Tar/soot 1450 K</td>
</tr>
</tbody>
</table>
Figure 36. C-13 CPMAS spectra of the Eastern bituminous coal (bottom), a matched tar/soot and char pair in the two (middle) spectra and a tar/soot at 1450 K (top) spectrum. Samples were collected at 1 3/8” HAB at 1 atmosphere pressure.

A single-pulse spectrum of an Eastern bituminous char formed at 1484 K and collected 2” HAB is shown in Figure 34. The proton 90 degree pulse, usually at around 4.1 µs for normal samples, has lengthened to about 6.2 µs at the same power for this very carbonized and conductive sample. Cross polarization would probably not see the inner aromatic carbon atoms in these very large condensed ring systems that must be present in this sample and are not close to the protons on the outer edge of these large ring systems. This is a totally aromatic system and NMR cannot give more information about this sample. A short contact time spectrum was attempted but showed no aliphatic material.

The C-13 CPMAS spectra of a tar/soot made from the eastern bituminous coal is shown in Figure 35. The spectrum taken with a 5 ms contact time exhibits all carbon types that are present in this sample. One notes, however, that the extended wings from the aromatic band masks the presence of other carbon types that may still be present in small quantities. These broad tails are present in all highly carbonized materials. This sample only slightly detuned the probe and hence, is much less carbonized than the companion char discussed above (see Figure 34). The spectrum taken at a much shorter contact time (5 us) shows a small amount (of the order of 1%) aliphatic material that is totally obscured in the 5 ms contact time spectrum when the nonprotonated carbons are also included. A dipolar dephasing experiment, using a 5ms contact time, of this material gave an upper limit of the average aromatic cluster size of about 200 carbons (assuming an all aromatic system that contained no biaryl or alkyl-substituted carbon functional groups).
Wyodak. Spectra of the Wyodak coal and two tar/soots samples collected at 1150 K and 1300 K at 3” above the burner are shown in Figure 37, and the corresponding structural parameters are given in Table 16. One can see even for the lowest temperature tar/soot (1150 K) considerable structural changes when compared to the parent coal. The carbonyl and carboxyl oxygen functional groups ($f_a^O$ and $f_a^{OO}$) have been lost, as has a considerable amount of the aliphatic groups dominated by the large methylene peak at about 34 ppm in the coal. The aromaticity, $f_a$, increases from 0.65 in the coal to 0.87 in the 1150 K tar/soot and moves to 0.93 for the 1300 K tar/soot. The aromatic cluster size is 11.2 for the coal. The average cluster size of the 1150 K tar/soot (which is 10) is slightly smaller but is still within the experimental error. The cluster size is 12.7 for the higher temperature tar/soot as slightly larger molecules are now lost from the lattice into the gas phase and/or a few secondary gas phase reactions may have occurred. One can see that the average number of attachments per aromatic cluster, $\sigma + 1$, for the tars is smaller (3.1 and 3.2) than that of the coal (5.2) as the more reactive (and smaller) structures are first released from the lattice as tar.

Figure 37. C-13 CPMAS spectra the Wyodak coal (bottom) and tar/soots made at 1150 K (middle) and 1300 K (top). Samples were collected at 3” HAB at 1 atmosphere pressure.
Two tar/soot and char pairs made from the Wyodak coal at 1350 K and supposedly at 1450 K and collected at 1 3/8 “ above the burner are shown in Figure 38, and the structural parameters are given in Table 17. The tar at 1350 K has an aromatic cluster size of 11.6, which is approximately the same size as the coal. The 1350 K char has a much higher cluster size of 17.9 as would be expected for a char sample made at this temperature. The aromaticity is 0.89 for both of these samples. These two samples have also lost phenolic groups that are very abundant in the coal. When one examines the tar/soot and char samples that were collected at 1450 K, one can clearly see by looking at the spectra that these samples are not carbonized enough to have reached this temperature. These spectra should be compared to the tar/soot at 1450 K from the Eastern bituminous coal shown in Figure 2. This is the amount of carbonization one would expect. When one has a cluster size of 17.9 at 1350 K and then measures (twice) a cluster size of 11.0, 12.8 for a sample made at 1450 K it is clear that the experimental temperature is incorrect. This shows that when one runs a series of samples at progressive temperatures NMR is sensitive to the loss of functional groups and can be used to monitor the extent of carbonization.
Figure 38. C-13 CPMAS spectra of the Wyodak coal (bottom) and 1350 K tar/soot and char pairs (2 and 3 from bottom) and 1450 K tar/soot and char pairs (4 and 5 from bottom). Samples were collected at 1 3/8” HAB and 1 atmosphere pressure.

Table 17. Wyodak coal and tar/soots and chars HAB 1 1/8”.

<table>
<thead>
<tr>
<th>Structural Parameters</th>
<th>Compound</th>
<th>$f_a$</th>
<th>$f_a^C$</th>
<th>$f_a^O$</th>
<th>$f_a^{OO}$</th>
<th>$f_a'$</th>
<th>$f_a^H$</th>
<th>$f_a^N$</th>
<th>$f_a^P$</th>
<th>$f_a^S$</th>
<th>$f_a^B$</th>
<th>$f_{al}$</th>
<th>$f_{al}^H$</th>
<th>$f_{al}^*$</th>
<th>$f_{al}^O$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>0.65</td>
<td>0.09</td>
<td>0.03</td>
<td>0.06</td>
<td>0.56</td>
<td>0.17</td>
<td>0.39</td>
<td>0.10</td>
<td>0.16</td>
<td>0.13</td>
<td>0.35</td>
<td>0.22</td>
<td>0.13</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Tar/Soot 1350 K</td>
<td>0.89</td>
<td>0.02</td>
<td>0.00</td>
<td>0.02</td>
<td>0.87</td>
<td>0.42</td>
<td>0.45</td>
<td>0.06</td>
<td>0.18</td>
<td>0.21</td>
<td>0.11</td>
<td>0.08</td>
<td>0.03</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Char 1350 K</td>
<td>0.89</td>
<td>0.03</td>
<td>0.01</td>
<td>0.02</td>
<td>0.86</td>
<td>0.31</td>
<td>0.55</td>
<td>0.06</td>
<td>0.18</td>
<td>0.31</td>
<td>0.11</td>
<td>0.07</td>
<td>0.04</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Tar/Soot 1450 K</td>
<td>0.90</td>
<td>0.04</td>
<td>0.02</td>
<td>0.02</td>
<td>0.86</td>
<td>0.40</td>
<td>0.46</td>
<td>0.05</td>
<td>0.18</td>
<td>0.23</td>
<td>0.10</td>
<td>0.07</td>
<td>0.03</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Char 1450 K</td>
<td>0.83</td>
<td>0.04</td>
<td>0.02</td>
<td>0.02</td>
<td>0.79</td>
<td>0.39</td>
<td>0.40</td>
<td>0.05</td>
<td>0.17</td>
<td>0.18</td>
<td>0.17</td>
<td>0.12</td>
<td>0.05</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Char 1450 K</td>
<td>0.83</td>
<td>0.04</td>
<td>0.02</td>
<td>0.02</td>
<td>0.79</td>
<td>0.36</td>
<td>0.43</td>
<td>0.05</td>
<td>0.17</td>
<td>0.21</td>
<td>0.17</td>
<td>0.12</td>
<td>0.05</td>
<td>0.06</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Lattice Parameters</th>
<th>Compound</th>
<th>$\chi_b$</th>
<th>$C$</th>
<th>$\sigma+I$</th>
<th>$P_0$</th>
<th>B.L.</th>
<th>S.C.</th>
<th>M.W.</th>
<th>$M_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>0.232</td>
<td>11.2</td>
<td>5.2</td>
<td>0.50</td>
<td>2.6</td>
<td>2.6</td>
<td>332</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>Tar/Soot 1350 K</td>
<td>0.241</td>
<td>11.6</td>
<td>3.2</td>
<td>0.88</td>
<td>2.8</td>
<td>0.4</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>
Surrogate. Under other funding, the investigators have previously performed a detailed study of biphenyl as a surrogate under a different pyrolysis environment. An extensive amount of analytical (NMR and very sophisticated GC/MS) data were obtained together with reaction pathways for formation of most of the tar components that were present (see Fletcher et al. 1990). The tar/soot spectra made from biphenyl at 1484 K and collected at 2” above the burner are shown in Figure 39. The two other biphenyl soot samples were collected at 1405 K and 2” above the burner were analyzed by GC/MS. The GC/MS analysis revealed several pyrolytic products: terphenyl (C_{18}H_{14}), 2-phenylnaphthalene (C_{16}H_{12}), fluoranthene (C_{16}H_{10}) and/or pyrene (C_{16}H_{10}) and either benzo[a]anthracene (C_{18}H_{12}), chrysene (C_{18}H_{12}), or triphenylene(C_{18}H_{12}). All of these compounds were observed in the large array of polyaromatic compounds identified in the tar/soot materials reported in (Winans et al. 2007).

<table>
<thead>
<tr>
<th></th>
<th>0.360</th>
<th>17.9</th>
<th>5.0</th>
<th>0.83</th>
<th>4.2</th>
<th>0.8</th>
<th>--</th>
<th>--</th>
</tr>
</thead>
<tbody>
<tr>
<td>Char</td>
<td>0.267</td>
<td>12.8</td>
<td>3.4</td>
<td>0.87</td>
<td>3.0</td>
<td>0.4</td>
<td>194</td>
<td>10</td>
</tr>
<tr>
<td>1450 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Char</td>
<td>0.228</td>
<td>11.0</td>
<td>3.1</td>
<td>0.77</td>
<td>2.4</td>
<td>0.7</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1450 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Char^{1}</td>
<td>0.266</td>
<td>12.8</td>
<td>3.5</td>
<td>0.77</td>
<td>2.7</td>
<td>0.8</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1450 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Repeat analysis of the same 1450 K char sample.

Figure 39. Two spectra of a tar/soot made from biphenyl at 1484 K. The (bottom) spectrum shows all carbon types and the (top) short contact time spectrum shows mostly carbons types that are protonated. Sample was collected at 2” HAB and 5 atmosphere pressure.
Biphenyl is a completely aromatic molecule but, in the case of the 1484 K sample, a few aromatic rings must have opened during pyrolysis as a small amount (~1%) of aliphatic carbons are visible around 35 ppm in the short contact time spectrum that identifies primarily protonated carbons. The 5 ms contact time spectrum also shown in Figure 5 represents all carbons. Notice how the small aliphatic signal is almost lost in the wings from the large aromatic signal when the non-protonated carbons are also present. When a sample is highly carbonized, wings from the main aromatic signal extend into the aliphatic region of the spectrum and also into the carbon/carboxyl region of the spectrum. Structural parameters depending on chemical shifts can no longer be calculated for these highly carbonized materials as they can be for samples produced at lower temperature. This aromatic signal still has a shoulder at about 139 ppm that represents the substituted carbons connecting aromatic rings with zero mass bridges. This shoulder represents the connecting carbons as biphenyl polymerizes to form longer chains of three, four or more rings connected by biaryl linkages (see Winans et al. 2007). As the carbonization proceeds further, these biaryl linkages will go away as acetylene present in the gas phase adds to the structure to make it fully condensed and it then becomes very conductive as noted for the sample discussed below.

Since preparing the PFFB to collect coal gasification data took longer than expected, there has not been sufficient time to analyze the soot yield data from the gasification experiments. Analysis of the trends in this data must be completed before development can begin on a soot formation model that includes pressure effects.

**Pressurized Pyrolysis**

Pyrolysis experiments were conducted on 3 bituminous coals and Wyodak subbituminous coal at four pressures and peak flame temperatures of ~1700 K. One of the bituminous coals is Kentucky #9. The other two bituminous coals were obtained in connection with a separate contract and cannot be named except by the designations “Eastern Bituminous Coal A” and “Eastern Bituminous Coal B.” Most of the experimental work for these two coals was done as part of another contract, but they are included here because the analysis was done as part of this contract and they add insight to the phenomena under investigation. As described in the “approach” section, fragmentation and soot contamination made interpretation of results from bituminous coals difficult. The separation procedure developed allows upper and lower bounds for swelling to be determined, but the bounds are fairly wide. The swelling data are presented in Figure 40. Table 18 presents the mass release data as determined by the ash tracer technique along with the changes in density and the calculated heating rates.
The Wyodak swelling is essentially constant, although there is a slight indication of a maximum at 5 atm. This is consistent with expectations for low-rank coals. Extensive low-temperature cross-linking occurs with coals that have high oxygen content. This early cross-linking prevents the formation of a viscoelastic phase that can expand in response to internally generated pressure. Instead, volatiles escape through the pore structure of the coal, generating greater porosity as they are released. SEM images of freshly pyrolyzed Wyodak show some signs of softening or smoothing on the surface, but internal void space occurs in the form of pores rather than large cavities (Figure 41). The low tar content of Wyodak

81
also explains the very low sensitivity of mass release and swelling to pyrolysis pressure. Only volatiles occurring as tar have vapor pressures low enough for pyrolysis yields and coal plasticity to be affected significantly by operating pressure. The heating rates calculated for Wyodak are somewhat low compared to other coals because the sample was dried before use so that the particles did not clog in the feed system of the PFFB.

Figure 41. SEM images of Wyodak char produced at ~1700 K. Left: 2.5 atm, 33 ms. Right: 15 atm, 44 ms.

The three bituminous coals exhibited maximum swelling ratios of about 1.4-1.8 in the pressure range of 10-15 atm. The Kentucky #9 did not exhibit a maximum in this range; it continued to increase in size up to at least 15 atm. Eastern Bituminous Coal A exhibited maximum swelling near 10 atm. Swelling appeared to be somewhat constant for the Eastern Bituminous Coal B between 5 and 15 atm, but the error bars were wide enough that it could have a maximum near 10 atm or continue to increase up to at least 15 atm. At 5 atm Eastern Bituminous Coal B swelled more than any of the others, which indicates that it is probably more vulnerable to fragmentation at the higher pressures, where it is expected to swell even more. Selective fragmentation of the largest, most fragile particles could explain the lack of a distinct trend for this coal.

These data suggest that the pressure at which maximum swelling occurs may vary somewhat with coal rank. They also show how the char collection method can alter the observed results. Greater care is being taken with ongoing experiments to collect unfragmented char and to remove the soot. The heating rates calculated for the bituminous coals are between $8 \times 10^4$ K/s and $10^5$ K/s at all conditions. The swelling ratios observed for these coals indicate that the changes in particle diameter are 50%-80% less than previously reported measurements of Illinois #6 at 8 atm and $\sim 10^4$ K/s (Lee et al., 1991). In fact, swelling of bituminous coals at 15 atm in the PFFB is less than the reported Illinois #6 results at 23 atm. These measurements of coals with ranks similar to Illinois #6 confirm that the heating rate strongly influences swelling at elevated pressures.

**Coal Swelling Model**

A first-generation atmospheric coal swelling model has been developed. The model is able to predict the
trends in swelling with heating rate for bituminous coals. It is also able to predict shrinkage for subbituminous coals and lignites. The swelling ratio is defined as the ratio of the char particle diameter to the initial coal particle diameter, \(d_0/d\). The form of the swelling correlation at heating rates greater than 7×10^3 K/s (denoted by the subscript HHR for high heating rate) is:

\[
\left( \frac{d}{d_0} \right)_{HHR} = \left( s_{\text{cluster}} + s_{\text{attach}} \right) \left( \frac{\dot{T}_{\text{Base}}}{\dot{T}} \right)^{c_3} + s_{\text{min}} \quad \text{(Equation 5)}
\]

where the individual terms are calculated as follows:

\[
\dot{T} = \left( \frac{dT_p}{dt} \right)_{\text{max}} \quad \text{(Equation 6)}
\]

\[
\dot{T}_{\text{Base}} = 5.7 \times 10^4 \text{ K/s} \quad \text{(Equation 7)}
\]

\[
s_{\text{cluster}} = \left( c_1 \frac{MW}{M_\delta} \right)^{c_2} \quad \text{(Equation 8)}
\]

\[
s_{\text{attach}} = \left( c_3 [\sigma + 1] \right)^{c_4} \quad \text{(Equation 9)}
\]

\[
s_{\text{min}} = \left( \left[ 1 - V_{\text{ASTM}} \right] \left[ 1 - A_{\text{ASTM}} \right] + A_{\text{ASTM}} \right)^{c_5} \quad \text{(Equation 10)}
\]

\(V_{\text{ASTM}}\) is the ASTM volatile matter expressed as a mass fraction of the dry, ash-free coal and \(A_{\text{ASTM}}\) is the ASTM ash fraction on a dry basis. The parameter \(s_{\text{min}}\) represents the theoretical lower limit of swelling at very high heating rates, assuming that the apparent particle density is constant and the trends in the volatiles yield with coal rank can be well-represented using the ASTM volatiles. Equation 6 defines the heating rate as the maximum derivative of particle temperature with respect to time. The parameters \(c_1, c_2, c_3, c_4, \text{ and } c_5\) are adjusted constants. The parameters \(s_{\text{cluster}}\) and \(s_{\text{attach}}\) represent contributions from cluster and attachment characteristics. The parameters \(MW, M_\delta, \text{ and } \sigma + 1\) are coal structural parameters used in the CPD model that can be determined from C-13 NMR measurements. In the development and application of this model, these parameters are estimated from correlations with \(V_{\text{ASTM}}\) and the coal ultimate analysis (Genetti et al., 1999). The ratio \(MW/M_\delta\) in the \(s_{\text{cluster}}\) term is the ratio of average molecular weight of an aromatic cluster (including attachments) to the average molecular weight of a single attachment; it is related to the aromaticity of the coal. The \(\sigma + 1\) term is the average number of attachments per aromatic cluster; it is related to the initial extent of cross-linking in the coal.
When the heating rate term has a value of 1, this approach yields an estimate of the swelling ratio at the heating rate for the Sandia flat-flame burner (Mitchell et al., 1992), which was calculated as $5.7 \times 10^4$ K/s. This form was chosen because of the superior fit for the Sandia experiments and because the values for the $s_{\text{cluster}}$ and $s_{\text{attach}}$ terms are within an order of magnitude of each other for most coals. This allows lower swelling observed for very high and low coal ranks to be explained in terms of the interplay between effects of aromaticity and cross-linking, eliminating the need for separate correction terms for low ranks and very high ranks.

It is important to note that no coals of ranks higher than low volatile bituminous were used to develop the correlation. Anthracites typically do not swell, but this correlation predicts a swelling ratio of 1.76 using ANL values for Buck Mountain Anthracite. The poor extrapolation to anthracites is not a serious liability; the value of $s_{\text{min}}$ can be used for anthracites. The value of $s_{\text{min}}$ is 0.988 for Buck Mountain Anthracite.

Two subbituminous coals were omitted for regression of parameters in order to improve the fit of bituminous coals and lignites. The swelling ratio for the Smith-Roland coal is slightly over-predicted, but the prediction for Blue #1 is somewhat low. This discrepancy could be due to experimental error, an inherent limitation of the model form, or limitations in either the correlations for NMR parameters or the estimate of $s_{\text{min}}$.

Since the basic rank model for swelling is specifically targeted at providing reasonable estimates for high heating rates, comparison of the model to data from electrically heated experimental facilities requires that the effect of heating rate be considered. A recent set of bituminous coal data designated as “BYU-GE Heating Rate Set” was chosen to fit the parameter $c_5$ because it covers a wide range of heating rates with a clear trend (Eiteneer et al., 2009; Shurtz and Fletcher, 2009). This coal is designated “Eastern Bituminous Coal A” elsewhere in this report. Sandia measurements that were excluded from the composition training set because of significant differences in heating rate were also used to fit the heating rate exponent (Fletcher and Hardesty, 1992; Mitchell et al., 1992). The heating rate exponent $c_5$ should be set to zero for anthracites, lignites, and most subbituminous coals to avoid predicting unrealistic swelling of these coals at heating rates near $10^4$ K/s. The results of the regression are shown in Figure 42. The values of parameters in the swelling model are listed in Table 19.
Figure 42. BYU swelling model with BYU and Sandia data. CBK swelling model shown for comparison.

Table 19. Parameters for swelling model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$c_1$</th>
<th>$c_2$</th>
<th>$c_3$</th>
<th>$c_4$</th>
<th>$c_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>0.017395</td>
<td>1.1209</td>
<td>0.16412</td>
<td>13.506</td>
<td>0.52048</td>
</tr>
</tbody>
</table>

At heating rates below $\sim$7×$10^3$ K/s, the trends of swelling with heating rate are significantly different. The data available in this range were not appropriate for direct regression due to large particle sizes that may introduce mass transfer limitations. However, several trends are apparent. For Illinois #6 coal, the swelling ratio appears to increase linearly with the logarithm of heating rate (Zygourakis, 1993). The swelling ratio appears to be constant at a value greater than 1 for heating rates below 1 K/s. This limiting value of the swelling ratio appears to be approximately equal to the swelling ratio at the base heating rate of 5.7×$10^4$ K/s. Based on these observations, a form of the swelling correlation was chosen for low heating rates that uses the composition dependence of the high heating rate correlation and captures the observed trends without fitting the data directly (Figure 43). The heating rate of maximum swelling was somewhat arbitrarily specified as 7×$10^3$ K/s for all coals because it allowed coverage of the available bituminous coal data near 10$^4$ K/s without large extrapolations. The swelling correlation at heating rates between 1 K/s and 7×$10^3$ K/s is:

$$\left(\frac{d}{d_0}\right)_{LHR} = \left(\frac{d}{d_0}\right)_{HHR,T_{peak}} \frac{1}{\log(T_{peak})} \log(T) + \left(\frac{d}{d_0}\right)_{HHR,T_{ave}}$$

(Equation 11)
Methods of predicting the effects of pressure on swelling and improving the predictive capabilities at atmospheric pressure are being pursued. Alternative formulations of composition dependence are being investigated, and the composition dependence of the heating rate and pressure terms are being investigated. Additional data from the literature is being gathered for these purposes.

Pressure dependence can probably be introduced into the correlation by multiplying the terms $s_{attach}$ and $s_{cluster}$ by a pressure term that has a value of 1 at 1 atm, increases to a peak value at some pressure between 8 and 20 atm, and then gradually decays to an asymptotic value of 1. A skewed distribution function such as the Weibull, Beta, or Gamma distributions could be used by applying vertical and horizontal offsets and a scaling factor. Attempts to use a Weibull distribution for this purpose have been difficult because the correct heating rate required for this correlation is seldom cited in literature sources. In the range of heating rates that drop-tube reactors operate in, the heating rate must be known very precisely (preferably with 2 significant figures) to quantify the effects of heating rate and pressure separately. Development of the pressure term in the swelling correlation will proceed as the quality and extent of swelling data available from the PFFB progress. This material is being updated and expanded for submission to a peer-reviewed journal.

**PFFB Gasification and Kinetic Modeling**

The large soot agglomerates collected with the char samples required a significant amount of extra labor to remove, but they also have interesting implications for gasifier design (Figure 8). Some soot agglomerates were comparable in size to the char particles. The soot yield in some cases appeared to be comparable to the char yield. However, this result is not certain because some soot was collected with the
char, and in some cases the material collected on the soot filters included very large, low-density char particles.

Because of its high surface area, radiation heat transfer from soot can lower local gas temperatures by up to 300 K (Brown and Fletcher, 1998). In the vicinity of char particles, this would significantly decrease gasification rates, increasing the required reactor size. Thermal radiation from soot may shorten the useful life of coal injectors and other components of gasifiers. The transformation of tar into soot greatly reduces the reactivity of the material. The agglomeration of primary soot particles into large structures inhibits gasification further by increasing the magnitude of mass transfer limitations. It is convenient in gasification modeling to represent char geometry as spherical, but soot agglomerates can be highly nonspherical and irregular compared to char. Hence, modeling gasification of soot in this form may be more difficult than modeling gasification of char, even considering the complex structures that have been observed in char.

The 1st order gasification model was used to fit the PFFB Wyodak steam gasification data at 2.5 atm. The model fit the data quite well at the three lower residence times, but there appears to be a transition from Zone II to Zone I near 147 ms (Figure 44). This decreased rate can be attributed to decreasing gas temperature and perhaps ash inhibition as well. This model is incapable of handling zone transitions; a more advanced model with more data will be needed to model the decrease in rate. The activation energy was driven to zero by the optimization software, which indicates that the particle was close enough to being isothermal at residence times below 147 ms for essentially constant rates to occur. Since the BYU-CBK/G model is designed to fit H₂O and CO₂ gasification simultaneously, it may be possible to fit this steam gasification data in conjunction with the other Wyodak data.

![Figure 44. Wyodak steam gasification in PFFB at 2.5 atm, ~1700 K with 1st order model.](image)

The 1st order model was applied to the CO₂ gasification data from the PFFB for all four coals. The Wyodak had sufficiently high reaction rates to measure significant differences in mass release and obtain a good fit of the data (Figure 45). The χ factors were on the order of 0.1-0.3 for all cases, confirming that these experiments were not limited by film diffusion. When viewed on a coalification diagram the Wyodak coal appears to be borderline in rank between subbituminous and lignite. The good fit of the
Wyodak data suggests that a simple 1st order model may be adequate to model gasification of subbituminous coals and/or lignites at moderate extents of reaction in Zone II.

Figure 45. Parity plot for Wyodak CO\textsubscript{2} gasification and 1st order model.

From the 1st order model it appears that the H\textsubscript{2}O gasification rate exceeds the CO\textsubscript{2} gasification rate for Wyodak by a factor of 340 at a particle temperature of 1158 K (the average of the ~30 K range where H\textsubscript{2}O gasification occurred), and reactant partial pressures (CO\textsubscript{2} or H\textsubscript{2}O) of 0.684 atm, with pyrolysis occurring at 2.5 atm and heating rates of ~8\times10\textsuperscript{4} K/s. This rate ratio is ~2 orders of magnitude higher than expected (Gadsby et al., 1946; Roberts and Harris, 2007).

The hypothetical effect of super-equilibrium O\textsubscript{2} concentration was investigated as a possible cause of the high ratio of H\textsubscript{2}O gasification rates to CO\textsubscript{2} gasification rates. Film diffusion limited oxidation rates (Zone III) were calculated assuming that all properties are evaluated at an average gas temperature of 1620 K (which overestimates the film temperature that should be used in the diffusivities). These calculations show that the mass release could be explained by the presence of ~2% O\textsubscript{2} reacting in Zone III. However, these conditions seem unlikely because soot was collected during the experiments (tar should be consumed preferentially to char) and the equivalence ratio of the flame was 1.07. The temperature was probably not high enough to reach Zone III; post-flame O\textsubscript{2} concentrations of greater than 2% would probably be needed to account for the high rates. The overall equivalence ratio could have been lower if the mass flow controllers have low accuracy for H\textsubscript{2} at the high flow rates used. Channeling of oxidizer to the outside of the burner is more probable for these experiments because the large 42 mm burner was used. If such was the case, tar released at the centerline of the burner at low residence times could have been transformed into less reactive soot in a fuel-rich zone. In this scenario, oxidation of char and soot would follow at longer residence times as O\textsubscript{2} diffused toward the center of the cylindrical flow path.
A second possible cause for the high ratio of H$_2$O gasification rates to CO$_2$ gasification rates is that the CO concentration in the CO$_2$ gasification environments was on the order of 10%; it was only slightly less than the concentration of CO$_2$. The CO concentration in the H$_2$O gasification environments was only 1%. CO can inhibit gasification rates by adsorbing onto char surface sites, blocking access to gasification reactants (Walker et al., 1959). This inhibition effect is also likely to be significant in industrial gasifiers where significant concentrations of CO are present in the syngas. The magnitude of this effect could be checked by lowering the equivalence ratio in the PFFB so that less CO is produced. Equivalence ratios greater than 1.15 were used in the CO$_2$ gasification experiments to assure that O$_2$ would not be present even in the presence of channeling or small inaccuracies in the calibration of mass flow controller.

A third possible cause of the low observed CO$_2$ gasification rates that should be investigated is that the Wyodak coal was not subjected to the same separation procedure as the bituminous coals because it produced less tar and soot. If there was sufficient soot mixed in with the char, it would artificially lower the observed extent of reaction as determined by tracer techniques. It appears that the average size of the soot agglomerates was much lower with the H$_2$O gasification conditions. Separation of char from soot should be more complete when soot agglomerates are small because the aerodynamic separation system is able to operate at its design conditions.

The extent of CO$_2$ gasification was very low for the bituminous coals compared to the Wyodak coal; it was on the order of 5% of the coal on a dry, ash-free basis. Results typical of the bituminous coals investigated are presented in Figure 46. Most of the observed gasification occurred between 40 ms and 120 ms because this corresponds to the region in the PFFB with the highest gas temperatures. One feature of the modeling results is that the span of the predictions exceeds the span of the measurements. At similar mole fractions of CO$_2$ the model over-predicts the extent of gasification at 15 atm and under-predicts gasification at 5 atm. This implies that the 1$^{st}$ order model is not adequate to model CO$_2$ gasification of bituminous coals; a lower reaction order would probably be more appropriate. A reaction order of 0.5 is commonly used to model char oxidation (Sun and Hurt, 2000). There is also a possibility that a significant part of the low apparent reaction order can be attributed to CO inhibition.
The CO$_2$ gasification rate constants optimized from the PFFB data using the 1$^{st}$ order model are presented in Figure 47. The thick solid portions of the lines correspond to particle temperatures predicted by the 1$^{st}$ order model where incremental changes of at least 1% were observed in the predicted extent of reaction. These rate constants are compared with the 1$^{st}$ order rate constants obtained by Goetz and coworkers in a previous study (Goetz et al., 1982). Goetz cites gas temperatures of 2000°F – 2650°F (1366 K – 1728 K). For comparison, the peak gas temperatures in the PFFB can exceed 1900 K but do not persist long; at particle residence times greater than ~250 ms the surrounding gas temperature was 1200-1300 K at 15 atm and up to 1500 K at 5 atm. Goetz used residence times of up to 900 ms, which is ~30% greater than the PFFB in its current configuration. The PFFB facility has the advantage of operating at elevated pressures. The PFFB particle heating rates (and hence the char structures and reactivities developed) are more representative of a full-scale gasifier. Most of the Goetz data was obtained using a CO$_2$ partial pressure of 0.3 atm, except for Pittsburgh #8 coal, which was studied at partial pressures of 0.15-0.6 atm. The PFFB conditions used partial pressures of 0.8-3 atm CO$_2$. 

Figure 46. 1$^{st}$ order CO$_2$ gasification model of Eastern Bituminous Coal A in the PFFB.

(a) 15 atm 1681 K
(b) 15 atm 1918 K
(c) 5 atm 1702 K
(d) 5 atm 1867 K
Figure 47. 1st order CO$_2$ gasification rate constants. Solid lines indicate PFFB particle temperatures.

The Wyodak rates exceed the Goetz rates for low-rank coals at all temperatures. The Wyodak activation energy of 157 kJ/mol is similar to the values of 165 kJ/mol and 178 kJ/mol obtained by Goetz for a Texas Lignite and a Wyoming Subbituminous C Coal, respectively. The bituminous coals investigated in the PFFB had rates that were 1-2 orders of magnitude lower than the Wyodak subbituminous coal. This is consistent with the rank trends observed by Goetz and implies that gasifiers designed exclusively for subbituminous coals and lignites can be much smaller and less expensive than gasifiers designed for bituminous coals. The PFFB bituminous coals also had very low activation energies compared to those obtained by Goetz; they differ by factors of 2-10. The Eastern Bituminous Coal A was the most reactive bituminous coal and Kentucky #9 was the least reactive. The PFFB bituminous coal gasification rates are very similar to the rates of the Goetz bituminous coals at the higher particle temperatures in the PFFB.

The trend in activation energies with rank is opposite the trend of Goetz; the results of these experiments predict higher activation energies for low rank coals compared to high rank coals.

The low activation energies for the Kentucky #9 coal and the Eastern Bituminous Coal B suggest that the gasification rates of these two coals may exceed those of eastern Bituminous Coal A and even Wyodak at very low temperatures. However, it is probable that the low activation energies for the two least reactive coals are caused by a low signal-to-noise ratio in the gasification data collected at the lower temperatures. The low temperature limits of the thick solid lines in Figure 47 were chosen to correspond to the temperatures at which the model predicted the last incremental change of 1% in the extent of reaction.

The existence of a higher minimum observed gasification temperature for the more reactive Eastern
Bituminous Coal A is evidence in favor of low signal-to-noise ratios for the low-temperature gasification data of the other two bituminous coals. It also seems unlikely that the Eastern Bituminous Coal A would have an activation energy more similar to Wyodak than the other two bituminous coals.

The similarity of coal gasification rates to those of Goetz at the temperatures where most measurements were made suggests that CO inhibition is not the cause for the large difference in the Wyodak H$_2$O and CO$_2$ gasification rates. More H$_2$O gasification experiments would be needed to gain a better understanding of the high observed H$_2$O gasification rate.

**Subtask 4.5 – Slag Formation and Slag-Wall Interactions**

Coal particles introduced into a high-temperature gasifier undergo three stages of conversion: (1) drying, (2) devolatilization, also known as pyrolysis, which forms a porous char, and (3) heterogeneous gasification reactions which convert the char to the final molten smelt product. The final degree of carbon conversion is driven primarily by how effective the heterogeneous reactions are. In order to achieve high conversion, the char particles must remain porous, with high internal surface area, so that the internal carbon sites are accessible.

Many studies on char conversion in gasifiers have been conducted over the past few decades, but most of these have focused on kinetics of gasification during the first 80-90% conversion. Very few studies have focused on late stages of conversion, when carbon burnout is high and ash concentration is correspondingly high. In particular, there have been no studies on the transition from porous, solid char to nonporous, molten slag. It is critical to understand this transition, since ultimate carbon conversion and even the fate of particles in the gasifier depends on the physical characteristics of the material.

This subtask aimed to shed light on this transition by evaluating the properties of coal char/ash particles generated under gasification (partial oxidation) conditions at temperatures both above and below the ash melting temperature. In particular, the project sought to identify the conversion at which the char-slag transition begins, and to quantify changes in physical properties of the material as this transition was taking place.

**Identification and Analysis of Char-Slag Transition**

Experiments to evaluate onset of the transition from char to slag were performed as described previously. The conversion of coal that was used in char and ash formation experiments was determined with a method used in previous studies (Tsai et al. 1987, Borrego et al. 2007). This method uses ash as a tie component (ash tracer). The coal conversion $X$ was calculated as

$$X = \left(1 - \frac{c_{\text{char}}^{\text{carbon}} c_{\text{ash}}^{\text{ash}}}{(1 - c_{\text{char}}^{\text{carbon}}) c_{\text{carbon}}^{\text{coal}}}ight) \times 100\%$$

where the superscripts ‘carbon’ and ‘ash’ indicate mass fraction of these components and subscripts ‘char’ and ‘coal’ indicate char formed during the char/ash formation experiments and the original dry coal, respectively.
The use of ash tracer in calculating coal conversion is based on three assumptions: (1) the conservation of ash before and after the reaction, (2) identical ash composition for the samples prepared in the LEFR and generated in proximate ash analysis and (3) the collected samples consisting of only carbon and ash. None of these assumptions are accurate. For example, vaporization of certain ash components is expected to occur because the mineral matter in the ash tends to exist as reduced or lesser-oxidized forms in a gasification environment particularly for the alkali and alkali-earth metals. The vaporized ash in the reaction gas can deposit on the collection probe when subjected to a quenching environment. Furthermore, the reaction conditions in the LEFR are different from those in proximate analysis, which can result in different mineral matter transformation and different ash composition. On the other hand, fine ash particles (submicron) liberated from char fragmentation is difficult to collect in the cyclone, thus reducing the ash content of the char particle determined using the LOI analysis. Borrego and Alvarez (2007) discussed the error of calculating the coal conversion using ash tracer method qualitatively. They concluded that the ash tracer method is acceptable for mainly comparative purposes between experiments performed at a single temperature varying only the reaction atmosphere.

**Particle Density Changes during Char-Slag Transition.** Particle density is a good signature of the char/slag transition, since it is known that porous char is relatively low density and slag has a higher density similar to that of its inorganic constituents. The particle densities of the parent coal, initial char formed after pyrolysis and gasified char/ash particles for the three different coals tested are presented in Figure 48.

The pyrolyzed char has a density that is much lower than that of the parent coal, which can be attributed to the swelling of char particles and loss of volatile matter during pyrolysis (Zeng and Fletcher 2005, Tsai and Scaroni 2007, Yu et al. 2007). Densities of the gasified particles are lower than those of the parent coal particle. During gasification, the carbon content in the char particle decreases and the ash content increases. Meanwhile, mineral matter in coal transforms into ash (mainly metal oxides, such as Al₂O₃, SiO₂, FeO, and MgO). These materials have densities above 2.0 g/cm³, which are much higher than the density of the carbon in the char (Bryers and Taylor 1976). Therefore, increasing the ash content in the char is associated with an increase in the particle density. One can expect that the slag particle (containing mostly ash) has a higher density than that of the parent coal (containing mostly carbon).

As seen in the figure, for much of the conversion the char particle density remained essentially constant and slightly lower than that of the initial pyrolyzed char, suggesting a porous structure similar to that of the pyrolyzed char. Maloney et al. (2005) observed that the char particle densities remained virtually unchanged with a slight upward trend up to 84% mass loss (comparable to conversion) during the combustion of a subbituminous Highvale blend coal. They attributed this phenomenon to the shrinkage of char particles with conversion, which tends to keep the porous structure. Hurt and colleagues (1988, 1993) also reported gasification-induced shrinkage up to 85% conversion. They concluded that shrinkage is due to densification of internal microporous structure and it reflects complex changes in internal morphology of the particle. Therefore, the constant particle densities throughout conversion suggest shrinkage of the char particles.
At higher conversion (88% for Illinois #6, 89% for Pittsburgh #8 and 94% for Black Thunder PRB), the particle density started increasing, and this trend continued throughout the burnout process. This suggests that the char–slag transition started at about these conversions. Maloney et al. (2005) observed an upward trend of particle density with decreasing particle size during char burnout process. Therefore, the particle density increase can be attributed to the size reduction of char and ash particles as conversion increased.

**Internal Surface Area Changes during Char-Slag Transition.** The effectiveness of coal gasification is associated with changes in the porous structure and associated internal surface area of the char. Heterogeneous gasification reactions require availability of carbon sites within the char particle, so a high internal surface area improves conversion. The evolution of the porous structure during char oxidation has been extensively studied using both experimental and modeling approaches. Bar-Ziv and Kantorovich (2001) reviewed these studies and concluded that surface area is one of the most widely used measures of reflecting the porous structure changes. However, few of these studies focused on the latter stage of coal gasification when char transforms into ash or slag.

Surface areas of the char and ash particles prepared by gasification of three coals were measured by BET analysis. The evolution in surface area is used to determine the point at which the char–slag transition started. To be used as an indicator of char–slag transition, the surface area must reflect the changes in both the carbon and the ash in the particle. Therefore, the particle internal surface area is evaluated per unit mass of the total particle (remaining carbon and ash) instead of the remaining carbon.
Figure 48. Particle densities of the parent coal, pyrolyzed char and gasified char samples. Top: Illinois #6. Middle: Pittsburgh #8. Bottom: Black Thunder PRB.
Internal surface areas of the char and ash samples from the three coals are presented as a function of conversion in Figure 49. The surface area started decreasing at higher conversions, indicating the transition from highly porous char to low porosity slag (i.e., the char–slag transition). For the Illinois #6 coal, surface area began to decrease at approximately 86% conversion, which is close to the 88% conversion at which density began to increase. For Pittsburgh #8, density increase and surface area decrease were observed at 89% and 91% conversion, respectively. For Black Thunder PRB, the respective values were both 94%. The good agreement between macroscopic (density) and microscopic (internal surface area) property shifts strengthens the concept of a char-slag transition and indicates that either property can be used to determine where the shift occurs.

At conversions above this critical point, the internal surface area of particles decreased throughout the burnout process. This trend is consistent with observations of other researchers who studied the variation of the porous structure of char particles in pulverized coal gasification (Simons 1983, Hurt et al. 1991). Internal surface area of char mainly arises from micropore and mesopores in the particle. Liu et al. (2006) attributed the decrease of char surface area at high temperatures to ash melting, which closed the pores of the char resulting in an inaccessibility of the pores to adsorptive gas. Lin et al. (1994) also pointed out that ash melting contributes to the decrease in the surface area of micropores and mesopores, especially at high conversion because the ash content increased with conversion.

The Illinois #6, Pittsburgh #8 and Black Thunder coals used in this study had ash flow temperatures of 1246, 1229 and 1191°C under reducing conditions, respectively. These temperatures are well below the temperatures at which the experiments were conducted (1400 and 1500°C). The ash in the char particles presumably melted at 1400 and 1500°C. Therefore, the decrease in the surface area can be attributed to ash melting in the char. In addition, the consumption of carbon at high conversions resulted in loss of micropores and mesopores, which also contributes to the decrease of micropore and mesopore surface area. The melting of ash and consumption of carbon in the char resulted in a substantial structural change: the transformation from porous char to molten, low-porosity slag.

**Morphological Changes during Char-Slag Transition.** In order to better understand the effect of ash melting on the internal surface area of the particle, scanning electron microscopy (SEM) images were captured with an Everhart–Thornley detector, which shows heavier elements as brighter regions. Mineral matter in coal is mainly composed of metal oxides, which are heavier than the carbon. Therefore, the ash minerals are always brighter than the carbon in the particle. The difference in brightness of different elements can be used to determine which part of the particle is rich in ash or carbon.
Figure 49. Internal surface area evolution of the char and ash particles prepared from Illinois #6 (top), Pittsburgh #8 (middle) and Black Thunder PRB (bottom).
The Illinois #6 coal used in this study is a bituminous coal, in which the included mineral matter is mainly present in the form of embedded mineral grains (Benson et al. 1993). SEM images of partially converted char and ash particles prepared from Illinois #6 coal at 1400 °C are presented in Figure 50. These images reveal the morphological changes of the particles during the char–slag transition, such as the shape of the particle and the association between the ash minerals and the carbon matrix.

Included minerals can become exposed from within the carbon matrix due to char surface receding in the burnout process. The exposed minerals can either remain attached on the char surface due to the molten ash surface tension or be liberated from the char particle by shedding. The minerals attached on the particle surface coalesce to form a few ash particles in the size range 10–20 µm (Sarofim et al. 1977). The minerals liberated by shedding produce thousands of small ash particles typically in the size range 1 to 8 µm (Helble et al. 1990). Wu and colleagues (1999, 2000) concluded that fragmentation plays a key role in the formation of a large amount of fine ash particles less than 10 µm in the early and middle stage of pulverized coal combustion, while coalescence of included minerals results in the formation of several coarse ash particles larger than 10 µm in the later stage of combustion, depending on the structure of the char. Baxter (1992) found that large char particles have a much higher tendency to fragment than small particles. Based on these studies, the char–slag transition process is described in terms of the association between the included minerals and the carbon matrix in the particle.

At low and medium conversions (Figure 50, parts a and b), the carbon material in the char was consumed to an extent that shrinkage occurred. Upon shrinking, char surface receded, and a few minerals (indicated by the bright droplets) became exposed on the char surface. However, most of the minerals were still encapsulated by the carbon matrix because the conversion was not sufficiently high. At the same time, some discrete ash particles appeared, which were formed from the excluded minerals and shedding of melted minerals from the char surface. As conversion proceeded, there was less carbon remaining in the char and the particle shrank further. As a result, more and more included minerals became exposed on the receding char surface. When sufficient minerals were exposed on the particle surface (Figure 50, part c), the char–slag transition started. In this stage, exposure of included minerals on char surface is mainly due to shrinkage of the particle (surface recession).

At high conversions, exposure of included minerals on the char surface is mostly caused by fragmentation. In the later stage of gasification, the char particle fragmented into a few particles of 20-30 µm. The exposed minerals likely remained attached on the particle surface due to the molten ash surface tension and became molten at temperatures above the ash fluid temperature. Because of the reduction in particle size, these minerals coalesced when they gradually met each other on the reduced particle surface (Figure 50, part d) and eventually merged with the minerals inside the particle (Figure 50, part e). When the coalescence of the minerals was completed, the char–slag transition was finished. The final ash particles (Figure 50, part f) narrowly sized in the range of 20–30 µm, indicating that most of the mineral matter in the coal particle coalesced to form a few coarse ash particles. In contrast to the coarse surface and irregular shape of the char particle, the coalesced ash particle has smooth surface and droplet (or spherical) shape because of the surface tension of molten ash. The smooth surface and droplet shape of the ash particles suggest that the residual carbon is encapsulated by molten minerals.
A complementary study on the char morphology using the Illinois #6 coal under combustion conditions showed that at temperatures below the ash flow temperature the particle still has a coarse surface and irregular shape (Figure 51) even at high conversions, while the particle has a smooth surface and droplet shape at temperatures above the AFT. This suggests that the formation of slag particle occurs at only temperatures above the ash flow temperature of the coal.

Figure 50 shows that shrinkage of the particle carbon matrix results in the exposure of included minerals in the initial stage of the char–slag transition, whereas fragmentation dominates the exposure of included minerals in the later stage of the transition. On the basis of the char–slag transition, the surface area evolution in Figure 49 can be explained as follows.

The internal surface area of a char particle is mainly created by micropores and mesopores in the particle. During the char–slag transition, a large amount of molten minerals became exposed on the particle surface. The melted minerals presumably have a tendency to block the pores on the char surface. The more melted minerals covered the particle surface, the more pores became closed, leading to further surface area loss. After the char–slag transition, the remaining carbon was completely enclosed by the molten slag, as indicated by its smooth surface and droplet shape. This kind of ash particle has the lowest internal surface area because of the high resistance for the adsorption gas diffusing into the particle. Consequently, the exposure of included minerals on the char surface is responsible for the sharp decrease in the surface area as shown in Figure 49.
Figure 50. SEM Photographs of Illinois #6 char during conversion to slag at 1400°C.
Figure 51. Comparison of the morphology of the ash particles (about 97% conversion) prepared under combustion conditions at different temperatures: left, 1200 °C; right, 1400 °C.

SEM images of partially converted char and ash particles prepared from Pittsburgh #8 coal at 1500°C are presented in Figure 52. The morphological changes of the Pittsburgh #8 char and ash particles follow the same trend as the Illinois #6 char and ash particles. However, the large amount of melted minerals did not appear on the particle surface until 91% conversion, suggesting that the char–slag transition took place at about 91% conversion. The critical conversion for transition is higher than that of the Illinois #6 coal while lower than that of the Black Thunder coal. This agrees well with the ash content (9.00%) of the Pittsburgh #8 coal, which is lower than that of the Illinois #6 coal and higher than that of the Black Thunder coal.

SEM images of partially converted char and ash particles prepared from Black Thunder coal at 1400°C are presented in Figure 53. The morphological changes of the Black Thunder char and ash particles follow the same trend as the Illinois #6 char and ash particles. However, the large amount of melted minerals did not appear on the particle surface until 94% conversion, indicating that the char–slag transition started at about 94% conversion. This corresponds with what was observed in the surface area evolution versus conversion shown in Figure 49. The conversion at which the char–slag transition of the Black Thunder coal took place is higher than that of the Illinois #6. This is probably due to the lower ash content (6.82%) of the Black Thunder coal compared with the Illinois #6 coal (10.89%). The lower ash content of the Black Thunder requires a higher conversion to consume the residual carbon in the particle for the included minerals exposing from the carbon matrix.
Figure 52. SEM Photographs of Pittsburgh #8 char during conversion to slag at 1500°C.
Figure 53. SEM Photographs of Black Thunder PRB char during conversion to slag at 1400°C.
Modeling and Prediction of the Char-Slag Transition Point. The char–slag transition is a process in which porous char transforms into molten slag at temperatures above ash fusion temperature. The transition starts from a porous char particle in which mineral matter is encapsulated by the carbon matrix and proceeds such that the encapsulated mineral matter becomes exposed on the particle surface as carbon is consumed. The transition completes when the particle surface is totally covered by the molten mineral, i.e., the remaining carbon is enclosed by the mineral. Exposure of included minerals is caused by shrinkage of the particle in the initial stages of the char–slag transition, whereas it is dominated by fragmentation of the particle in the later stages of the char–slag transition.

In a partially converted char particle, the two main components are residual carbon and ash. When there is adequate residual carbon to encapsulate the included minerals, the particle behaves as a solid char. When the ash starts encapsulating the carbon, the char–slag transition occurs and the particle is an intermediate between char and slag. When the residual carbon is encapsulated by the ash, the transition is finished and the particle transforms into molten slag. This indicates that the char–slag transition occurs when the ash content in the char particle reaches a specific value.

By assuming the conservation of ash in the conversion process, the ash content in a partially converted char particle can be calculated as

\[ c_{\text{char}}^{\text{ash}} = \frac{c_{\text{coal}}^{\text{ash}}}{1 - c_{\text{coal}}^{\text{carbon}}} X \]

where \( X \) indicates fractional coal conversion, \( C \) indicates mass fraction, the subscripts refer to the material being analyzed and the superscripts refer to the component whose mass fraction is measured. A more simplified expression for particles containing only carbon and ash is

\[ 1 - c_{\text{char}}^{\text{carbon}} = \frac{c_{\text{coal}}^{\text{ash}}}{1 - c_{\text{coal}}^{\text{carbon}}} X \]

The critical conversion \( X \) at which the char–slag transition occurs can be expressed in terms of residual carbon content and coal ash content as

\[ X = \frac{c_{\text{coal}}^{\text{ash}}}{c_{\text{coal}}^{\text{carbon}} (1 - c_{\text{char}}^{\text{carbon}})} + \frac{1}{c_{\text{coal}}^{\text{carbon}}} \]

On the basis of analyzing the changes in density, size, internal surface area and morphology of the char and ash particles at different conversions, the critical conversions at which the char–slag transition occurs were determined separately. By comparing the critical conversions determined based on different property changes, an appropriate critical conversion was identified for each coal. The critical conversions, the parent coal ash contents and the parent coal carbon contents are summarized in Table 20. Data in Table 20 suggest that the critical conversion increases with decreasing ash content in the parent coal because the coal with lower ash content needs a higher conversion to burn enough carbon for the included minerals to become exposed from the carbon matrix and to cover the particle surface. This indicates that
the critical conversion is dependent upon the parent coal ash content in the equation above, which can be further simplified as

\[ X = mC_{coal}^{ash} + b \]

where \( m \) and \( b \) are constants. Using the data from Table 20, the expression above was fit using regression to a straight line with the resulting constants being \( m = -1.44 \) and \( b = 1.04 \). The expression thus becomes

\[ X = -1.44C_{coal}^{ash} + 1.04 \]

The fit between this expression and data from Table 20 is shown in Figure 54. The fit is very good and trends according to the mechanism described above; one would expect that a coal with a lot of ash would melt, or collapse into slag, at lower conversion than coal with a higher carbon/ash ratio.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Critical Conversion (%)</th>
<th>Coal Ash (wt %, mf)</th>
<th>Coal Carbon (wt%, mf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illinois #6</td>
<td>88</td>
<td>10.89</td>
<td>76.30</td>
</tr>
<tr>
<td>Pittsburgh #8</td>
<td>91</td>
<td>9.00</td>
<td>86.49</td>
</tr>
<tr>
<td>Black Thunder</td>
<td>94</td>
<td>6.82</td>
<td>77.40</td>
</tr>
</tbody>
</table>

Figure 54. Char–slag transition model fit to experimental data.
This empirical model can be used to predict the critical conversion at which the char–slag transition takes place on the basis of the parent coal ash content that is determined from the proximate analysis. However, caution needs to be taken when using the model to predict the char–slag transition because the char–slag transition is strongly affected by the fragmentation behavior of char particles. For example, if fragmentation occurs in the early stage of char oxidation, large amounts of included minerals will be liberated and the char–slag transition is expected to occur earlier. The fragmentation of char particles is highly dependent on the coal rank and type, char structure and reaction conditions. The constants in this empirical model were based on the properties of two bituminous and one subbituminous coals. When applied to other coal ranks, the constants need to be modified for optimum results.

In addition, the critical conversions for the transition of the three coals were determined at temperatures above the ash fluid temperatures of the coal ashes. In some practical coal gasifiers, coal particles are mixed with additives for achieving a slagging operation condition. The additives might affect the char–slag transition by interacting with the coal ash and lowering its ash fluid temperature.

**Workshop on gasifier refractory performance, slag-wall interactions and mechanisms of refractory degradation**

This workshop differed somewhat from the original scope of work. It was somewhat smaller and located at NETL’s Albany Research Center. Due to NETL’s commitments to other projects and travel of key people, it was difficult to schedule this meeting. After several delays and attempts at reschedule, the investigators decided to hold a workshop at NETL instead of Utah.

NETL/Albany, the University of Utah, and Brigham Young University met in Albany, Oregon on May 3, 2011 to discuss mutual interests in and progress on the interaction of gasifier slag with refractory. The primary representatives of each institution were James Bennett, Kevin Whitty, and Larry Baxter, respectively. Several NETL personnel attended specific portions of the workshop, with Kyei-Sing and Jin Nakano attending essentially all of it. During this meeting, NETL presented research results and plans on refractory-slag interactions and details of slag chemistry, University of Utah presented a status report on their developing gasification systems, and BYU presented experimental and modeling results of ash deposition, deposit properties, and refractory-slag interactions in approximately equal time slots. The material from Albany contained proprietary aspects and is not available, but notes on their presentation are appended below (courtesy of Kevin Whitty). In addition to the prepared presentations, the investigators discussed agreements, disagreements, implications, and critical questions based on the presented data and models.

Some of the major conclusions of the workshop include:

- Refractory-slag interactions remains the largest or one of the largest barriers to making coal-based gasification cost effective and reliable.
- Minor modifications in refractory or slag composition can have large impacts on dissolution rate.
- Spalling rates are perhaps the least-well understood of the refractory degradation mechanisms and are almost certainly a combination of chemical, physical, and design properties of the gasifier.
Chemical interactions depend strongly on thermodynamics and transport mechanisms, both of which are difficult to theoretically compute or experimentally discern. Ultimately, however, chemical interactions drive refractory degradation. These commonly couple with physical and design properties to produce spalling, which is physical failure of refractory driven by underlying chemical interactions with the slag.

Slag/wall temperature, slag chemistry, refractory porosity, and refractory composition all have major impacts on wear rates, consistent with NETL measurements and BYU models.

The presence of running slag has a major influence on failure rate, but the amount of running slag has a minor influence, again consistent with NETL predictions and the BYU models.

Refractory failure commonly occurs in a relatively isolated zone of the gasifier – typically the highest temperature zone. It is highly non-uniform, with respect to location, again consistent with NETL observations and model predictions.

Predictions suggest that refractory wear does not change monotonically with slag composition, although this is difficult to verify experimentally since operating conditions typically vary substantially and refractory degradation measurements lack accuracy and especially continuity (typically available only single-time-step SEM images after exposure).

Current high-performance refractory include chromia as the primary phase with minor phosphorus content, though these are both expensive and health concerns because of potential Cr VI formation.

Many of these conclusions would not be obvious from the work of just one of the institutions involved, indicating the value of the workshop. Continued interactions between NETL and the universities will be pursued as possible depending on available funding.

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

**Injector Performance**

**Cold Flow Injector Testing.** Tests were performed using the atmospheric pressure ex situ injector described previously, using air and water through the oxygen and slurry channels, respectively. The three factors that were evaluated were the impingement angle, respective flow rates, and the pressure drop.

To study impingement angle, three nozzles with different impingement angles (25°, 45° and 65°) were evaluated. The angles represent the angle of the outer directional cone which forces oxygen (air) in towards the slurry stream. All angles are measured from the vertical, so the 25° nozzle has the least severe impingement angle with the flow largely in line with the slurry stream and the 65° nozzle has an impingement angle that is almost perpendicular to this stream. Figure 55 shows the effect of impingement angle for the three nozzles at constant oxygen (air) and slurry (water) flow rates. Overall, impingement angle does not have a significant influence on the characteristics of the spray. It is difficult to tell from the photographs, but it was observed that the 65° nozzle provided more consistent behavior and resulted in a more finely atomized spray.
A key design parameter is the pressure drop of the oxygen channel, which is responsible for atomizing the slurry stream. Ultimately, one would like to have very high pressure drop, but this can create operational challenges. For the system at the University of Utah, a lower pressure drop allows higher overall system pressure since the oxygen supply pressure is fixed. To test the influence of pressure drop, a series of tests was performed with the same nozzle and constant slurry (water) flow rate, but with different pressure drops (achieved by varying the gap width of the nozzle). Representative results from this study are shown in Figure 56. Clearly, higher pressure drop results in much better atomization. The conclusion from these studies was that atomization behavior improves with pressure drop up to approximately 40 psi. Higher pressure drop beyond 40 psi did not noticeably affect atomization performance.

A complementary study to the one described above for pressure drop was to vary the slurry flow rate at constant air pressure drop. A series of tests was performed with one injector, holding the air flow rate constant and maintaining a pressure drop of 40 psi. The water flow rate was varied by a factor of roughly five, with flow rates corresponding to those in the pilot-scale system corresponding to near-atmospheric pressure and higher pressure. As seen in Figure 57, even over this wide range of water flow rates, good atomization was achieved.
Figure 56. Both injectors shown have the $65^\circ$ nozzle and the same flow rates of water and air. The injector on the left is operating at a 10 psi pressure drop, whereas the injector on the right is operating at a 50 psi pressure drop.

Figure 57. Both injectors have the $45^\circ$ nozzle tip installed. The injector on the left has a water flow rate corresponding to an EFG system pressure of 25 psia. The injector on the right has a flow rate corresponding to an EFG system pressure of 115 psia. Both injectors are operating at a 40 psi air pressure drop.

**Influence of Injector Performance on Gasification Behavior.** The adjustable injector was evaluated during EFG operation to determine its effect on the EFG temperature profile and the syngas composition.
The pressure drop across the nozzle was varied by adjusting the gap width while maintaining constant flow rates of slurry and oxygen. For each injector pressure drop the system was allowed to equilibrate for 30-40 minutes. Figure 58 shows the temperature profile through the reactor for different injector oxygen pressure drops. TC1 is the top thermocouple, located near the “roof” of the reactor. TC2 through TC5 are spaced equidistant down the length of the reactor such that TC5 is approximately 70% of the length of the reactor. (Thermocouples at lower positions cannot be installed due to the presence of a large pressure vessel flanges.) It is interesting that higher pressure drops, which have been demonstrated to give superior atomization, result in lower temperatures. Several factors can be responsible for this. With finer atomization, more of the slurry is evaporated, devolatilization of the coal is more complete, and the heterogeneous gasification reactions \((C + H_2O \rightarrow CO + H_2)\) and \((C + CO_2 \rightarrow 2 CO)\). All of these are endothermic processes that require heat and will result in lower temperatures. With poor atomization, it is likely that much of the coal is not converted, resulting in a higher effective \(O_2/coal\) ratio and correspondingly higher temperatures.

![Temperature profile through the reactor for different injector oxygen pressure drops.](image)

Figure 58. Reactor temperature profiles during operation with the 45° nozzle at specific injector oxygen pressure drops. The thermocouples are number in order of their position from the top of the reaction zone, so TC1 is closest to the injector and TC5 is furthest away. The thermocouples are 11 in from the adjacent thermocouple.

Table 21 presents concentrations of the main syngas species at different injector pressure drops. As the pressure drop across the injector was increased, the quality of the syngas increased. More \(H_2\) and \(CO\) was produced and less \(CO_2\) was produced. This also is an indication of better conversion and a lower effective \(O_2/coal\) ratio at high pressure drop.
Table 21. Syngas composition (dry, normalized N₂-free) from EFG testing.

<table>
<thead>
<tr>
<th>Injector O₂ Pressure Drop (bar)</th>
<th>H₂ (vol%)</th>
<th>CO (vol%)</th>
<th>CO₂ (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>25.9</td>
<td>35.7</td>
<td>38.2</td>
</tr>
<tr>
<td>1.4</td>
<td>27.1</td>
<td>37.3</td>
<td>35.4</td>
</tr>
<tr>
<td>2.1</td>
<td>27.9</td>
<td>38.3</td>
<td>33.6</td>
</tr>
</tbody>
</table>

Reactor Operation – High-pressure Testing

**Oxygen/fuel ratio.** Over the course of the project, various campaigns were conducted to study how oxygen/fuel ratio, pressure and residence time affect performance. An example of results from a campaign to study how O₂/fuel ratio affect performance is given in Figure 59. As one would expect, increasing this ratio results in higher temperatures, a lower heating value syngas and production of CO₂ at the expense of CO.

![Figure 59](image1.png)  
**Figure 59.** Temperatures (left) and concentrations of major gas species (right) as a function of oxygen/coal ratio. Operation at 5 bar with Utah Skyline coal and a constant coal feed rate of 12 kg/hr dry.

**Influence of System Pressure.** This was studied in each of the campaigns performed under this program. An example of the change in pressure and syngas composition is depicted in Figure 60, which shows a stepwise progression from low to high pressure. For these tests, the coal slurry and oxygen feed rate were maintained as pressure increased. The top graph in the figure shows the system pressure as it was increased from 50 to 200 psi. The middle graph shows temperature and the bottom graph presents concentrations of the major syngas species. It should be noted that as pressure increases at constant fuel and oxygen feed rate, the residence time in the reactor also increases, providing better opportunity for conversion.

Temperature in the reactor was relatively constant, perhaps decreasing slightly at higher pressure due to better conversion resulting from the longer residence times. TC2 broke early in this run, so its temperature is not displayed. TC5 had been broken but began to register a signal around 15:40, although
that measured temperature was unrepresentatively low. Such problems with thermocouples are common in high-temperature coal gasifiers, and the University of Utah’s system is no exception.

The syngas composition improved significantly as pressure increased, as seen in part (c) of the figure. The CO₂ concentration became nearly half as much at 200 psi as at 50 psi, and CO and H₂ both increased notably. This is a consequence of more time for conversion, particularly due to heterogeneous gasification reactions, at higher pressure.

![Graphs](image)

**Figure 60.** Stepwise pressure increases versus time on 12/15/2010.

**System Balance**

It is important to be able to perform a mass balance around the gasifier. This involves measuring the flows of material entering and exiting the system. Oxygen flow (lb/hr) can be measured very accurately with the coriolis-style flowmeter/totalizer. Slurry flow is measured with the ultrasonic flow meter and then compared against the loss in slurry height in the feed tank over an hour or more. The slurry is regularly tested for density and coal solids content so it is possible to determine the mass flow rates of slurry water and coal. Syngas flow rate is measured with a v-cone (orifice-type) flowmeter and
composition is measured and recorded with a gas chromatograph. Water discharge from the quench bath can be determined by monitoring quench bath height and discharge frequency.

The operation data log and gas chromatograph data were used to perform material balances around the gasifier during periods of steady state operation, generally about an hour. Three different periods were chosen for operation at 200 psi, based on the stability of the data. System closure was defined as follows:

\[
\text{system closure} = \frac{(\text{total mass of material exiting})}{(\text{total mass of material entering})} \times 100\%
\]

Closure for the system during the three periods ranged from 118% to 144%. This is not especially good. Not only does it appear that more material is exiting the system than is entering (obviously impossible), but the range of values is unacceptably far from 100%. After scrutinizing the data, it was concluded that the measurement of syngas flow rate contributes most to poor system closure. That flowmeter is relatively low-tech and old, and it is susceptible to fouling by soot and other particulate in the gas. Although it is cleaned regularly, any fouling of the flowmeter will result in a higher pressure drop, which is what is measured to calculate flow. So, the observed flow rate becomes higher than the actual flow rate. The length of time used for balancing may also contribute to the wide range of values. Ultimately, several hours of operation should be used.

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 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), physical processes (Subtask 4.5), and the development 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. One of the most significant conclusions of the work performed was the implementation of a sequential process for assembling response surfaces. This was significant not just because of the process laid out, but because each step of the assembly revealed important information about the behavior of the system response. An input/uncertainty map containing input variables expected to be significant was constructed after discussions with modelers and experimentalists; it was found that four of these parameters were very clearly significant (devolatilization reaction activation energy, wall temperature, coal mass flowrate, and mean particle size), while the remaining two (devolatilization reaction pre-exponential constant and char oxidation reaction activation energy) were insignificant. Perhaps the most important observation was that the devolatilization reaction activation energy was not only significant near the inlet in the devolatilization zone, but that its effect propagated throughout the system, and it was the single most significant parameter throughout the entire gasifier. This is consistent with the findings of Smith (1990). Additionally, the construction of a response surface from the results of a factorial design set of runs performed with the Arches gasification code was significant and important.
**Subgrid-scale modeling.** The efforts on subgrid-scale modeling focused on three primary areas: (1) Developing and assessing the efficacy of the ODT model in reproducing DNS statistics; (2) Exploring the use of PCA to obtain controlling parameters for use in developing combustion models; and (3) Interfacing TabProps with the ARCHES code to enable a common interface for a variety of models. In each of these areas, significant progress was made. Developments in ODT resulted in a new formulation for the ODT model and validation activities for the software that implemented it. PCA was shown to be an excellent method to obtain a reduced set of variables that can parameterize the thermochemical state of a reacting system with high accuracy, although parameterizing source terms remains a challenge. The TabProps interface for ARCHES has been completed and is in use now.

**Char and soot kinetics and mechanisms.** The work on char and soot kinetics focused on experiments and subsequent analysis from the PFBB, including the development of soot from a coal and from a coal tar surrogate on the measurement of coal swelling ratios during pyrolysis and gasification rates. A model was developed to predict coal swelling. Swelling observed in the PFFB is low compared to results from pressurized drop-tube reactors due to the higher heating rate. First-order kinetic modeling of gasification rates show some agreement with published rate constants, but with lower activation energies for bituminous coals. Analyses revealed very large soot agglomerates, which have the potential to significantly impact heat transfer and gasification rates in gasifiers.

While the samples studied in this work were not systematically developed into a closed set of experimental conditions for the two coals and surrogate tar/sample, sufficient experiments were conducted to demonstrate a number of experimental conditions, which affect the transformation of different coals under pyrolysis conditions. Differentiation between the structural elements of char and tar/soot samples under similar pyrolysis conditions are evident. The structural elements in the Wyodak and Eastern Bituminous coals were distinctly different. Some evidence exists that the HAB collection point has an affect similar to residence time in the pyrolysis temperature zone. It is clear that the structural parameters of coals are related to their behavior under pyrolysis conditions.

**Slag formation and slag-wall interactions.** During high-temperature gasification, coal particles quickly devolatilize to form char with relatively low density, approximately 40-80% the density of the original dry particle depending on the coal. The internal surface area of the char is high and can exceed 200 m²/g. Experiments performed under this study indicate that char density remains relatively constant and that internal surface area per mass of remaining char increases somewhat as the char undergoes most of its conversion. However, at high coal conversion and at temperatures exceeding the ash fluid temperature, the particle begins to experience partial melting of the inorganic inclusions, causing a dramatic increase in density and decrease in internal surface area as the particle “collapses.” For the three coals used in this study, the onset of this transition ranged from 88 to 94% coal carbon conversion. At even higher conversions, 95% and above, the particles are essentially molten, with density much higher than the original char and very low surface area. The remaining few percent carbon in the sample is encapsulated in the particles, making final conversion by heterogeneous reactions with gasifying agents inefficient and slow. This is a key reason why achieving very high carbon conversion in such gasifiers is difficult.
The conversion corresponding to the onset of the critical char-slag transition depends on the ash content in the coal. Provided that the environment is hotter than the ash fluid temperature, coals with higher ash contents will begin to undergo char-slag transition at lower conversions. The critical conversion for the onset of char-slag transition can be estimated based on the ash content in the coal. An empirical expression for that onset was developed based on data from the three coals tested in this program, and suggests that for each percent increase in ash mass fraction, the critical conversion for the onset of coal-slag transition is about 1.5% lower.

*Acquisition of Validation Data in an Entrained-Flow Gasifier.* Over the course of this project, the University of Utah’s pilot-scale entrained-flow coal gasifier was commissioned and methodically brought to the point where it can operate at the maximum pressure possible with the current oxygen supply system. Overall, the system operates in a manner representative of an industrial-scale gasifier. The synthesis gas composition closely matches what equilibrium modeling indicates it should. Syngas properties and reactor temperatures vary with oxygen/fuel ratio and residence time as predicted; higher O₂/fuel ratios result in higher temperatures, more CO₂ and less CO and H₂. Operationally, injector design and avoidance of slag buildup at the reactor outlet present the largest challenges and will undoubtedly remain priority areas for research for several years to come.

**LIST OF PEER-REVIEWED PUBLICATIONS**


**REFERENCES**


Sutherland, J. C. TabProps Wiki, 2010 a. URL [https://software.crsim.utah.edu/trac/wiki/TabProps](https://software.crsim.utah.edu/trac/wiki/TabProps).

Sutherland, J. C. TabProps Software Repository, 2010 b. URL git://software.crsim.utah.edu/TabProps.git.

119


